

**RESEARCH ARTICLE****DEVELOPMENT OF SODIUM ALGINATE-13X ZEOLITE-FILLED MIXED MATRIX MEMBRANES FOR PERVAPORATION DEHYDRATION OF ISOPROPANOL****<sup>1</sup> H.Sudhakar,<sup>1</sup> Y.Maruthi,<sup>1</sup> P.Kumara Babu, <sup>4</sup> M.Naveen,<sup>3</sup> B.Chandra SekharaRao,<sup>2</sup> U.Sajankumarji Rao,<sup>2</sup> Sudbha.M.C.S.,<sup>1\*</sup> K. Chowdoji Rao**<sup>1</sup>Department of Polymer Science & Technology, Sri Krishnadevaraya University Anantapuramu, India<sup>2</sup>Department of chemistry, Sri Krishnadevaraya University, Anantapuramu, India<sup>3</sup>Department of Biotechnology, Sri Krishnadevaraya University, Anantapuramu, India<sup>4</sup>AAP Pharma Technologies India Pvt Ltd., Genome Valley, Alexandria Knowledge Park, Turkapally, Shameerpet (M), Ranga Reddy, India**ARTICLE INFO****Article History:**Received 12<sup>th</sup>, April, 2014Received in revised form 22<sup>th</sup>, April, 2014Accepted 15<sup>th</sup>, May, 2014Published online 28<sup>th</sup>, May, 2014**Key words:**

Pervaporation, sodium alginate, glutaraldehyde, 13X zeolite, isopropanol-water.

**ABSTRACT**

Novel polymeric composite membranes were prepared by solution casting method by the incorporation of different amounts of 13X zeolite into Sodium Alginate. Membranes were cross-linked with glutaraldehyde and tested for pervaporation dehydration of isopropanol at 30<sup>o</sup> C. The mixed matrix membranes were characterized by FT-IR, X-RD, TGA, DSC and SEM, and we found that flux and selectivity increased systematically with increasing amount of zeolite in the SA matrix. In case of zeolite membrane containing 30wt. % highest selectivity 2300 was observed of which was attributed to the combined effects of molecular adhesion between zeolites and SA matrix as well as enhanced hydrophilicity due to the zeolite.

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**INTRODUCTION**

Pervaporation (PV), a membrane separation process, has gained widespread acceptance in the chemical industry as an effective process for the separation of azeotropic mixtures. This technology will be more economical compared to conventional separation processes, such as distillation or adsorption, since it is more energy efficient. In addition, it is more environmental friendly because unlike in distillation, no third component is added. On the other hand, zeolite membrane has additional advantages in separating mixtures with molecular sieve differences. Therefore, pervaporation with zeolite membrane has attracted great interest in many important industrial processes. Pervaporation with zeolite membrane has been more successful in dehydrating organic compounds than separating organic compounds from organic mixtures. For the past ten years, significant progress has been made in understanding separation mechanisms of zeolite membranes. Among many kinds of materials, zeolites are promising candidates due to their high-performance, because of the unique characteristics of zeolite crystals such as molecular sieving, ion exchange, selective adsorption and catalysis (Lin *et al.*, 2000). Although there are many papers on the synthesis and gas permeation of various kinds of zeolite membranes, only a limited number of publications deal with pervaporation studies (Okamoto *et al.*, 2001; Kondo *et al.*, 1997; Kumakiri *et al.*, 1999; Kita *et al.*, 1997; Sano *et al.*, 1994, 1995).

Zeolite membranes have several advantages over the conventional plain polymer membranes and are suitable for molecular sieving-based separations when used in pervaporation (PV) separation of aqueous-organic mixtures (Shah *et al.*, 2000; Cui *et al.*, 2003; Bowen *et al.*, 2004; Bein

1996). Numbers of studies have been devoted to molecular based separations using zeolite-filled polymer membranes for gas (Yong *et al.*, 2001; Ersolmaz *et al.*, 2000; Jia *et al.*, 1991) and liquid separations (Moermans *et al.*, 2000; Boom *et al.*, 1998; Adnadjevi *et al.*, 2003). There have been earlier reports by Koros and co-workers (Moore *et al.*, 2005; Vu *et al.*, 2003; Zimmerman *et al.*, 1997) on mixed matrix membranes used in membrane applications. Isopropanol forms an azeotrope at 12.5 mass% of water and hence, its separation by PV would be more advantageous than the conventional distillation. Previous reports on PV separation of water-isopropanol mixture through the modified NaAlg membranes did not offer high selectivity to water (Toti *et al.*, 2004; Moon *et al.*, 1999). However, Okumus *et al.* have reported that, incorporation of zeolite A and 13X zeolite into cellulose acetate (CA) and polyacrylonitrile (PAN) have caused a decrease rather than an increase in separation factor due to porous cave-like structures as reflected by SEM examination results, and increased porosity subsequently lead to an increase in the flux (Okumus *et al.*, 1994; Okumus *et al.*, 2003). 13X Zeolite have been used in the development of NaCMC/PVA mixed matrix membranes because of their intrinsic properties, including their thermal resistivity and chemical stability helps to improve their pervaporation performance (Venkata Prasad *et al.*, 2012). Deficiencies in both polymeric and purely molecular sieving media suggest the need of the development of composite membranes.

However, in this investigation, it is demonstrated by incorporating 13X zeolite into SA membrane, one could achieve water selectivity as high as 2300. The present study, PV performance of the SA membranes loaded with, 10, 20 and 30 wt. % of 13X zeolite is compared with the SA membrane in

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separating isopropanol–water mixtures. PV results are discussed in terms of the extent of molecular sieve loading.

## Experimental

### Materials

Sodium alginate (SA) was purchased from Loba Chemicals, Mumbai, India. Isopropanol (IPA), glutaraldehyde (GA), and hydrochloric acid were all purchased from s.d. fine Chemicals, Mumbai, India. 13X zeolite was kindly supplied by M/S Zeolite and Allied products Pvt. Ltd., Mumbai. All the chemicals were of reagent grade and used without further purification. Deionized water generated by reverse osmosis system in the laboratory was used throughout the research work.

### Membrane preparation

A solution of SA (2 wt %) was prepared by stirring vigorously and then filtered to separate any undissolved matter and get bubble-free solution. The resulting solution was then cast onto a glass plate with the aid of a doctor's blade in a dust-free atmosphere at room temperature for 1-2 days. The completely dried membrane was subsequently peeled-off and designated as SA-0. To prepare 13X zeolite filled SA membrane, a known amount of 13X zeolite was added into the SA solution. The amount of SA solution was kept constant for each membrane. The zeolite filled solution was stirred for about 2 h and then it was kept in an ultrasonic bath for 30 mins at 30°C to break the aggregated crystals of 13X zeolite and enhance its dispersion in the polymer matrix. The resulting solution was poured on to a glass plate and the membrane was dried as mentioned above. The prepared membranes were then cross linked 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 amount of 13X zeolite with respect to SA was varied 0, 10, 20 and 30 mass%, and the membranes thus obtained were designated as SA-0, SA-10, SA-20 and SA-30 respectively. The SA was cross linked with glutaraldehyde to reduce the extent of swelling. A model scheme of the possible interaction is shown in Figure 1 which represents the structure of SA cross linked with glutaraldehyde.

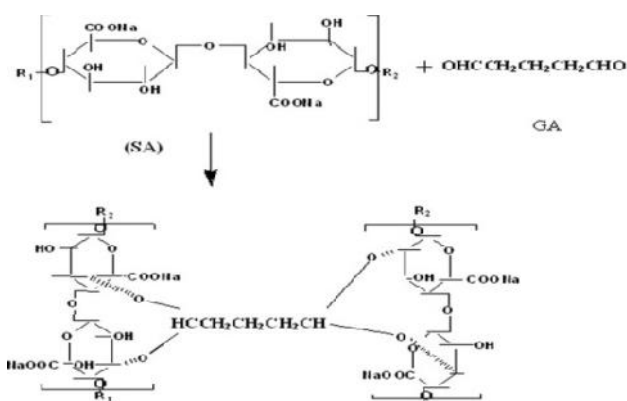


Figure 1 Schematic representation of SA cross linked with glutaraldehyde.

## Membrane Characterization

### Fourier transform-infrared (FTIR) spectroscopic studies

The FTIR spectrum of SA(uncross linked), SA-0 and 13X zeolite filled composite cross linked membranes were scanned

in the range between 4000 cm<sup>-1</sup> and 500 cm<sup>-1</sup> by using ABB Bomen model MB-3000, Canada.

### X-ray diffraction (XRD) analysis

A Siemens D 5000 (Germany) X-ray diffractometer was used to study the solid-state morphology of membranes incorporated with zeolites in different compositions. X-rays of 1.5406 Å<sup>0</sup> wavelengths were generated by a Cu-K source.

### SEM Studies

Scanning electron micrographs (SEM) of the surface and the cross-section of zeolite filled SA membranes; were taken using a software controlled digital scanning electron microscope–JEOL JSM 5410, Japan.

### Thermal analysis

Thermal stability and DSC curves of SA and their mixed matrix membranes were examined using TA instruments sequential thermal analyzer (Model: SDT Q600, U.K) in the temperature range of 25–600 °C at a heating rate of 10 °C/min, with nitrogen flushed at 100 ml/min. The samples were subjected to TGA and DSC both before and after incorporation of zeolite to determine the thermal stability and decomposition characteristics.

### Mechanical properties studies

Mechanical tests were performed at room temperature using the tensile testing machine (Shimadzu make and AGS-10 kNG model) with an operating head load of 5kN and keeping speed of testing was set at the rate of 12.5 mm/min. Cross-sectional area of the sample of known width and thickness was calculated. Tensile strength was calculated using the equation.

$$\text{Tensile strength} = \frac{\text{Max load}}{\text{Cross sectional area}} \text{ N/mm}^2 \quad (1)$$

### Pervaporation experiments

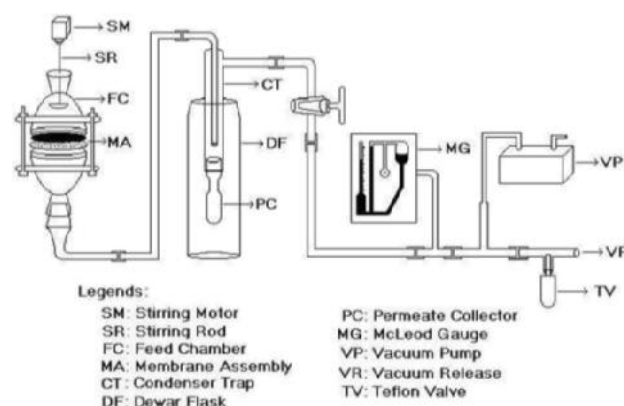


Figure 2 Schematic diagram of laboratory pervaporation set-up.

Pervaporation experimental apparatus is shown in Figure 2. The equipment used to perform the PV experiments remained the same as described earlier (Sudhakar *et al*, 2010; 2011; 2013). Flux ( $J_i$ ) was calculated using the Equation 2. The feed was kept in continuous stirring mode using an overhead stirring motor to minimize the concentration polarization.

$$i = \frac{W_i}{At} \quad (2)$$

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

The selectivity,  $\alpha$ , of the 13X zeolite-filled membranes was evaluated by Equation 3, which is the ratio of permeability coefficient of water to that of isopropanol, which is calculated from their respective wt. concentrations in feed and permeate as given below:

$$\alpha = \frac{y(1-x)}{x(1-y)} \quad (3)$$

Where  $y$  is the permeate weight fraction of water and  $x$  is its feed weight fraction.

### Sorption experiments

Interaction of the membranes with the pure liquid components of the feed mixture was determined by gravimetric sorption experiments. Dried membranes of known weight were immersed in different IPA-water mixtures for 48 hrs. When the sample attained constant weight, the membrane was carefully wiped off with filter papers to remove surface liquid, and then quickly weighed. Degree of swelling was calculated as:

$$\text{Degree of swelling} = \frac{M_s}{M_d} \quad (4)$$

Where  $M_s$  is mass of the swollen membrane in (g) and  $M_d$  is mass of the dry membrane in (g). The percent sorption was calculated using the equation:

$$\% \text{ Sorption} = \left[ \frac{M_s - M_d}{M_d} \right] \times 100 \quad (5)$$

## RESULTS AND DISCUSSION

### FTIR analysis

Figure 3 shows the FTIR spectra of the SA (uncross linked), SA-0 and 13X zeolite filled cross linked membranes. Figure 3(a) of SA, two strong absorption peaks at 1609 and 1416  $\text{cm}^{-1}$  are seen. They can be assigned to the antisymmetric and symmetric stretching vibration of the carboxyl ate group, respectively (Rao *et al*, 1963; Sartori *et al*, 1997). It is noticed from this spectrum, that a peak at 3320  $\text{cm}^{-1}$  exhibits, which corresponds to O-H stretching vibrations of plain SA. The curve, at 1630  $\text{cm}^{-1}$  has a broad band, which refers to carboxyl groups of  $-\text{COONa}$  of uncross linked SA. The weak band at 2930  $\text{cm}^{-1}$  which corresponds to aliphatic C-H stretching and two strong bands at 1090 and 1034  $\text{cm}^{-1}$  which corresponds to C-O stretching are noticed.

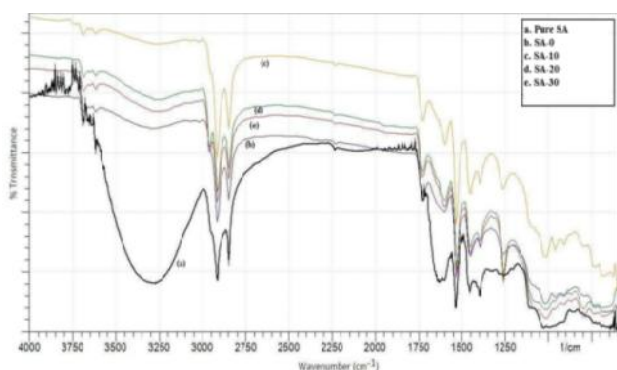


Figure 3 FTIR patterns of pure (a) SA (uncross linked) (b) SA-0; (c) SA-10; (d) SA-20 and (e) SA-30 13X zeolite cross linked membranes.

In cross linked curve Figure 3(b) the peak observed at 3320  $\text{cm}^{-1}$  confirms the utilization of O-H groups of SA during cross linking reaction. A sharp peak at 1270  $\text{cm}^{-1}$  refers to C-O stretching vibration due to cross linking reaction. Figure 3(b-d) shows a strong peak observed at around 1020  $\text{cm}^{-1}$  which is

assigned to C-O stretching of SA. The Si-O band (Chavasit *et al*, 1988) also appeared at the same wavelength upon loading zeolite in the polymer matrix and hence, C-O and Si-O bands are almost overlapping in the spectra, it is noticed that the transmittance decreases with increases of 13X zeolite content in the SA membranes. This can be attributed that molecular cohesion between SA and zeolites were more adhesion which interm decreases in the transmittance.

### X-ray diffraction

In general, it is important to take into account the crystalline changes in the polymer matrix which occurs due to the presence of zeolites. Figure 4 shows that the gain in crystallinity due to the incorporation of zeolites where a progressive increase in peak intensity is observed with increasing zeolite.

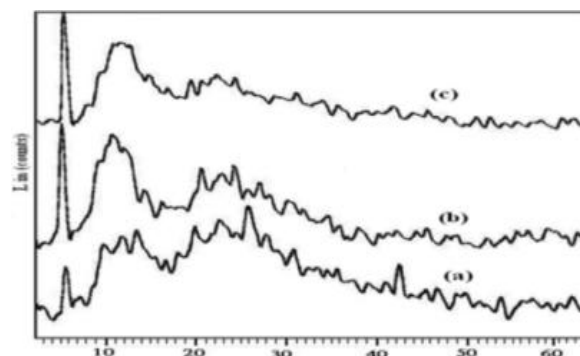


Figure 4 Wide angle X-ray Diffraction Patterns of Zeolite filled Sodium alginate membranes: (a) SA-10; (b) SA-20; and (c) SA-30.

### SEM analysis

Figure 5 shows the typical surface SEM micrograph of zeolite filled SA membranes in which zeolite particles are distributed homogeneously throughout the SA matrix. Figure 5A and 5B represent surface and cross-section of the zeolite filled SA membranes respectively. This uniform distribution of zeolite particles in SA matrix facilitates an easy penetration of water.

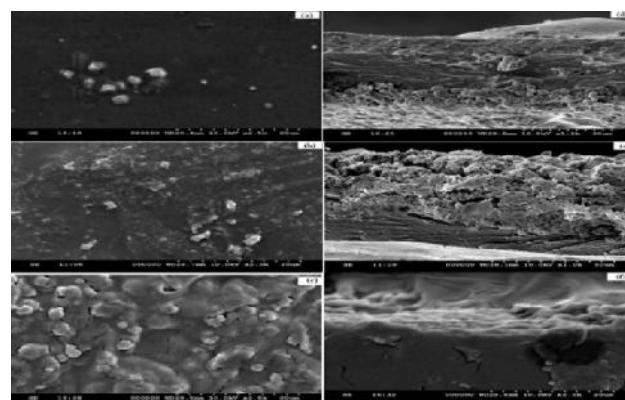


Figure 5 (A) SEM pictures Surfaces of the: (a) SA-10; (b) SA-20; (c) SA-30. (B) SEM pictures of the (cross section): (d) SA-10; (e) SA-20; (f) SA-30.

### TGA studies

Figure 6 displays thermal degradation of SA-0 and zeolite filled membranes by Thermo gravimetric analysis. From the Table 1 it is noticed that with increase in zeolite content in the polymer matrix, % wt. loss decreases. This is due to the increase in crystallinity with increase in zeolite content in composite membrane. The trends in the thermo gravimetric stability

(Table 1) of various zeolite membranes are as follows: 10 % zeolite < 20 % zeolite < 30 % zeolite. This may due to the more adhesion between SA and zeolite with increase in zeolite concentration in the composite membrane.

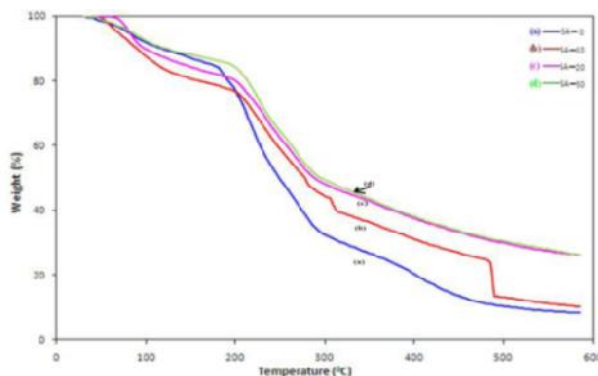


Figure 6 TGA analysis of (a) SA- 0; (b) SA-10; (c) SA- 20; (d) SA-

Table 1 Thermo gravimetric Stability Data of SA and 13X Zeolite Composite membranes.

Materials	% weight loss (temperature °C)			
	150	250	350	550
SA	87.1	49.6	26.7	8.9
10 % zeolite	79.2	55.9	28.1	3.8
20 % zeolite	81.3	65.5	46.9	30.4
30 % zeolite	97.8	75.7	55.3	37.7

**DSC studies**

DSC thermograms of SA-0 and zeolite filled SA-0 membranes illustrated in Figure 7. SA-0 membrane shows a sharp endothermic melting point 190°C. The melting endotherm range shifted to higher values, i.e. 210–230 °C in zeolite filled SA membranes with increase in zeolite content in the composite membranes which is in accordance with the conclusion drawn from TGA studies.

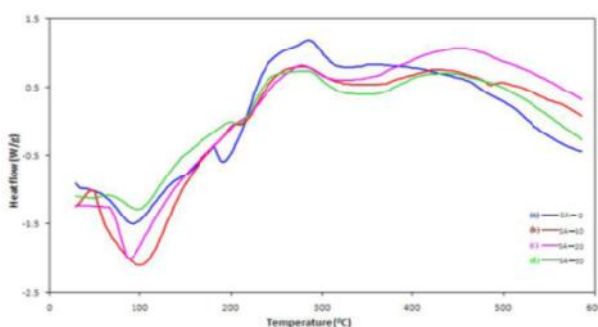


Figure 7 DSC analysis of (a) SA- 0; (b) SA-10; (c) SA- 20 and (d) SA - 30

**Mechanical properties**

SA-0, SA-10, SA-20 and SA-30 cross linked composite membranes exhibited tensile strengths of 16.42, 19.83, 21.38 and 22.87N/mm<sup>2</sup>, respectively, calculated from the stress–strain curves, which showed an enhancement in mechanical strength after incorporation of 13X zeolite.

**Membrane sorption properties**

Figure 8 compares the plots of %degree of sorption of plain SA and zeolite incorporated composite membranes at 30°C for 10–50 wt. % water containing feed of water. Notice that membranes are swollen to a higher extent in IPA-water feeds

due to stronger interactions (hydrogen bond type) between IPA and water for all the feed mixtures. Also, at the same time from the Figure 8 it is noticed that zeolite incorporated SA membranes were swollen to a lesser extent in all the feeds mixtures than the SA-0 membrane.

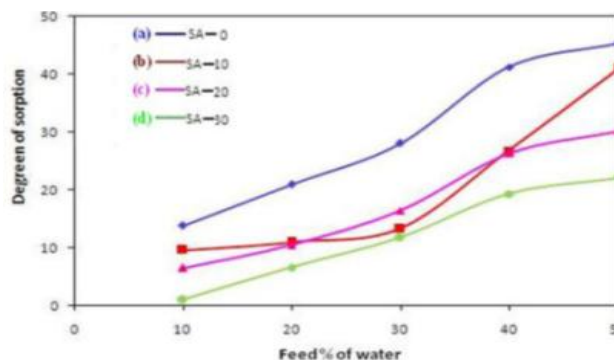


Figure 8 Plots of Degree of sorption vs. Percentage of water (a) SA-0; (b) SA -10; (c) SA -20 and (d) SA -30 incorporated 13X zeolite cross linked membranes.

**Pervaporation properties**

Membrane performance was studied for dehydration of IPA at 30°C and displayed in Table 2 and Figure 9. It is observed that with an increase in the feed water content, in use of all the membranes under consideration it is observed that there is a decrease in the permeate water content, and increase in permeation flux. These results are possibly attributed to the enhancement of water sorption in the polymer matrix. When water is sorbed in the polymer matrix, it swells the matrix, especially for the hydrophilic polymers with flexible structures. Therefore, it is reasonable to observe an increase in flux and a decrease in the permeate water content for all the membranes with increase feed water content.

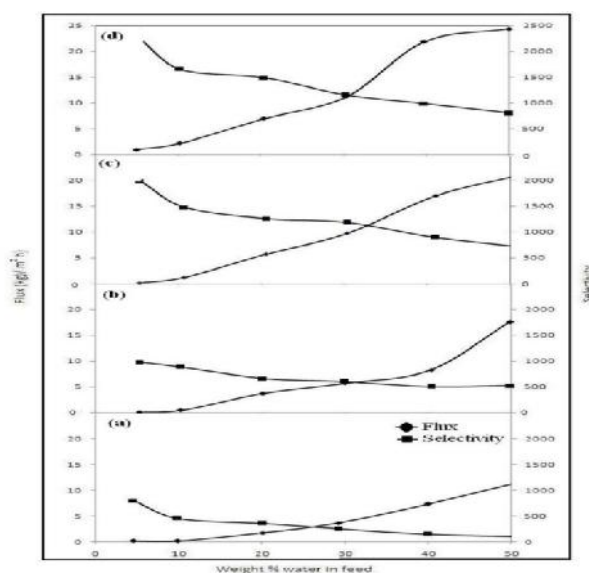


Figure 9 Effect of feed compositions on pervaporation performance of (a) SA- 0; (b) SA-10; (c) SA- 20; (d) SA- 30 incorporated zeolite crosslinked membranes.

Figure 9 shows the flux and selectivity vs water concentration for the SA and composite membranes. In the entire composition range, water permeates predominantly and water is preferentially permeable through the membranes. The fluxes increase with water concentration in the feed solution. Owing to the high hydrophilicity of the SA material, the SA

membranes swell more significantly in the solution with high water content. As the water concentration in feed increases, the amorphous regions of the membrane are more swollen, and the polymer chains become more flexible and increase the space available for diffusion, thus increase in flux is observed.

**Table 2** Pervaporation data of IPA and water mixtures at 30°C permeate pressure (1 mmHg).

Feed compositions		Permeate compositions (wt %)		Selectivity	Flux (kg/m <sup>2</sup> h)
Water(x)	IP(1x)	Water (y)	IPA (1-y)		
SA -0					
4.561	95.439	98.214	1.786	798.53	0.18
9.865	90.135	96.785	3.215	455.82	0.20
20.123	79.877	94.687	5.313	359.54	1.78
29.145	70.855	93.749	6.251	253.89	3.65
40.012	59.988	89.357	10.643	152.36	7.38
51.236	48.764	86.679	13.321	102.89	11.68
SA -10					
5.321	94.679	98.568	1.432	976.38	0.02
10.325	89.675	98.018	1.982	885.36	0.45
20.148	79.852	96.258	3.742	661.25	3.65
30.012	69.988	93.689	6.311	601.25	5.68
40.328	59.672	91.238	8.762	504.68	8.24
49.856	50.144	88.985	11.015	519.68	17.5
SA -20					
5.289	94.711	99.296	0.704	1987.28	0.09
10.631	89.369	99.123	0.877	1475.68	1.19
20.485	79.515	97.698	2.302	1258.36	5.68
30.254	69.746	95.892	4.108	1189.36	9.68
40.948	59.052	93.012	6.988	896.78	16.98
50.658	49.342	90.125	9.875	714.57	20.89
SA -30					
4.968	95.032	99.758	0.242	2300.87	0.98
10.198	89.802	99.012	0.988	1658.35	2.19
20.389	79.611	97.889	2.111	1487.36	6.97
30.284	69.716	96.532	3.468	1157.38	11.25
39.684	60.316	96.987	3.013	987.34	21.87
50.00	50.00	93.257	6.743	801.32	24.35

The data for selectivity as a function of feed concentration of water are also given in Table 2 and exhibited in Figure 9. Interestingly, high selectivity for water removal is observed at high isopropanol concentrations. Hence, the membranes are effective especially for the dehydration of high concentrations of isopropanol including isopropanol- water azeotrope. This is what we desired for the proposed separation using SA based membranes. The decrease in selectivity is noticed with increase in water content in the feed as seen in Figure 9.

The increase in the isopropanol concentration restricts the degree of swelling of the membranes, thus reducing the diffusivity of the permeating species. Since the molecular size of isopropanol is greater than those of water, the flux of the former is more affected than that of the latter.

At 30° C, the selectivity for the SA and SA -30 composite membranes for 90 wt. % isopropanol feed concentration were 455 and 1658, respectively. When the isopropanol concentration was increased to 95 wt. %, the selectivity for the SA and SA -30 composite membranes increased to 798 and 2300, respectively. Note that for the whole range of feed composition, the selectivity for the composite membranes is higher than that of plain membrane.

**CONCLUSIONS**

This work presents the effect of incorporating 13X zeolite materials into hydrophilic SA to study the permeation behavior

of binary aqueous organic mixtures of industrial importance as well as to understand the dehydration of organic compounds. The composite membranes exhibited high resistance to organic components, which are more permeable to water. The PV performance of 13X zeolite filled composite membrane was explained by the type and nature of interactions of the dual pore systems of the fillers used as well as the hydrophilic nature of the SA matrix and also on the basis of adsorption-diffusion-desorption concepts. Membranes of this study exhibited higher affinity towards the hydrophilic nature of the zeolites, thus the preternatural water adsorption could occur by hindering the organic components through the hydrophilic micropores of the zeolite due to wearing interaction with the membrane matrix. The present membranes, if commercialized may be used to extract water from organic pollutants containing isopropanol.

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