



Novel adsorbent membranes of poly (vinyl alcohol) and ZSM-5 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 ZSM-5 i.e., zeolite in different compositions from 1 to 10 wt. % that are used for pervaporation (PV) dehydration of ethanol at azeotropic point from aqueous mixtures of 4.1 wt. % water 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 ZSM-5 zeolite particles that are also hydrophilic. The membranes were crosslinked with tetraethyl ortho silicate (TEOS) and confirmed by Fourier transform infrared spectroscopy (FTIR) and by calculating the 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 membranes. It is observed that flux and selectivity increased with increasing amount of ZSM-5 particles in the PVA matrix. In case of hybrid adsorbent membrane containing 10 wt. % of ZSM-5, selectivity for water was 1320 and a flux of 0.366 kg/cm² h was attributed to combined effects of molecular adhesion between particle surfaces and PVA matrix. Higher selectivity of the adsorptive membrane was found compared to the plain PVA membrane.

Keywords: pervaporation, dehydration, poly (vinyl alcohol), hybrid adsorbent membrane, zeolite ZSM-5

1. Introduction

Pervaporation is polymeric membrane process used in separation of binary or multi-component liquid mixtures of different industrially important liquids. The separation of the liquid mixtures is effected by means of the pervaporative membranes. The membranes, non-porous ('dense') pervaporation membranes made of polymeric materials and they exhibit different philicity towards different components, as a result, the desired separation of the liquid components [1, 2].

The liquid mixture Separation via partial vaporization of liquid through a membrane (nonporous or dense) is the basic separation principle in the pervaporation. This yields in collection of permeating mixture in the vapor form, which may be either eliminated by flowing an inert sweep medium or by means of applying low pressure on the permeant side. The main driving force in pervaporation process is the gradient in chemical potential, corresponding to the concentration gradient between phases on the opposite sides of the interfacial barrier. The solution diffusion model is employed to explain the transport properties on the basis of change in the molecular size instead of boiling point like distillation. Hence, it is effectively utilized as economical substitute azeotropic mixture separations. In addition to there is no intermediate of third components and need of low energy consumption are the add-on the side of advantages [1, 2]. In the last few decades, pervaporation is getting an extensive range of areas for its application such as liquid hydrocarbons separations (petrochemical application, alcohol/ether

separations) [3-5], removal of volatile organic compounds (VOCs) from aqueous medium [6, 7], elimination of water from glycerin [8], and dehydration to intensify esterification reaction [9, 10].

Pervaporation (PV) separation has been the widely used method for separating aqueous-organic azeotropes [11]. 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 that of plain polymeric membranes. In the prior literature, several hybrid adsorbent membranes loaded with inorganic zeolite particles have been developed and used for dehydrating organics [12-14]. Separation using zeolite-filled PV membranes occurs by adsorption-desorption and molecular sieving effects due to the presence of small particles [15].

The incorporation of inorganic silicate particles into a polymeric matrix has been explored extensively as an efficient way for improving separation performance as well as thermal stability, optical properties, electrical properties, catalytic reactivity, and transport properties of the membranes. 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 membranes [16].

Organic-inorganic hybrid membranes in which inorganic filler

with specific physicochemical characteristics is spatially dispersed into the bulk of polymeric membranes is a facile and feasible approach to cross the trade-off hurdle by combining the high selectivity with desirable mechanical properties of inorganic materials and tunable flexibility with excellent processability of polymeric materials [11, 12]. Many studies have demonstrated that the dramatically improved separation properties of organic-inorganic hybrid membranes could be realized by incorporating porous or nonporous inorganic absorbents, including zeolite, silica, carbon molecular sieve and activated carbon into the matrices of glassy and rubbery polymers. There are also some studies on incorporating mineral flakes into polymeric membranes to develop selectively permeable membranes [13, 14] or impermeable barriers [15]. 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 not only on the intrinsic properties of the inorganic material and polymer as well as interaction between the two phases, but also inorganic content and particle size. Maxwell [17], te Hennepe *et al.* [18, 19], Koros *et al.* [20] have subsequently proposed 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 [21]. They pointed out that the dispersed phase might cause an undesirable void at the interface or create varying degrees of regasification in the surrounding polymer. Until now, no similar report specifically dealing with the pervaporation can be found. Therefore, in this study, we focus on a detailed investigation and elucidation on the organic-inorganic hybrid pervaporation membranes with simultaneously enhanced permeability and selectivity.

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 [22-24]. 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.

The purpose of this study is therefore, to find a strategy for 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)-ZSM-5 adsorbent membranes were prepared and characterized by FTIR, SEM, DSC and TGA techniques. The effects of ZSM-5 zeolite particle content on pervaporation properties of the adsorbent

membranes for separation of ethanol/water mixture at azeotropic composition were systematically investigated. The reversal of tradeoff effect was actually found and tentatively elucidated.

2. Experimental

2.1 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.

2.2 Particle size measurement of zeolite ZSM-5

Particle size was measured by Zetasizer (Model 3000HS, Malvern, U.K). The sizes of the completely dried zeolite ZSM-5 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.

2.3 Membrane Fabrication

2.3.1 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.

2.3.2 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 ZSM-5 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 caste membranes allowed drying and once dried membranes are peeled off. The hybrid adsorbent membranes are designated as ZSM-5-PVA-1, ZSM-5-PVA-2.5, ZSM-5-PVA-5, ZSM-5-PVA-7.5 and ZSM-5-PVA-10 that contained 1, 2.5, 5, 7.5 and 10 wt % of ZSM-5 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 $2.5\mu\text{m}$).

2.4 Scanning electron microscopy

SEM micrographs of the plain PVA and ZSM-5-PVA hybrid adsorbent membranes containing 2.5 wt. % of ZSM-5 and 10 Wt. % of ZSM-5 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.

2.5 FTIR

Pristine and crosslinked membranes ground well with KBr to make pellets using a hydraulic pressure of 400-450 kg/cm². 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.

2.6 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 cm² 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 (kg.m⁻².h⁻¹) using weight of liquids permeated, W (kg), effective membrane area, A (m²) and measurement time, t (h) as:

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

The analysis of feed and permeate samples was done using 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 μL . Pure hydrogen was used as the carrier gas at 0.75 kg/cm² 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, α 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 α were taken under similar conditions of temperature and feed compositions to confirm steady-state pervaporation.

2.7 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 ZSM-5 incorporated PVA hybrid adsorbent membranes were taken on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) to an accuracy of ± 0.01 mg. Samples were placed inside the specially designed airtight test bottles containing 30 cm³ 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_∞ and W_0 are the weights of swollen and dry membranes, respectively.

3. Results and Discussion

3.1 Reaction of PVA and TEOS

The crosslinking reaction between PVA and TEOS are shown in Scheme 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.

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 1000–1100 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 (-CH₂-CH-) of PVA. However, -Si-O- stretching is also observed in the same region as that of C-O stretching.

3.6 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 ZSM-5 loaded PVA membrane was displayed in figure 4 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 4 compare the plots of % degree of swelling of the plain PVA and ZSM-5 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 ZSM-5 particles in PVA. For 1 wt. % ZSM-5-loaded PVA membrane, a slight decrease in % DS is observed over that of plain crosslinked PVA membrane. However, for 10 wt. % ZSM-5 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.

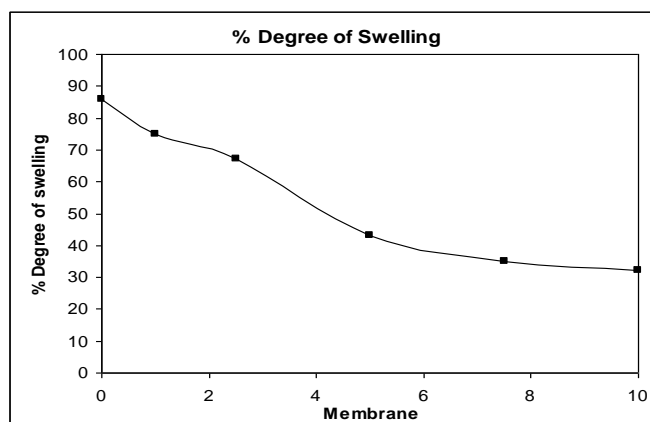


Fig 4: % Degree of sorption for the different membrane.

3.7 Pervaporation separation Index

Figure 5 displays the variation of PSI with the extent of loading zeolite ZSM-5 in the PVA membrane. The PSI values increased linearly with increasing ZSM-5 content, signifying that membranes that contained a higher amount of filler would show improved PV performance for water-ethanol feed mixtures. The incorporation of ZSM-5 particles into the PVA membrane would not only affect membrane hydrophilicity, but also its rigidity. Thus, increased hydrophilic-hydrophilic interactions between ZSM-5 and PVA exert a significant effect on diffusion of water through composite membranes by retaining organic components on the feed side.

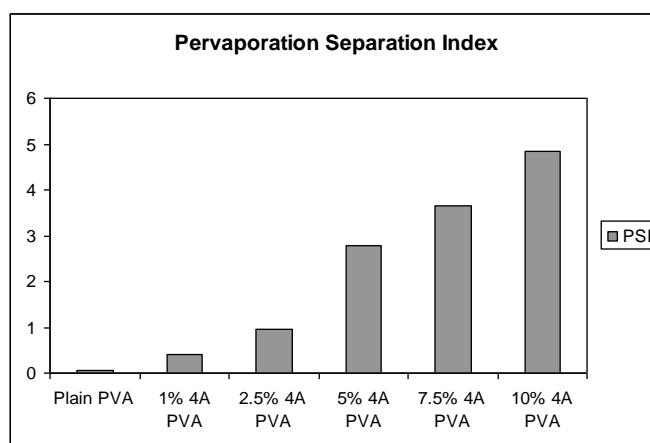


Fig 5: Pervaporation separation index.

3.8 Membrane performance

Since transport is very sensitive to sub nanometer 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 ZSM-5 particles. Zeolite ZSM-5 is a well-known molecular sieve with a pore diameter of 3.8 Å and 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 ZSM-5 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 Figure 6 (a) and (b), for plain crosslinked PVA membrane, flux and selectivity data for ethanol–water are much lower than those observed for adsorbent membranes. 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 ZSM-5 zeolite particles, indicating an increased hydrophilicity of the hybrid adsorbent membranes due to the presence of ZSM-5 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. % ZSM-5 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. % ZSM-5 zeolite loaded mixed matrix PVA membranes was able to remove 91 % of water from feed (see also Table-I for numerical data). On the other hand, for the 10 wt.% ZSM-5 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 ZSM-5 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 ZSM-5 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 ZSM-5 zeolite particles.

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.% ZSM-5 zeolite < PVA/2.5 wt.% ZSM-5 zeolite < PVA/5 wt.% ZSM-5 zeolite < PVA/7.5 wt.% ZSM-5 zeolite < PVA/10 wt.% ZSM-5 zeolite. It was noticed that addition of ZSM-5 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 ZSM-5 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 ZSM-5 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 ZSM-5 zeolite particles, thus allowing an easy transport of water, since large number of water molecules are being adsorbed onto ZSM-5 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/m² 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.

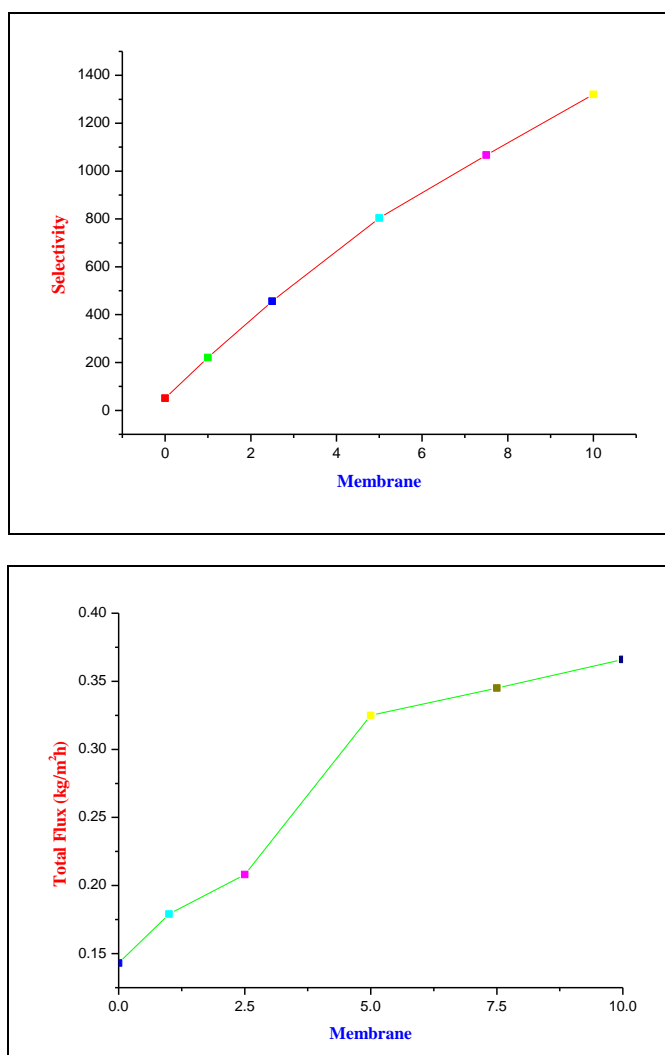


Fig 6: Total Flux and selectivity with respect to Membrane.

4. Conclusions

To improve the 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 ZSM-5 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 ZSM-5 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 ZSM-5 particles, whose addition to another hydrophilic polymer like PVA greatly improved the overall membrane performance.

5. References

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