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PERVAPORATION SEPARATION OF IPA-WATER MIXTURES THROUGH ZSM-5 ZEOLITE-FILLED GUARGUM MEMBRANES

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ABSTRACT

ZSM-5 zeolite filled Guargum membranes were prepared by solution casting method by varying the zeolite content ranging from 10 to 30 wt % with respect to GG weight. Membranes were cross-linked with glutaraldehyde and tested for Pervaporation (PV) dehydration of aqueous IPA at 300 C. These membranes were characterized by Fourier Transform infrared spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and X-ray diffraction (X-RD) techniques. From FTIR results it is noticed that the formation crosslinking is observed in these blend membranes. Further from DSC & X-RD results it is observed that the peaks of Si-O increased with increase in zeolite content which confirms that there is no chemical interaction between zeolite & GG. Morphology of the membranes was assessed by SEM and the results concluded that the zeolite particles are uniformly dispersed in GG membranes. Sorption studies have been performed to evaluate the extent of interaction and degree of swelling of the membranes with pure GG and zeolite mixed membranes at different IPA-water contents in the feed mixture. The pervaporation results it is observed that the flux decreased and the selectivity increased systematically with increasing amount of zeolite in the GG matrix. The membrane containing 30 mass % of zeolite gave the highest separation selectivity of 249.15 for 10 mass % of water containing feed mixture at 30°C. Increase in water selectivity of the membrane was explained due to a reduction in free volume by increasing zeolite content of the membrane. The presence of hydrophobic nature of zeolite also responsible for the above trends.

KEYWORDS: Separation techniques; Membranes; Isopropanol-water; Zeolite; Selectivity;

INTRODUCTION

Membrane phenomena can be traced back to eighteenth century when Abbe Nollet invested the word “osmosis” to describe permeation of water through a diaphragm in 1748. Pervaporation is a process using membrane to separate mixtures of dissolved solvent through evaporation of volatile components through a non-porous selective membrane. The first paper was published by Kober, who discovered the potential of Pervaporation. With increasing experience and confidence in the new technology, more and more new membranes have been developing for separation of gases and liquids mixtures purpose via Pervaporation (1). Pervaporation is not an “ideal” technology, but just a new unit operation which is attractive when weighed against other competitive process (2). The problems of Pervaporation technology that are highlighted are selectivity and reliability (3). Pervaporation technique has a great potential for separations where the more conventional techniques, such as distillation, are not possible to be realized or too expensive. This includes the separation of azeotropes, of mixtures of components with only a slight difference in volatility, and of components that are pressure or temperature sensitive. These separations occur in the (petro) chemical and as well as the food industry and in waste water treatment (4-7). For dehydration purposes, hydrophilic

membranes are used. Up to now, mostly polymeric membranes have been used on an industrial scale. Zeolites have unique properties that are very attractive features because of their well-defined micropore structure, good thermal and structural stability, high mechanical strength, feasible for steady-state operation, low energy consumption, resistance to relatively extreme chemical environment (8,9). In particular, the acid sites due to the presence of aluminum, the high specific surface and the well-defined pore dimensions have imposed them as selective catalyst materials.

The crystalline nature of zeolites offers the opportunity to obtain membranes with a regular 3D network of micropores at the molecular scale and they are therefore able of separating mixtures of substances on the basis of differences in the molecular size and shape (10), such as, for example, isomers (11), compounds with similar molecular weight and also azeotropic mixtures (12). The advantage of using a zeolite membrane is that it can potentially separate molecules in a continuous way. For example, modules of hydrophilic zeolite A (LTA) membranes were recently commercialized for alcohol dehydration by pervaporation (13). The incorporation of zeolite or porous fillers in dense membrane can improve the separation performance of the membranes (14-18) due to combined effect of molecular sieving action, selective adsorption, and difference in diffusion rates. In addition, zeolites have high mechanical strength, good thermal and chemical stability, and thus, the membranes, when incorporated with these fillers, can be used over the wide range of operating conditions.

Silicate and ZSM-5 zeolites having the MFI-type structures have been widely studied in membrane applications (19-22). Silicate is pure silica zeolite having straight channels interconnected by zigzag channels. The straight channels in ZSM-5 zeolite are elliptical, with an opening of 0.51 x 0.57 nm, and the sinusoidal channels are almost circular, with a diameter of 0.54 nm (23). Guar gum is a polysaccharide prepared from cellulose. It contains both methyl and hydroxyl propyl substitutes. It is a good film-forming properties, which has been studied extensively as a PV membrane studies in various applications. GG membranes are known to exhibit high swelling due to the presence of hydroxyl groups. To improve the membrane performance, it is necessary to maintain a balance between hydrophilicity by the addition of hydrophobic groups to achieve higher selectivity than the virgin GG membrane.

The present study aims at maintaining a proper balance between hydrophilicity and hydrophobicity of the membrane by incorporating different amount of hydrophobic ZSM-5 zeolite (particle size: 0.35 -0.75 μm , pore size: 5.6 Å, Si / Al ratio: 5-100) in the Guar gum (GG) polymer matrix. The resulting membranes were tested for the PV separation of water-isopropanol mixtures at 30°C. Swelling experiments were performed to understand the effects of zeolite loading and feed compositions on the PV performance of the membranes.

MATERIALS AND METHODS

Materials

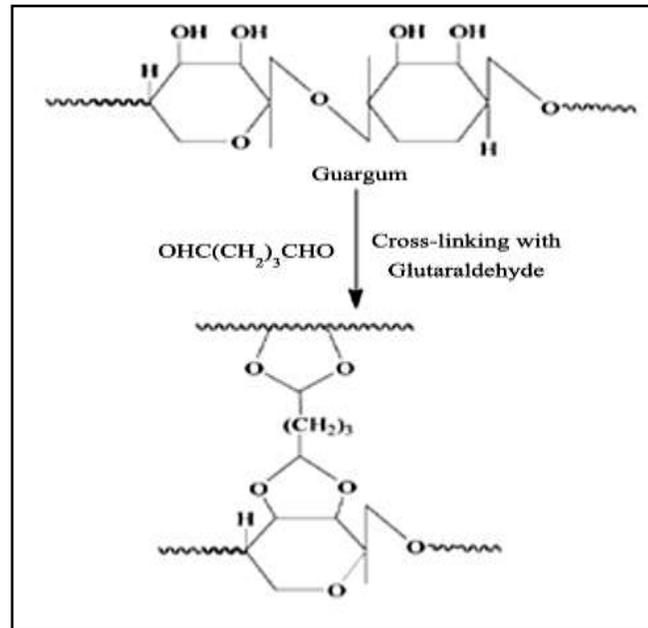
Guar gum (A.R. Grade, M.W - 1, 40,000), Glutaraldehyde (GA), Iso-propanol (IPA) (AR-grade), Hydrochloric acid (HCl) and Acetone were purchased from s.d. fine chemicals, Mumbai, India. ZSM-5 Zeolite was kindly supplied by M/S Zeolite and Allied products Pvt Ltd, Mumbai. All the chemicals were of analytical grade samples used without further purification. Deionized water with a conductivity of 20 $\mu\text{s/cm}$ was produced in the laboratory using (Technico pilot plant, Vadodara, India.) through a nano filtration membrane module and used for all the experiments.

Preparation of membrane

Guar gum (2g) was dissolved in 100 ml of deaerated distilled water at room temperature with a constant stirring for about 24 h. The solution was then filtered to separate any undissolved matter and allowed to bubble-free solution. The resulting homogeneous solution was spread onto a glass plate with the aid of a doctor's blade in a dust-free atmosphere at room temperature. After being dried for about 48 h, the membrane was subsequently peeled-off and designated as GG-0.

To prepare zeolite-incorporated GG membrane, a known amount of ZSM-5 zeolite was added into a GG solution. The amount of GG was kept constant for each membrane. 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, and then kept stirring for overnight to get a homogeneous solution. The resulting solution was poured onto a glass plate and the membrane was dried as mentioned above and the membranes were peeled off. The prepared membranes were then crosslinked in a bath containing with 84 vol. % isopropanol, 10 vol. % water, 5 vol. % of glutaraldehyde crosslinker and 1 vol. % hydrochloric acid catalyst for a period of 2 hours.

The crosslinking reaction between Guar gum with glutaraldehyde was shown in scheme 1. The amount of ZSM-5 zeolite with respect to GG varied as 0, 10, 20 and 30 wt. %, and the membranes thus obtained were designated as GG-0, GG-10, GG-20 and GG-30 respectively.



Scheme 1. Structural representation of ZSM-5 Zeolite incorporated Guar gum membranes crosslinked with glutaraldehyde.

Pervaporation experiments:

Schematic pervaporation experimental setup were performed in an apparatus designed in the Dept. of Polymer Science & Technology, S.K.University, Ananthapur and it was used elsewhere and the procedure used in pervaporation has been described by many researchers [24, 25]. The pervaporation cell consist 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 is used as the feed chamber. The membrane is supported by a stainless steel porous plate which is embedded with an SS mesh/screen. Teflon gaskets are fixed by means of high-vacuum silicone grease on either side of the membrane, and the sandwich is placed between the two glass column couplers and secured tightly. The effective membrane area in contact with feed is almost 20 cm² in all cases. The feed side pressure is maintained at atmospheric pressure and the vacuum in the downstream side at about 0.5 mmHg using a vacuum pump (Ind high vac, ED-18 model Bangalore, India). The permeate was collected in liquid nitrogen cold traps for a period of 8 hrs followed by analyzing the compositions of the feed and permeate at 35°C using Abbe Refractive meter (Atago, Model: DR-A1, USA) and comparing with standard graph of refractive index versus mixture composition. From the PV data, selectivity (α) was calculated,

$$\alpha = [Y_A / 1 - Y_A] / [1 - X_A / X_A] \quad \dots (1)$$

Where X_A is the mole fraction of water in the feed and Y_A is the mole fraction of water in permeates. Flux, J (kg/m²h) was calculated using the weight of the permeate, W [kg], effective membrane area, A (m²), and time, t (h) as

$$J = W/At \quad \dots (2)$$

In all cases, results were obtained in triplicate but averages (3% standard error) are reported. Calculated values of flux and selectivity are presented in Table2.

Swelling measurements:

The degree of swelling of zeolite-incorporated membranes was determined in different compositions of water and isopropanol mixtures for 24h at 30°C using an electronically controlled oven (WTB Binder, model-BD-53, Germany).

The masses of the dry membranes were first determined. The dry membranes were equilibrated by soaking in different composition of the mixture in a sealed vessel, at 30°C for 24 hours and then the swollen membranes were weighed immediately after careful blotting on a single pan Adam digital microbalance (model AAA 160L, Switzerland) having a sensitivity of ± 0.01 mg. The % degree of swelling (DS) was calculated as:

$$DS (\%) = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (3)$$

Where W_s and W_d are the mass of the swollen and dry membranes, respectively.

CHARACTERIZATION TECHNIQUES

Fourier transforms infrared spectra

Dispersion of different amounts of ZSM-5 zeolite in the GG matrix confirmed by FTIR (Bomem, MB-3000, Canada) spectrophotometer. About 2 mg of the sample was grounded thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm². Dry membranes were characterized in the range of 4000 to 400cm⁻¹ at a scan rate of 25 cm⁻¹ under N₂ atmosphere.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermo grams of crosslinked GG membranes were obtained on a Rheometric Scientific (Model TA-600, Germany). Thermo grams were recorded from 30°C to 600°C at a heating rate of 10°C / min in a nitrogen atmosphere.

X-ray diffractometry (XRD)

To investigate a change in membrane structure with crosslinking density, a wide-angle X-ray diffractometer (Simens D 5000, Germany) with a scintillation counter detector using Cu K α - radiation as a source was used. Angles (2θ) ranged from 2° to 50°. All samples were films with thickness of 11-13 μ m in order to identify any changes in the crystal structure and intermolecular distances between intersegmental chains after modification.

Scanning Electron Microscope (SEM)

SEM micrographs surface of the membranes were obtained unfilled GG membrane and zeolite filled GG membranes, under high resolution (Mag 800X3.0kv) (Using JEOL Model JSM 5410 Japan), scanning electron microscope (SEM), equipped with phonix dispersive analysis.

RESULT AND DISCUSSION

FTIR Studies

FTIR spectra of the crosslinked GG membranes and those of different amounts of ZSM-5 zeolite loaded membranes are given in Figure 3.1. A characteristic strong and broad band appearing at around 3040 cm⁻¹ corresponds to O-H stretching vibrations of the hydroxyl group of GG. This O-H frequency shifted and moved towards lesser frequency in case of zeolite loaded and crosslinked blend membranes which indicates the crosslinking of -OH group of GG with -CHO group of glutaraldehyde. On close observation of peak intensity of the zeolite-loaded samples it is observed that the intensity did not change, indicating that hydroxyl groups of GG are not involved in any chemical reaction with the zeolites. A sharp intense band appearing at around 1100 cm⁻¹ is assigned to Si—O stretching, (26) and the multiple bands appearing between 700 and 100 cm⁻¹ are assigned to the stretching of Al—O vibrations (27) due to the presence of zeolite. The intensity of these bands increased further with increasing the amount of zeolite in the membranes, which ascertains the complete dispersion of zeolite in the crosslinked GG membranes.

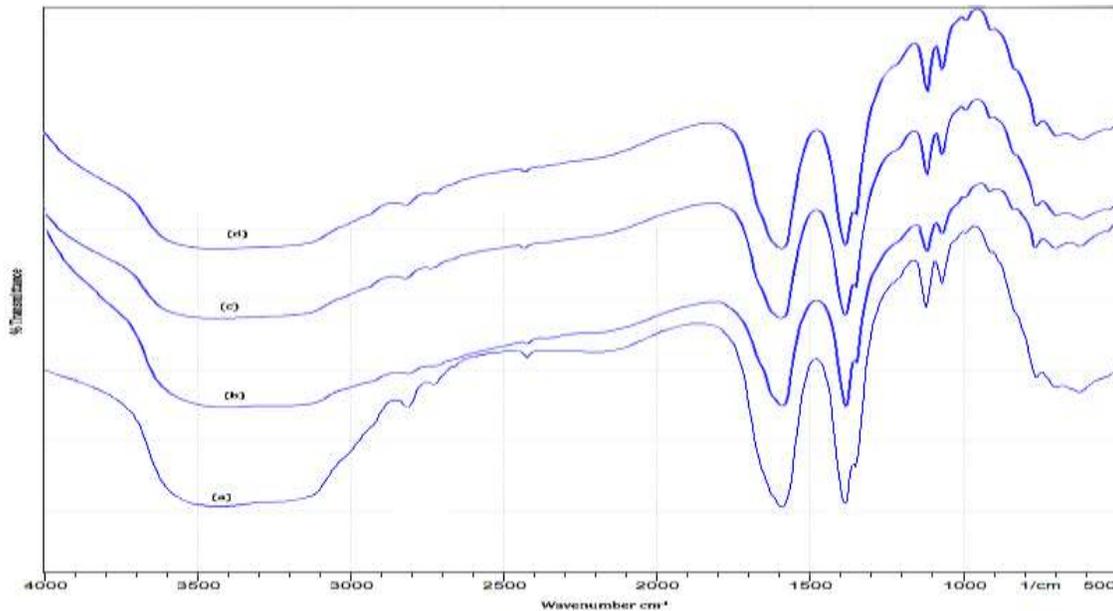


Fig: 3.1. FTIR spectra of crosslinked GG Membrans (a) GG-0 (b) GG-10 (c) GG-20 (d) GG-30.

DSC Studies

In an effort to study the effect of zeolite loading on the membrane morphology, the glass transitions of the different membranes were studied. Effect of zeolite loading on T_g of the crosslinked GG membranes is shown in Figure 3.2. The T_g of the crosslinked GG membrane increased systematically with increasing the amount of zeolite, indicating that the free volume of crosslinked GG membrane decreased. This is because segmental motions of the chains are restricted by increasing the zeolite loading. This confirms the presence of zeolite in the membranes and also indicates that there is no chemical reaction on between zeolite and GG.

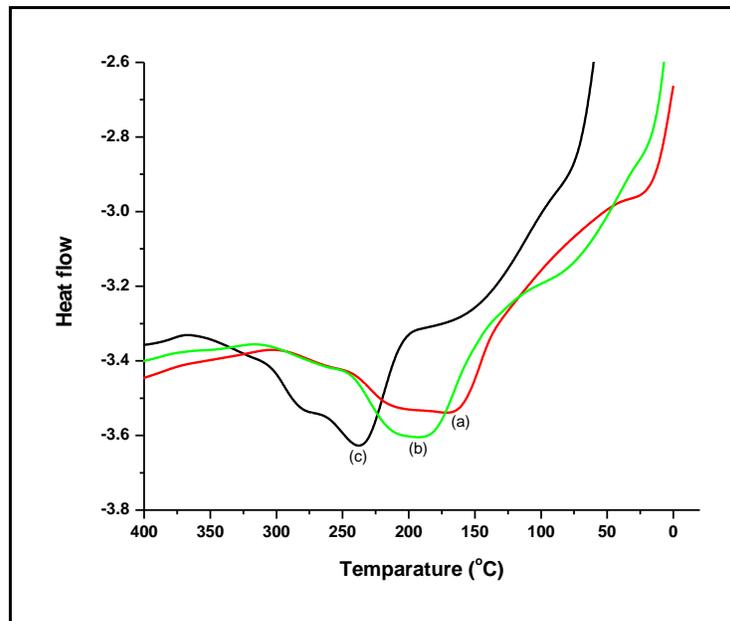


Fig: 3.2. DSC thermograms of crosslinked GG membranes : (a) GG-10 (b) GG-20 (c) GG-30.

X-ray diffraction Studies:

X-ray diffraction patterns of with and without zeolite loaded the membranes are presented in Fig: 3.3. The X-ray diffraction patterns of the membranes (a & b) shows that as the loading of zeolite increased, peak intensity of the crosslinked GG membranes decreased at around $2\theta = 20$. This revealed that the relative crystallinity of GG crosslinked membranes decreased with increasing loading of the zeolite. An additional peak has appeared as the zeolite content was increased at around $2\theta = 23$ degree. This is due to the presence of ZSM-5 zeolite in the membranes, whose intensity further increased as the zeolite content increased in the membranes from (a & b).

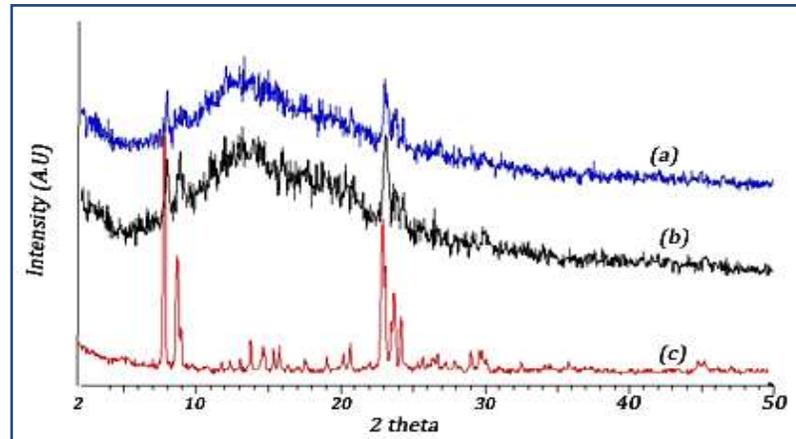


Figure.3.3: X-ray diffraction patterns for the membranes (a) GG-20 (b) GG-30 (c) GG-0.

SEM Analysis:

Fig.3.4. showed the scanning electron micrographs of ZSM-5 particles and the pure GG-0, GG-10, GG-20 & GG-30 membranes. As can be seen from Figure 3.3 (e), ZSM-5 zeolite as a rectangular parallelepiped block particles was about $3\sim 5\ \mu\text{m}$. From Figure 3.3 (a), no appreciable pore could be observed, indicating that defect-free dense membrane was synthesized. It could be seen from fig (b-d) that ZSM-5 particles were uniformly dispersed in the membrane matrix.

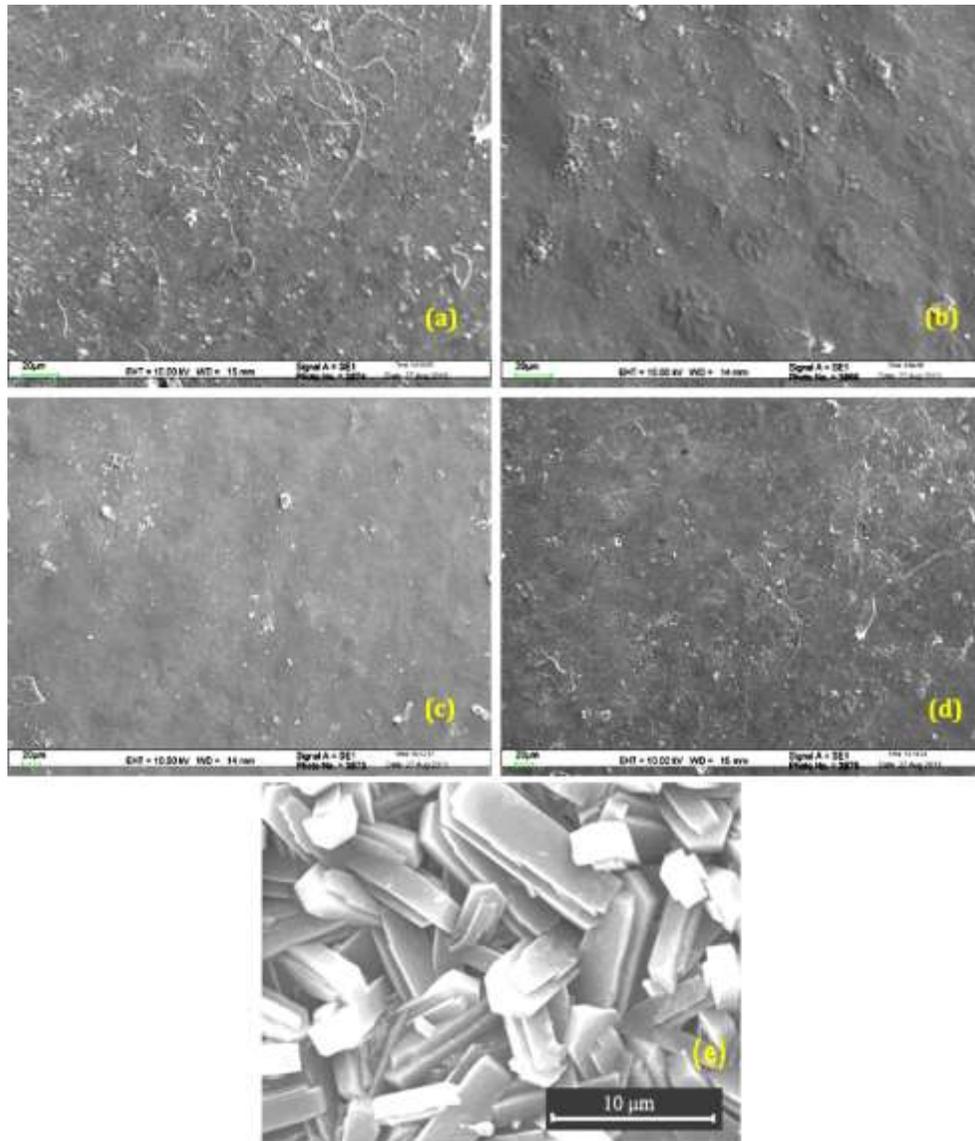


Figure.3.4: SEM photographs of Membranes (a) Pure-GG (b) GG-10 (c) GG-20 (d) GG-30 and (e) plane ZSM-5 zeolite

Effect of feed composition on membrane swelling

In PV experiments, membrane swelling controls the transport of permeate molecules under the gradient of chemical potential. When the polymer matrices are filled with highly symmetrical zeolite particles, then it is likely that the pores of the membranes might have been occupied by the zeolite particles. Because, in the present investigation, hydrophobic property is predominant in the type of zeolite used, it hinders the chain mobility due to loss in free volume. Therefore, both solubility and diffusivity of the permeant molecules through the zeolite – filled membrane might have decreased during the PV process with increased zeolite loading.

Figure 3.5 shows the swelling behavior of different mass % of zeolite – filled membranes as a function of feed mixture composition at 30° C. This data (Table-1) observed that degree of swelling increased with increasing feed water concentrations up to 30 mass % and then decreased for all the membranes as the water concentrations increased beyond 30 mass % in the feed. This unusual tendency is not only due to the free volume available in the membrane matrix but also due to the cluster formation of water molecules at higher concentration of water in the feed.

Table-1 Results for degree of swelling of membranes in Water + IPA mixture at 30°C

Water in mixture (wt%) water+IPA	GG-10	GG-20	GG-30
10+90	1.561	4.524	7.261
20+80	2.324	5.862	8.541
30+70	2.814	6.239	10.723
40+60	2.120	4.871	7.925

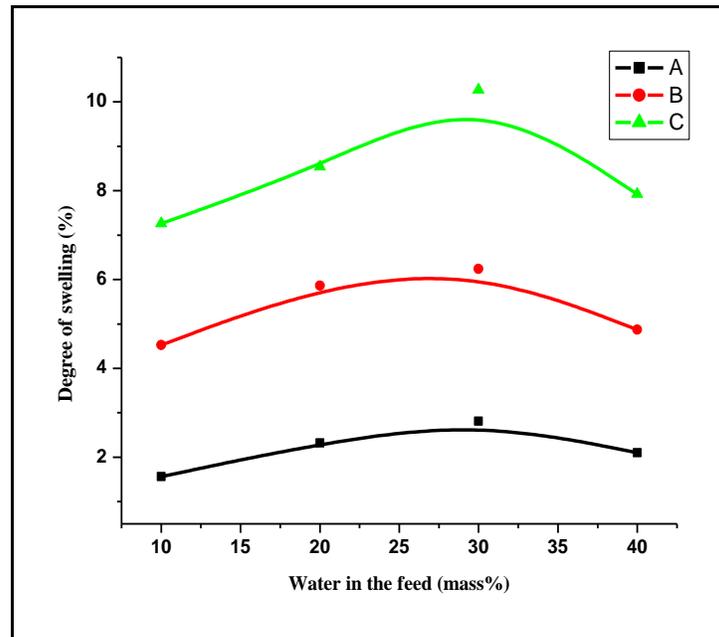


Figure 3.5: Variation of degree of swelling with different mass% of water in the feed for different loadings of zeolite in cross-linked (A) GG-10 (B) GG-20 and (C) GG-30.

Effect of feed composition on Pervaporation studies

The effect of water composition on the total permeation flux is shown in Figure 3.6(a). It is observed that permeation flux increased with increasing the amount of water in the feed mixture, reaching a maximum at around 30 mass % of water, and then it decreased steeply with further increase of water composition in the feed. Such a decreasing tendency after attaining a maximum value is due to the hindrance in permeating process occurred in the membrane owing to the formation of water clusters. At higher water contents in the feed, clustering of water molecules will be more, and cluster size might continue to increase with increasing amount of water content in the feed (28-30).

On the other hand, selectivity as shown in Figure 3.6(b) decreased drastically up to 20 mass % of water, and then it remains constant over the entire composition of water in the feed mixture, showing not much variation beyond 20 mass % in the feed with the varying amounts of zeolite in the membranes.

Calculated results of total flux and selectivity, measured at 30°C for different composition of feed with respect to zeolite loading in the membranes (GG-10, GG-20 and GG-30), are presented in Table-2 respectively. It is observed that there is a systematic decrease in total flux and with increasing amount of zeolite. For all the membranes, flux values of water are much higher than those obtained for isopropanol indicating the water selectivity of the membranes.

Table: 2. Pervaporation Flux (J) and Separation Selectivity (α) data for different mass % of Water in the Feed Mixture at 30°C for different Membranes:

Feed compositions		Permeate compositions (wt %)		Selectivity (α)	Flux (kg/m ² h)
Water (x)	IPA (1-x)	Water (y)	IPA (1-y)		
GG-10					
10.325	89.675	98.018	1.982	116.87	0.41
20.148	79.852	96.258	3.742	70.76	1.64
30.012	69.988	93.689	6.311	46.72	3.12
40.328	59.672	91.238	8.762	29.23	2.26
GG -20					
10.631	89.369	99.123	0.877	156.24	0.38
20.485	79.515	97.698	2.302	80.25	1.50
30.254	69.746	95.892	4.108	62.32	2.66
40.948	59.052	93.012	6.988	41.29	1.87
GG -30					
10.198	89.802	99.012	0.988	249.15	0.32
20.389	79.611	97.889	2.111	112.12	0.92
30.284	69.716	96.532	3.468	84.25	2.48
39.684	60.316	96.987	3.013	60.24	1.37

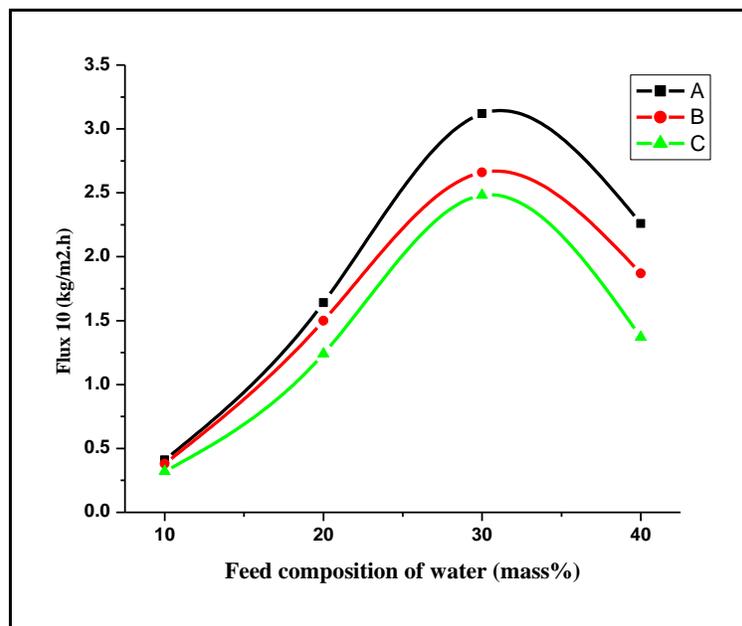


Fig 3.6(a): Variation of flux (J) with different mass% of water in the feed for (A) GG-10 (B) GG-20 (C) GG-30

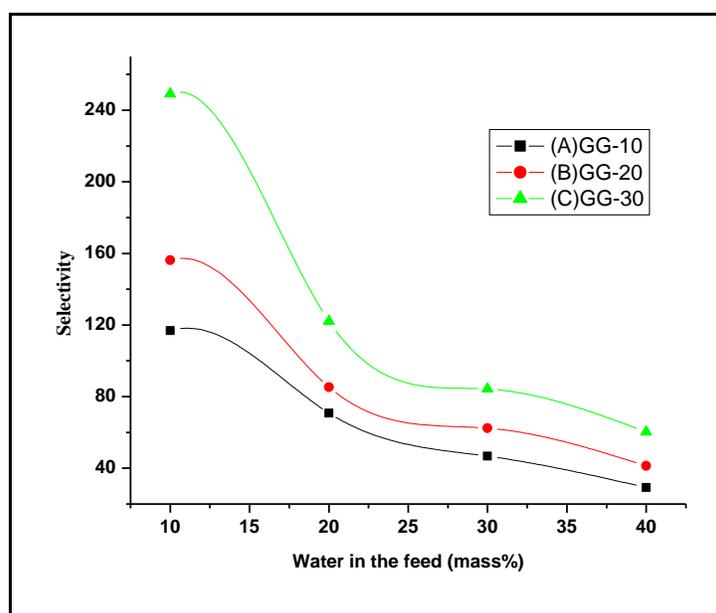


Fig 3.6(b): Variation of separation selectivity (a) with different mass% of water in the feed for (A) GG-10 (B) GG-20 (C) GG-30

CONCLUSION

Incorporation of ZSM-5 zeolite in GG has shown an improvement in the membrane performance while separating water-isopropanol mixtures. Selectivity increased significantly from membranes GG-10 to GG-30 due to a reduction in free volume as well as packing density with increasing zeolite content. However, selectivity decreased drastically up to 20 mass% of water in the feed and remained almost constant when the water concentration increased beyond 20 mass%, signifying that separation selectivity is much influenced at lower composition of water in the feed. Highest separation selectivity is found to be 249.15 for 10 mass% zeolite loading in the membrane at 30°C without sacrificing permeation flux significantly. This was explained on the basis of the cluster formation of water molecules. Molecular transport in the present system not only depend upon morphology of the polymer and free volume of the polymer matrix, but also depends on the cluster formation of water molecules as well as zeolite loading. With regard to temperature effects, permeation flux increased, but selectivity decreased when the temperature increased, suggesting that ZSM-5 filled GG membranes are good for the dehydration of isopropanol.

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