

Separation of isopropanol/water mixtures by Nanocomposite SA-GL membranes: Membrane synthesis, Characterization and Pervaporation performance

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Abstract:

Novel composite membranes of Sodium alginate (SA) and Gelatin (GL) incorporated with 4A zeolite were prepared by solution casting and solvent evaporation method for the use of pervaporation dehydration of isopropanol (IPA) solvent. These mixed matrix membranes (MMM's) were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (X-RD), Thermal Gravimetric Analysis (TGA) and Scanning Electron microscopy (SEM) techniques. FTIR results confirm crosslinking and useful to assess their intermolecular interactions. Crystallinity and thermal stability of these MMM's examined from X-RD and DSC studies. SEM studies indicated the surface morphology of the membranes. Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of membranes, in pure liquids as well as in binary mixtures. Extent of zeolite loading and effect of water/isopropanol feed composition on the pervaporation performance of the membranes were evaluated. Experimental results showed that both flux and selectivity increased simultaneously with increasing zeolite content in the membrane. The blend membrane containing 30 % wt. of 4A zeolite exhibited the highest separation selectivity of at a substantial flux of 0.545 kg/m²h for azeotropic feed composition (87.5 % IPA) and at ambient temperature (30⁰C). These observations were explained on the basis of enhancement of hydrophilicity, selective adsorption and molecular sieving action by the creation of selective openings in the blend matrix through zeolite incorporation.

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

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1. INTRODUCTION:

In recent years there has been increased interest in the use of pervaporation membranes for dehydration water/organic liquid mixtures. A major advantage of this process is the ability to separate azeotropic mixtures such as water/alcohol system. According to the solution diffusion theory, many hydrophilic membranes have been investigated for the dehydration of water/alcohol azeotropic mixtures [1, 2]. Great efforts have been made to develop new effective membranes because it is the key to commercialize the pervaporation process. Mixed matrix membranes (MMM's) usually show good mechanical strength, high flux and separation factor.

Pervaporation (PV) is an important and attractive unit operation among the current research areas in membrane technology for recovery of pure organic compounds from aqueous solutions [3]. In PV, the minor component is preferentially transported through the membrane which is selected on the basis of its affinity for this component in terms of hydrophilic or hydrophobic nature. For the dehydration of organics containing <10% water a hydrophilic membrane is preferred. PV is economical and attractive when the permeating species is present in low concentrations due to the phase change involved [4]. In PV process, mass transfer can be described by the solution–diffusion mechanism. Diffusion through a dense membrane is the rate controlling step since it affects the overall permeation rate owing to the fact that different species have different molecular sizes and consequently varying kinetic diameters. In solution–diffusion model, a study of mass transfer through a dense membrane necessitates independent analysis of sorption and diffusion phenomena.

To improve the performance of the membrane, modification by cross linking significantly decreases the degree of swelling in aqueous solutions [5, 6]. Formation of hydrogen bonds and ionic linkages induces variation in performance parameters [7, 8]. Membrane performance can also be modified by using a porous substrate, which provides mechanical strength, feasibility of scale-up and long life [9-11].

Zeolites are microporous, crystalline aluminosilicates with well defined structures that can reinforce polymer membranes due to their stability, physicochemical property as well as nanoporous morphology [12]. Zeolites preferentially adsorb water molecules when the pore size of zeolite is almost equal to the size of the water molecules. When a membrane is filled with hydrophilic zeolite it gives higher water flux and selectivity over the pristine polymeric membrane [13, 14]. When the sodium ion of zeolite 4A is replaced by other cations such as Ca^{2+} , the zeolite pore size increases to 5 Å. Similarly when it is replaced by K^+ , the pore size reduces to 3 Å [15]. Hydrophilic zeolite 4A with pore size of 0.4 nm that is

marginally larger than the water molecule (0.26 nm) [16] and hence chosen for this study based on its capability to preferentially permeate water molecules.

Sodium alginate (SA), a naturally occurring polysaccharide, extracted from seaweed is a linear copolymer of β -(1-4)-linked D-mannuronic acid and α -(1-4)-linked L-guluronic acid units. It is found to have an excellent performance as a membrane material for pervaporation-based dehydration of organic solvents [17]. Gelatin (GL) is a biodegradable, environmentally friendly 'green' polymer. Gelatin, which has been intensively studied in biomedical areas [18–21], is thought to be a candidate of green polymer for membrane materials. It is well known that blending is an effective and convenient method to improve the performance of polymer materials.

Isopropanol (IPA) is one of the important solvents used on a large scale in the chemical industry in oils, gums, waxes and cosmetics as well as in pharmaceutical laboratories. Further, it is also used in semiconductor and liquid crystal display industries as water-removing agent [22, 23]. Isopropanol is also more effective than ethanol for medical applications. Isopropanol and water form an azeotropic mixture at 87.5 mass% of alcohol [24] and hence, the separation of these mixtures by conventional methods such as solvent extraction, rotavapor or distillation could prove uneconomical for obtaining absolute IPA. Several membrane materials have been modified recently for the selective separation of water from aqueous mixtures of isopropanol. [25].

In the present study, Sodium alginate blending with Gelatin has been explored for pervaporation based separation. 4A zeolites could be a suitable filler for efficient removal of water from isopropanol. SA-GL blend solution was incorporated with a hydrophilic 4A Zeolite in different ratios. The structure, morphology, and thermal properties of these membranes were systematically investigated. Effects of 4A zeolite content on the sorption and diffusion properties of the mixed matrix membranes were discussed.

2. EXPERIMENTAL

2.1. Materials

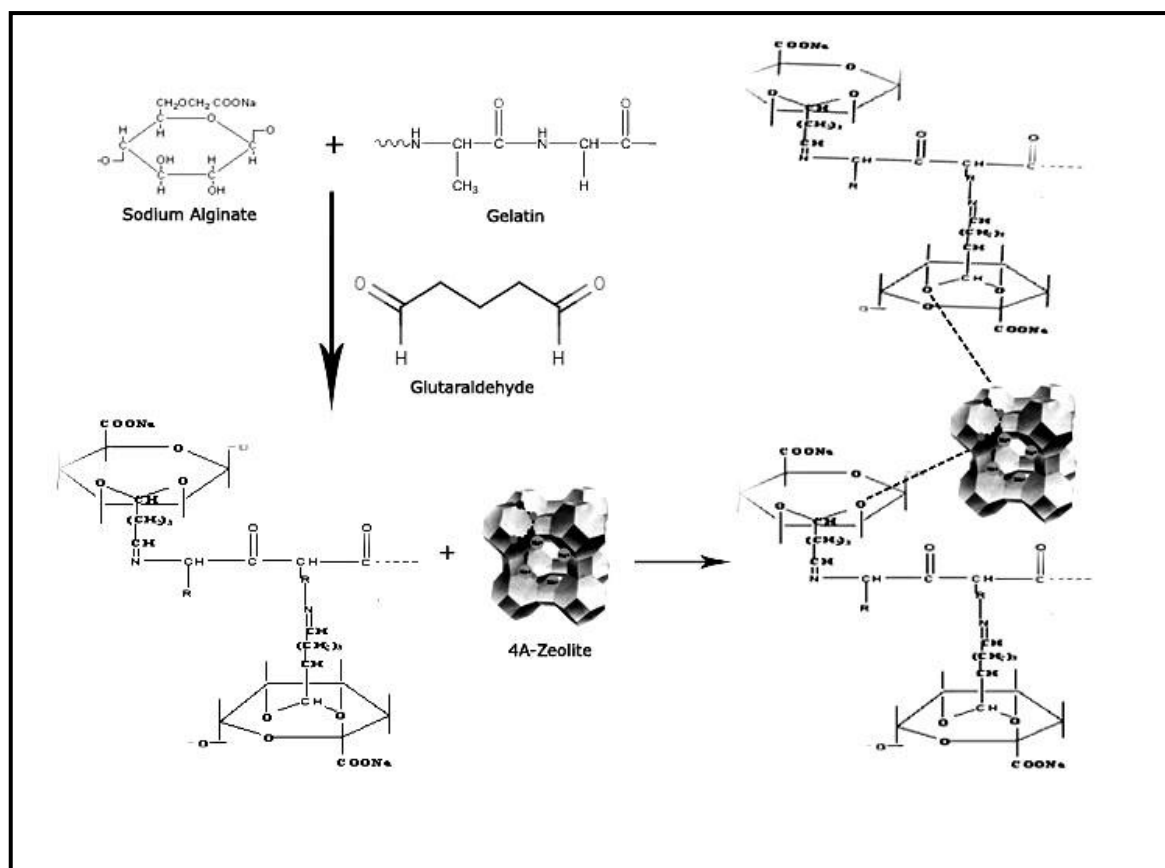
Sodium alginate (SA), Gelatin (GL), Glutaraldehyde (GA) solution (25%), Hydrochloric acid (HCl), Isopropanol (AR- grade sample) and Acetone were purchased from S.d.fine chemicals, Mumbai, India. 4A zeolite (Particle Size- 4A^o) was kindly supplied by M/S Zeolite and Allied products Pvt. Ltd., Mumbai. All the chemicals were of analytical grade samples used without further purification. Deionized water with a conductivity of 20

$\mu\text{S} / \text{cm}$ 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. Preparation SA-GL and 4A zeolite filled blend membranes

4A Zeolite-filled blend membranes of SA/GL were prepared by solution casting method. 2g of SA was dissolved in 45ml of distilled water and 2g of Gelatin was dissolved in 45ml distilled water at room temperature (30°C). These two solutions were mixed through by constant stirring the mixture for 30 min to form a homogeneous solution. After uniform mixing, the solution was filtered to remove any suspended particles. The 10,20 and 30 wt% of 4A zeolite particles (with respect to the weight of the polymer) dispersed in 10 ml DI water separately by sonication for 30 min; these two solutions were separately added to the previously prepared blend solution (of 90 ml) and then the whole mixture was kept under stirring for another 24h. The blend solution was poured onto to a prelevelled glass plate in dust-free atmosphere to cast the membranes with uniform thickness. Membranes thus formed were allowed to dry at ambient temperature and then peeled-off from the glass plate and then crosslinked with glutaraldehyde [2.5ml] containing 85:15 acetone water mixture in which 2.5ml HCl was added as activator and allowed for crosslinking reaction for 2h. Acetone being a non-solvent prevents the initial dissolution of the membrane and water present in the feed leading to swelling in the membrane there by facilitating an easy penetration of GA into the membrane matrix for an effective crosslinking. Crosslinking reaction takes place between the $-\text{OH}$ groups of SA/GL and $-\text{CHO}$ groups of GA because of the formation of ether linkages by eliminating water molecules. The crosslinked membranes were removed from crosslinking bath and washed repeatedly with distilled water to remove the adhered GA and unreacted molecules and then dried in hot air oven at 50°C to constant weight.

Membranes were designated as SA-GL-0, when there was no 4A Zeolite, and 4A Zeolite-fill membranes were prepared in the same manner by dispersing 10wt.%, 20wt.% and 30wt.% of 4A Zeolite and designated as SA-GL-10, SA-GL-20 and SA-GL-30, respectively. Membrane thickness was measured using a micrometer screw gauge and was found to be around $35\text{-}40\mu\text{m}$. The SA-GL blend was cross linked with glutaraldehyde to reduce the extent of swelling. A model scheme of the possible interaction is shown in **Schme.1** which represents the structure of SA-GL crosslinked with glutaraldehyde.



linked with glutaraldehyde.

2.3. Pervaporation experiments:

Schematic pervaporation experimental setup were performed in an apparatus designed in the Dept. of Polymer Science & Technology, S.K.University, Ananthapuramu and it was used elsewhere and the procedure used in pervaporation has been described by many researchers [26, 27]. 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 cm^2 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 (INDVAC, 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 30°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, flux, J_i is calculated as given below:

$$J_i = \left(\frac{W_i}{At} \right) \quad \text{.....(1)}$$

Here W_i represents the mass of water in permeate (kg), A is the membrane area (m^2) and t represents the permeation time (h).

Membrane selectivity, α , is the ratio of permeability coefficients of water to that of isopropanol, which is calculated from their respective concentrations in feed and permeate as given below:

$$\alpha = \left(\frac{y(1-x)}{x(1-y)} \right) \quad \text{..... (2)}$$

Where 'y' is the permeate weight fraction of water and 'x' is its feed weight fraction. In all cases, results were obtained in triplicate but averages (3% standard error) are reported.

2.4. Sorption Experiments

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:

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

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

3. Characterization techniques:

3.1. Fourier Transform Infrared (FTIR) Spectroscopic Studies

Dispersion of different amounts of 4A zeolite in the SA/GL matrix was 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.

3.2. Differential Scanning Calorimetry (DSC) Studies

Differential scanning calorimetry (DSC) thermo grams of crosslinked SA/GL blend membranes were obtained on a differential scanning calorimeter (Model-SDT Q600, USA). Thermo grams were recorded from 30°C to 600°C at a heating rate of 10°C / min in a nitrogen atmosphere.

3.2. X-Ray Diffraction (XRD) Analysis

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 (2 θ) 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.

3.4. Scanning Electron Micrograph (SEM) Studies

Scanning electron micrographs (SEM) of surface were taken for the unfilled SA/GL membrane and zeolite filled SA/GL membranes, using software controlled digital scanning electron microscope–JEOL JSM 5410, Japan.

4. Results and discussion

4.1. FTIR analysis

Fig:1 shows the FTIR spectra of the zeolite loaded and unloaded crosslinked blend membranes (SA-GL-0, SA-GL-10, and SA-GL-20). The FTIR spectrum of zeolite filled membranes, show the carboxylic group at 1650 cm⁻¹ and peaks appearing in the range 3693–

3413 cm^{-1} corresponding to O–H stretching vibrations. This can be confirmed by the presence of a peak at 1195 cm^{-1} due to Si–O groups of 4A Zeolite.

It is observed that as the zeolite content increases the intensity of the peaks did not alter, instead the peaks shifted to lower wavelength from membrane SA-GL-10 to SA-GL-20 (curve b, and c). This is due to the increase of Si–O groups of zeolite [28]. The strong bond at 1726 cm^{-1} could be indicative of the free carboxyl group of sodium alginate. All these evidences ascertain the increase of zeolite incorporation in the membrane matrix.

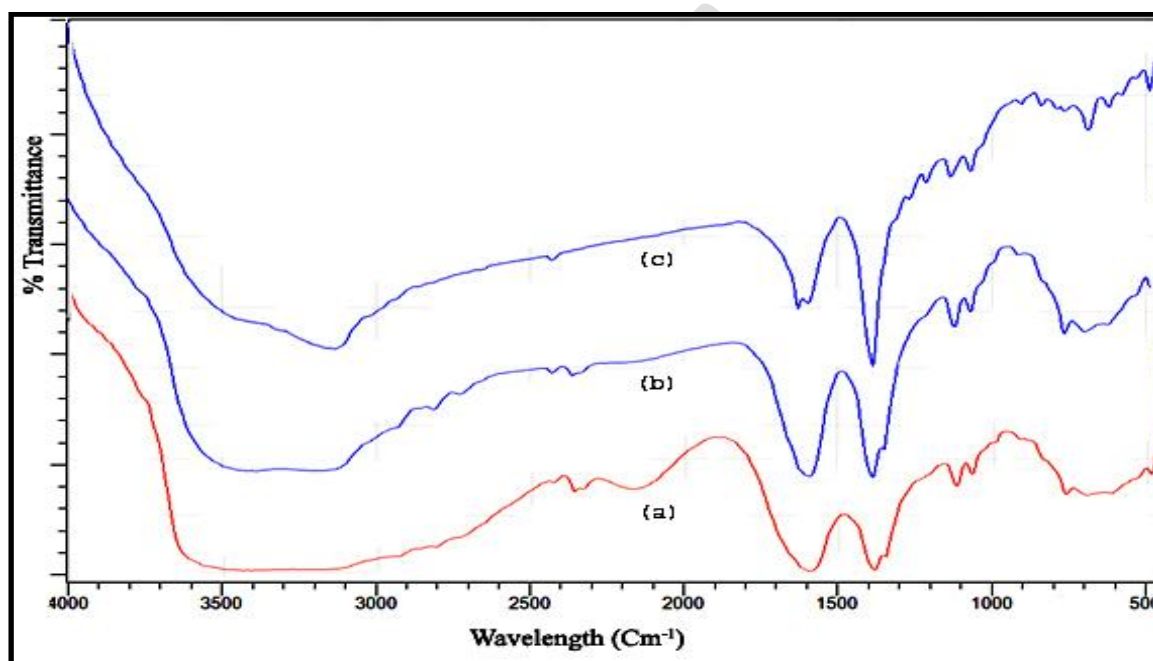


Fig: 1. FTIR patterns of (a) SA-GL-0 cross linked membrane and 4A zeolite loaded (b) SA-GL-10 and (c) SA-GL-20

4.2. Differential scanning calorimetry studies:

DSC thermograms of SA-GL and its MMM's are illustrated in **Fig.2**. In comparison with SA/GL membrane, MMM's exhibited higher T_g values due to the presence of Si–O groups of 4A zeolite. In case of within the MMM's, containing 20w% of zeolite (SA/GL-20) showed higher T_g than the membranes containing lower amount of zeolite (0, and 10). This indicates that addition of zeolite to SA/GL membranes increases the overall thermal stability of the membrane

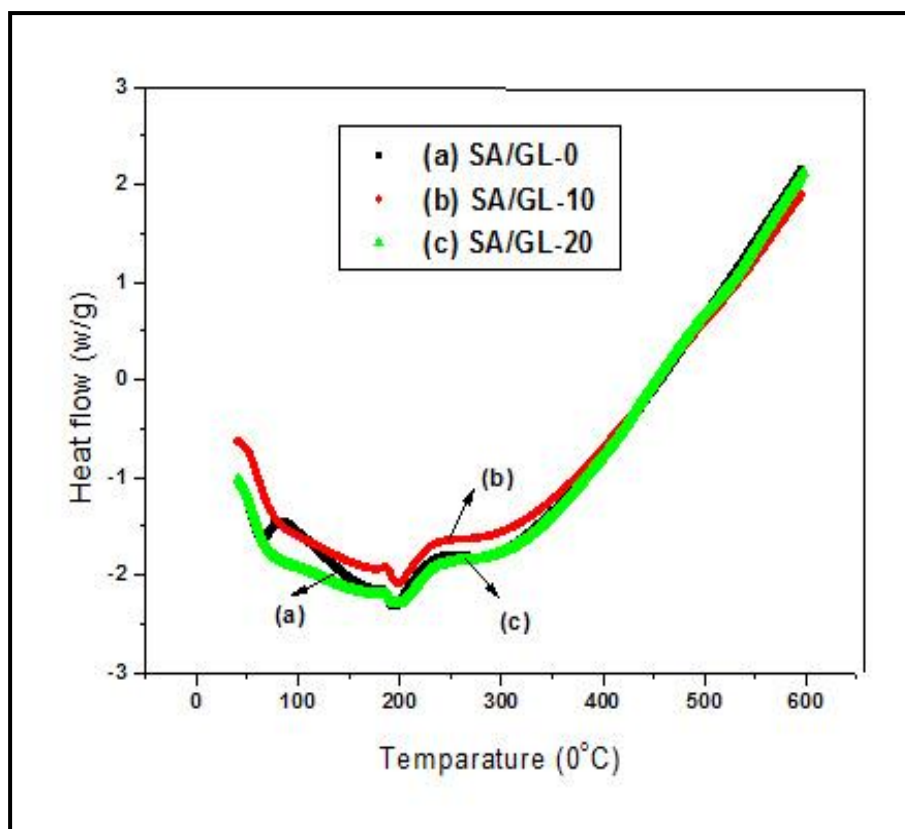


Fig : 2. DSC analysis of Zeolite filled SA/GL membranes: (a) SA/GL-0 (b) SA/GL-10 and (c) SA/GL-20.

4.3. X-ray diffraction studies:

The X-RD patterns of pure 4A zeolite (a), zeolite unloaded (SA-GL-0) (b) and zeolite loaded crosslinked blend membranes (SA-GL-10, SA-GL-20 & SA-GL-30) (c-e) are presented in **Fig:3** The X-ray diffraction patterns of the membranes (c to e) show that as the of zeolite loading increased, peak intensity of the crosslinked membranes decreased at around $2\theta = 20^\circ$. This revealed that the relative crystallinity of SA-GL crosslinked blend membranes decreased with increasing loading of the zeolite which indicates the uniform distribution of the zeolite. But an additional peak has appeared as the zeolite content was increased at around $2\theta = 23^\circ$. This is due to the presence of 4A zeolite in the membranes, whose intensity further increased as the zeolite content increased in the membranes from c to e.

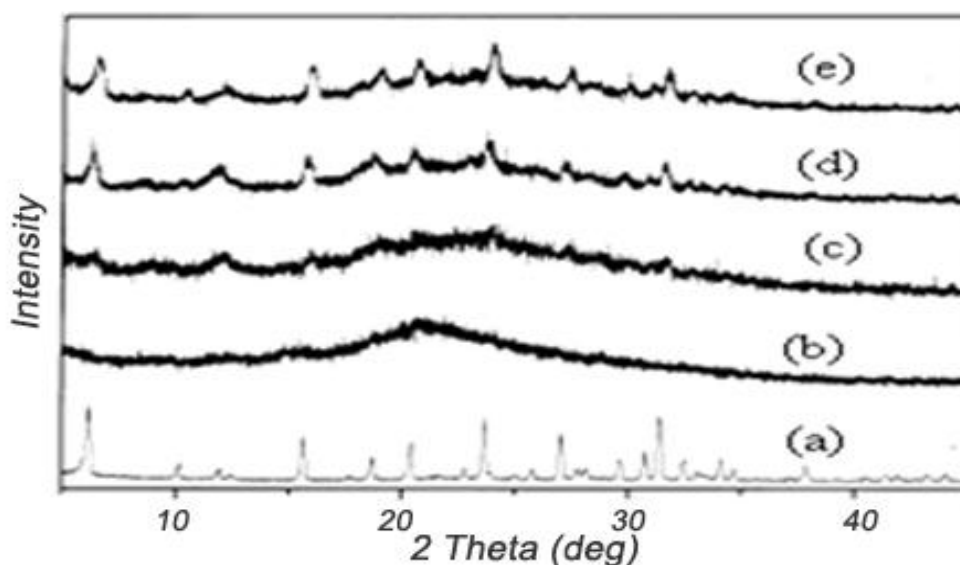


Fig: 3. X-ray Diffraction Patterns of (a) Pure 4A Zeolite (b) SA-GL-0; (c) SA-GL-10; (d) SA-GL-20 and (e) SA-GL-30.

4.4. Scanning electron microscope studies:

Fig .4. represents the SEM micrographs of surface morphology of the SA/GL-0 and its 4A zeolite-incorporated membranes. The SA/GL-0 SEM graph shows the complete miscibility of the blend membrane. But the zeolite loaded micrographs confirm that the zeolite distribution increased from membrane SA/GL-10 to SA/GL-30 (c to d) with increasing zeolite loading. Further it is also observed that the zeolite was distributed evenly throughout the SA/GL matrix this would help to facilitate an easy transport of water molecules through the membranes [29]. Furthermore, the micrographs clearly show that the zeolite crystals were embedded in the membrane matrix, with no voids around them upto 30% zeolite content in the membrane. This ensured that the zeolite-incorporated membranes obtained here were free from possible defects upto 30% zeolite.

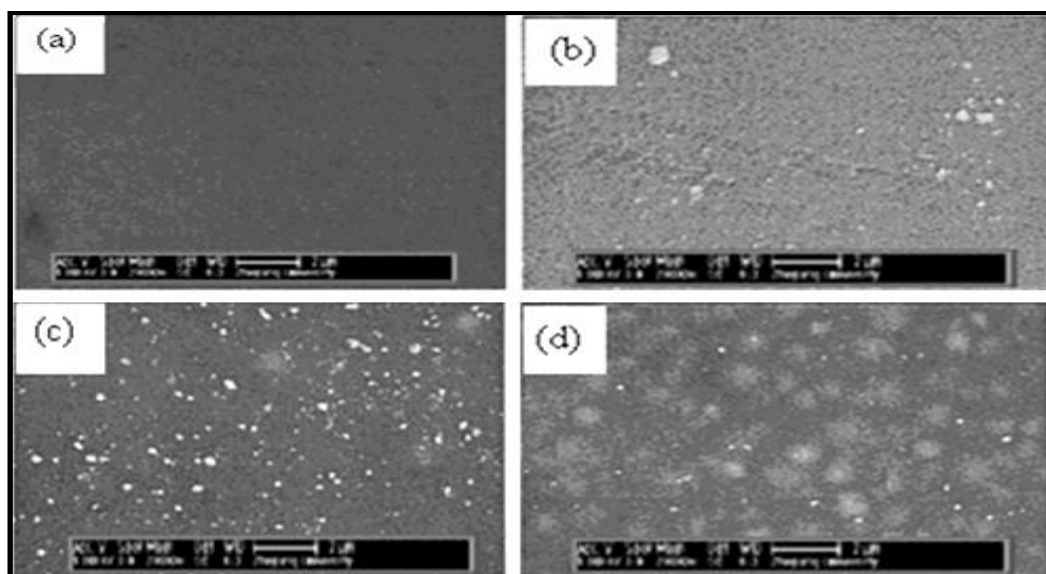


Fig 4: SEM micrographs of surface SA-GL-0 (a), SA-GL-10 (b), SA-GL-20 (c) and SA-GL-30 (d).

4.5. Effect of 4A 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**. **Fig.5** present the results of % degree of swelling of SA-GL-0, and it's MMM's filled with 4A zeolite membranes in different mass % of water/IPA mixture at 35°C.

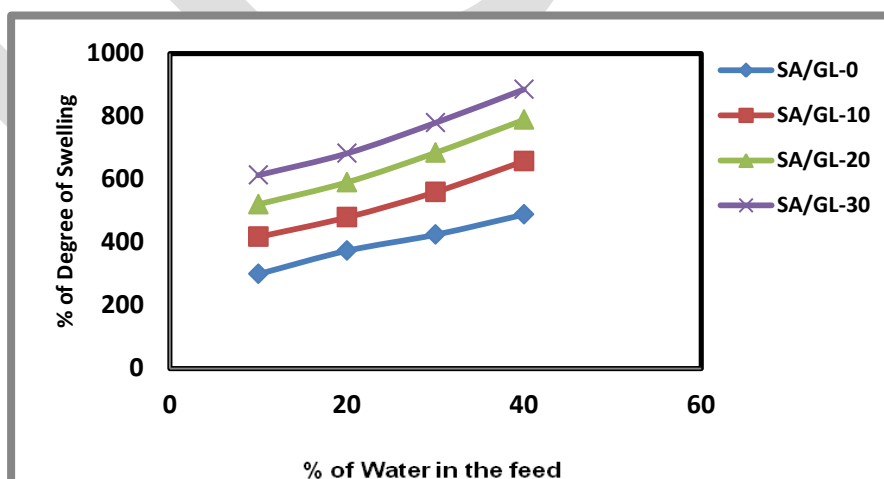


Fig: 5. Plots of degree of swelling of zeolite unfilled (SA/GL-0) and 4A zeolite incorporated membranes (SA/GL-10, SA/GL-20 and SA/GL-30) Vs % of water in the feed

The results in **Table-1** indicate that the swelling ratio of SA/GL increases with increase in the zeolite content upto 30%. Both 4A zeolite and SA-GL-0 blends are

hydrophilic, so 4A zeolite-filled MMM's can be used effectively in dehydration of IPA by PV, mainly at azeotropic mixtures. The zeolite-filled membranes are maintained by the strong interaction between 4A zeolite and SA/GL-0. During the PV processes, when water molecules diffuse into the membrane, the membranes become swollen; swelling leads to increase the interaction between 4A zeolite membranes and SA/GL-0; this might result in the formation of some tiny cracks developing at the interface between the zeolite and SA/GL, which allows water molecules to pass through. This also confirms the reason that the 30 mass % 4A zeolite-filled SA/GL-30 membranes show good stability through the PV process.

Table:1 Percentage of Sorption data of IPA/Water mixtures in SA/GL and Zeolite filled membranes at 30°C.

% of Water in the feed	% Sorption in different membranes			
	SA/GL-0	SA/GL-10	SA/GL-20	SA/GL-30
10	300	374	425	489
20	418	480	560	658
30	521	591	685	790
40	614	683	780	886

5. Pervaporation studies

5. (i). Influence of 4A zeolite loading on PV Performance:

In the PV process, the overall performance of the membranes can be assessed based on the flux and selectivity. In order to calculate these parameters the developed membranes were subjected to a Pervaporation experiment with 10 to 40% of water in the feed. The resulting data of both flux and selectivity are presented in **Table:2**.

The amount of zeolite added into the polymer matrix is an important parameter in the preparation of MMM's [30-32]. Zeolites that are having molecular sieving properties [33, 34] enhance the selectivities of polymeric membranes either because of their intrinsic properties or by modifying the membrane morphology [31, 35].

The effect of zeolite loading between 10-30% in SA/GL was tested, since addition of zeolite gave varying flux and selectivity for the MMM's. The MMM's showed improved performance than that of SA-GL-0 membrane, this may be due to the filler-polymer and membrane-solvent interactions. The effect of zeolite content on membrane performance was investigated for feed containing different amounts of water with increasing loadings of 4A zeolite. Both flux and selectivity were increased upon increasing zeolite content up to 30% in the membrane; the reason would be the hydrophilic nature and pore size (pore size of 4A

zeolites is smaller than IPA molecules and larger than water molecules) of 4A zeolite, which absorbs large amount of water through the pores, thereby creating free channels for transportation of water molecules through the membranes. Hydrophilic-hydrophilic interactions would reject the organic (in the present case IPA) component of the feed, but allows water molecules. This leads to an increase in the flux with increasing the zeolite loadings up to 30% in the membrane for all the studied range concentrations of water in the feed as shown in **Fig: 6 (a & b)**. A strong interaction between 4A zeolite (hydrophilic) and water molecules would allow water to transport through the membrane at 30w% zeolite loading. Hence, higher water flux of $0.584 \text{ kg/m}^2\text{h}$ obtained at a feed concentration of 40 wt% in the water/IPA mixture.

Table: 2.Pervaporation results of Water/IPA mixtures for different membranes at 30°C.

S.No.	% of water in feed	Water flux J [$\text{kg m}^{-2} \text{h}^{-1}$]	Selectivity (α)
SA/GL– 0			
1	10	0.081	4680
2	20	0.162	2365
3	30	0.252	1480
4	40	0.384	1123
SA/GL – 10			
1	10	0.097	5612
2	20	0.182	3468
3	30	0.325	2801
4	40	0.437	1489
SA/GL – 20			
1	10	0.106	6325
2	20	0.253	4682
3	30	0.395	3890
4	40	0.502	2687
SA/GL– 30			
1	10	0.112	6975
2	20	0.280	5841
3	30	0.480	4960
4	40	0.584	3885

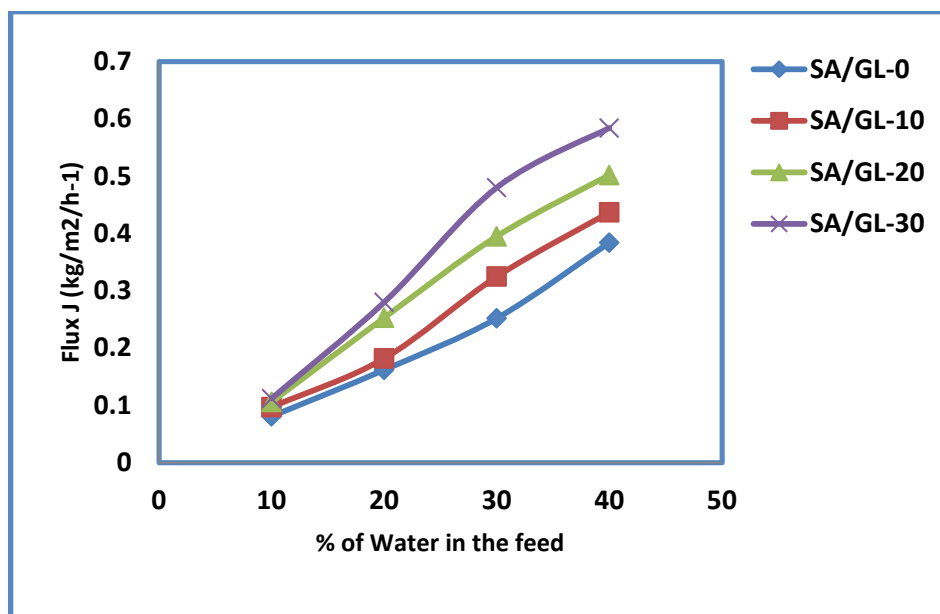


Fig: 6. (a). Plots of water flux Vs weight % water in feed SA/GL-0 and SA/GL incorporated 4A zeolite membranes.

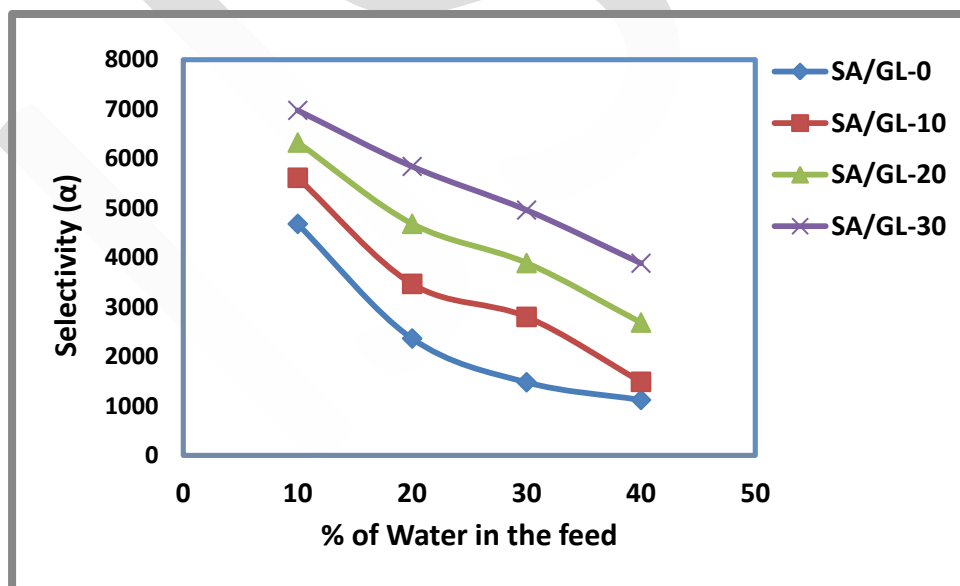


Fig: 6. (b). Plots of Selectivity Vs weight % water in feed SA/GL-0 and SA/GL incorporated 4A zeolite membranes.

5. (ii). Effect of feed water composition:

In PV process, the overall selectivity of a membrane is generally explained on the basis of interaction between the membrane and permeating molecules, molecular size of the permeating species. Fig. 6.a displays the effect of water compositions on the flux for all the membranes prepared with different amounts of 4A zeolite in SA-GL matrix and the results are also tabulated in **Table 2**. It is observed that the flux of water in the feed increased drastically for all water/IPA compositions under the studied zeolite concentration range (10 to 30 mass%). At higher concentration of water in the feed, the membranes swell greatly due to the formation of a strong interaction between the membrane and water molecules. This might have led to allow water molecules to pass through the membranes [36]. As a result, flux of water increases drastically at higher concentration of water in the feed, irrespective of the amount of zeolite loading in the membrane matrix.

On the contrary, the selectivity decreased significantly from 10 to 40 upon increasing the water content in the feed. This can be clearly observed from **Fig. 6.b** showing the variation of selectivity as a function of wt% of water in the feed in the membrane for different mass% of 4A zeolite (10-30 wt %) in the membrane. Generally, with increasing the water content in the feed compositions, the permeation flux increases and selectivity decreases [37]. Similar observations were also observed in the present case with increasing water content in the feed composition. The highest flux observed for SA-GL-30 is 0.584kg/m²/h at a feed composition of 40 wt% feed mixture. Whereas, highest selectivity observed is 6975 for SA-GL-30 at 10wt% of water a in the feed.

6. Conclusions

The effect of zeolite content significantly influenced the characteristics of SA/GL membrane. Membranes containing lower amount of 4A zeolite has the weak hydrogen-bonding interactions between SA/GL and zeolite substantially loosed the blend polymer chains, and the free volume cavity size was increased correspondingly. The transport of IPA in all the membranes was mainly controlled by the diffusivity. Hydrophilic zeolite preferentially adsorbed IPA, leading to increase in water uptake, swelling and decreased IPA permeability.

The IPA permeability was slightly decreased with the zeolite content, indicating that only a small portion of IPA passed through the zeolite filled membrane. The IPA

permeability of the MMM's reduced with increase in zeolite content, most probably due to the increase in diffusion resistance. The MMM's membranes displayed desirable thermal and mechanical stabilities within the working temperature range.

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