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# Dehydration of dioxane by pervaporation using filled blend membranes of polyvinyl alcohol and sodium alginate

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ABSTRACT

Pervaporation membranes were made by solution blending of polyvinyl alcohol (PVA) and sodium alginate (SA). Accordingly, five different blends with PVA:SA weight ratio of 75:25, 50:50, 25:75, 20:80 and 10:90 designated as PS1, PS2, PS3, PS4 and PS5, respectively, were prepared. Each of these blends was crosslinked with 2, 4 and 6 wt% glutaraldehyde and the resulting fifteen (5 × 3) membranes were used for pervaporative separation of 90 wt% dioxane in water. The membranes made from PS4 and PS5 were not stable during pervaporation experiments. Among the stable membranes PS3 membrane crosslinked with 2 wt% glutaraldehyde showed the best results for flux and selectivity. Thus, it was filled with nano size sodium montmorillonite filler and used for separation of dioxane–water mixtures over the entire concentration range of 80–99.5 wt% dioxane in water. The membranes were also characterized by mechanical properties, FTIR, SEM, DTA–TGA and XRD.



## 1. Introduction

Biopolymers have been explored extensively for synthesis of pervaporation membranes. Most of the biopolymers like carboxymethyl cellulose, ethyl cellulose, chitosan, sodium alginate, gour gum, etc., are made from natural polysaccharide. Sodium alginate is a water soluble polysaccharide obtained from brown seaweeds. It consists of linear chain structures of 1-4-linked D-mannuronic acid and L-guluronic acid arranged in block. This polymer can be easily crosslinked with glutaraldehyde, 1,6-hexane diamine, bi-functional organic compounds or by immersing in a solution of multivalent ions. Sodium alginate has been identified as a potential dehydrating membrane for pervaporation and its performance exceeds those of other polysaccharides and even polyvinyl alcohol (PVA) (Huang, Pal, & Moon, 1999). However, the mechanical integrity of this otherwise excellent membrane is poor. Thus, sodium alginate membrane has been modified either by incorporating various adsorptive fillers to produce mixed matrix membranes (Bhat & Aminabhavi, 2006a, 2006b; Lokesh, Krishna Rao, Mallikarjuna Reddy, Chowdoji Rao, & Srinivasa Rao, 2008; Patil, Bhat, Halgeri, Vijayalakshmi, & Kumar, 2009) or it has been blended with other polymers like chitosan, gour gum and PVA (Bhat & Aminabhavi, 2007). Pervaporation membranes based on sodium alginate were used for dehydrating various solvents like ethanol, isopropyl alcohol, 1,4-dioxane (Huang et al., 1999), and isopropyl alcohol (Bhat & Aminabhavi, 2006a, 2006b; Huang et al., 1999). 1,4-Dioxane is extensively used as an important organic solvent in petrochemical and pharmaceutical industries. It is miscible with water in all proportion and it forms an azeotrope at a concentration of 82 wt% in water. Dehydration of 1,4-dioxane above 80 wt% by distillation is difficult and expensive (Srinivasa Rao, Smitha, Sridhar, & Krishnaiah, 2006a; Srinivasa Rao, Smitha, Sridhar, & Krishnaiah, 2006b). Thus, dehydration of this solvent above 80 wt% in water by pervaporation has been tried by many researchers. Various hydrophilic blend membranes like blends of PVA with chitosan (Anjali Devi, Smitha, Sridhar, & Aminabhavi, 2006), polyethyleneimine (Srinivasa Rao et al., 2006a, 2006b), poly(methyl methacrylate) (Adoor, Manjeshwar, Naidu, Vijay Kumar, & Aminabhavi, 2006), mixed matrix membranes of sodium alginate (Bhat & Aminabhavi, 2006a, 2006b), blends of calcium alginate and chitosan (Reddy, Kalyani, Kumar, Boddu, & Krishnaiah, 2008), blends of chitosan and nylon 66 (Smitha, Dhanuja, & Sridhar, 2006) were tried for dehydration of dioxane by pervaporation. Blend membranes are generally made by solution blending of two or more polymers in a common solvent while mixed matrix or filled membranes are prepared by incorporating micro or nano size adsorptive filler in the matrix of the polymer. The objective of the present work was to combine the advantages of blend and mixed matrix membranes by incorporating a filler in a blend membrane and crosslinking the blend with a

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common crosslinker. In this case the filler and crosslinker improves the stability and water selectivity of the membrane in highly concentrated corrosive solvent like dioxane (>80 wt% in water). Further, the hydrophilicity of the membranes will increase due to adsorptive hydrophilic filler and multifunctional chemical crosslinker. Several membranes may also be synthesized by varying blend, filler and crosslinker composition. In one of our previous works type and amount of a crosslinker and also amount of hydrophilic filler was varied to produce filled and crosslinked PVA membrane which showed optimum flux and selectivity for pervaporative dehydration of isopropyl alcohol (Das, Ray, Kuila, Samanta, & Singha, 2011). In the present work PVA and sodium alginate were chosen as the blend forming polymers since these polymers are soluble in water and thus a stable blend of these two polymers may be prepared by solution blending from water. Because of strong polymer–polymer interaction the blend membranes obtained by solution blending shows excellent permeability and selectivity for different solvents (Minnath, Unnikrishnan, & Purushothaman, 2011). This apart, PVA and sodium alginate can be chemically crosslinked with a common crosslinker like glutaraldehyde. Among the various crosslinkers, glutaraldehyde crosslinked PVA showed optimum flux and selectivity for pervaporative dehydration of IPA (Das et al., 2011). Thus, in the present work blend and filled membranes were prepared from PVA and sodium alginate. These membranes were crosslinked with glutaraldehyde and used for separation of dioxane–water mixtures over the concentration range of 80–99.5 wt% dioxane in water.

## 2. Experimental

### 2.1. Materials

Natural polymer sodium alginate (average molecular weight 500 kDa and degree of deacetylation 84%) was procured from Merck and used as it is without any further purification. Polyvinyl alcohol (PVA) of number average molecular weight of 125 kDa and degree of hydrolysis of 98–99% was obtained from S.D. Fine Chemicals, Mumbai. It was also used without any further purification. High purity, HPLC grade 1,4-dioxane and crosslinker glutaraldehyde (25% aqueous solution) was also purchased from S.D. Fine-Chem, Mumbai, India. Nano size sodium montmorillonite (Na+MMT, polymer grade containing 98% montmorillonite, particle size 30–90 nm, aspect ratio 300–500, mineral's thickness 1 nm and cation exchange capacity 120 mequiv./100 g) clay was kindly supplied by Amrfeo Pte. Ltd., Kolkata and used after drying in hot oven at 110 °C for 2 h. Deionized water (conductivity of 20 μS/cm) was produced in the laboratory itself from a reverse osmosis module.

### 2.2. Synthesis of blend membranes

PVA solution was made in a 250 ml glass beaker by gradual addition of required amount of PVA to boiling water in several intervals with constant stirring to obtain a viscous but clear polymer solution. Sodium alginate solution was made in a similar way. Both of these solutions were mixed and further stirred for another 1 h for homogeneous mixing. For preparing filled membranes, required amounts of the nano fillers were added in the blend solution and it was mixed in a sonicator for 1 h followed by mechanical stirring for 8 h to get the filler incorporated stable polymer dispersion. The blend solutions (for blend membranes) and polymer dispersions (for filled blend membranes) were then mixed with required amount of aqueous glutaraldehyde solutions at a certain pH maintained by adding sulfuric acid (10 wt% in water), acetic acid (10 wt% in water) and methanol (50 wt% in water) in the blend solution (Peppas & Wright, 1998). Thus, blend and filled membranes were prepared by casting the blend solutions or dispersion with an applicator on a clean and smooth glass plate. It was kept overnight at room temperature and then dried at 60 °C for 2 h under vacuum. The thickness of the membranes was maintained at around 50 μm and it was measured by Test Method ASTM D374 using a standard dead weight thickness gauge (Baker, Type J17).

### 2.3. Membrane characterization

#### 2.3.1. Mechanical properties of the membranes

The mechanical properties of the blend membranes, i.e., tensile strength and elongation at break were evaluated by a Lloyd-Tensile tester (Lloyd instruments, England). The experiment was performed according to ASTM D882-97 (Das & Ray, 2013).

#### 2.3.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectral measurements of the unfilled blend membranes were performed with a Perkin Elmer (model-Spectrum-2, Singapore) spectroscope using a thin film (~10 μm) of the polymer (Das et al., 2011).

#### 2.3.3. X-ray diffraction (XRD)

The wide angle X-ray diffraction pattern of the membrane samples was studied at room temperature with a diffractometer (model – X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu $K_\alpha$ radiation ($\lambda = 1.5418$ Å) and a scanning rate of 2°/s (Das et al., 2011).

#### 2.3.4. Differential thermal analysis and thermogravimetric analysis (DTA–TGA)

DTA and TGA of the membrane samples were carried out in a Perkin Elmer instrument (model – DTA-TGA 7, Singapore) in nitrogen atmosphere at the scanning rate of 10 °C per minute in the temperature range of 60–600 °C (Das et al., 2011).

#### 2.3.5. Scanning electron microscopy (SEM)

The membrane samples were coated with gold (Au). The morphology of the unfilled and filled membranes were observed by using SEM (model – S3400N, VP SEM, Type-II, made by Hitachi, Japan) with the accelerating voltage set to 15 kV (Das et al., 2011).

### 2.4. Swelling study

#### 2.4.1. Total sorption

Sorption experiments were carried out by immersing known weight ($w_d$) of the dry membrane sample in dioxane–water mixtures of varied compositions and it was allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. The membrane sample was then taken out from the solution and weighed ($w_e$) after the superfluous liquid was wiped out with tissue paper (Áres, Perrin, Durand, Arnold, & Lochon, 1998). Total sorption ($S_t$) of water and dioxane mixtures by the membranes (g/g dry membrane) is obtained as

$$S_t = \frac{w_e - w_d}{w_d} \quad (1)$$

Similarly, total sorption in terms of number of moles ($N_t$) per g of dry membrane may be obtained as (Randová, Bartovská, Hovorka, & Friess, 2009)

$$N_t = \frac{S_t}{x_{im}M_i + (1 - x_{im})M_j} \quad (2)$$

Here $x_{1m}$ is mole fraction and $M_1$ is molecular weight of the preferentially sorbed (i.e., water) component 1.

*2.4.2. Membrane phase composition and preferential sorption*

For determining the membrane phase composition in sorption experiments the total amount of water and dioxane sorbed by the membranes ($S_t$) was collected in a trap immersed in liquid nitrogen and connected to a vacuum pump. The composition of water and dioxane in membrane was analyzed by a digital refractometer (Anton Paar, model – Abbemat-HP, precision up to 5 decimal). During sorption component *i* (water) is sorbed more than component *j* (dioxane) and the excess of number of the moles of preferentially sorbed *i* in comparison to its feed concentration per g of dry membrane may be expressed in terms of a parameter called preferential sorption ($\Omega$) (Randová et al., 2009)

$$\Omega_i = N_t(x_{im} - x_{ib}) \tag{3}$$

where $x_{im}$ and $x_{ib}$ are mole fraction of preferentially sorbed component *i* (i.e., water in the present system) in membrane and bulk feed, respectively which is obtained from sorption experiments. Combining Eqs. (2) and (3)

$$\Omega_i = \frac{S}{x_{im}M_i + (1 - x_{im})M_j}(x_{im} - x_{ib}) \tag{4}$$

*2.4.3. Sorption by filler*

The total sorption by filler ($S_f$) was obtained by subtracting the sorption by membrane ($S_m$) from the total sorption ($S_t$), i.e., using Eq. (5)

$$S_f = S_t - S_m \tag{5}$$

In the present work PS3 membrane was filled with sodium montmorillonite filler. Hence, total sorption by filler in filled membranes, i.e., F1PS3, F2PS3 and F3PS3 was obtained by subtracting total sorption of PS3 (containing 0 wt% filler) membrane ($S_m$) from the total sorption ($S_t$) of the three filled membranes (Kuila & Ray, 2011).

*2.4.4. Sorption thermodynamics*

*2.4.4.1. Interaction parameter between solvents ($\chi_{ij}$) in feed and membrane.* Interaction parameter between solvents, i.e., $\chi_{ij}$ is determined from feed concentration using Eq. (6) (Mulder & Smolders, 1984)

$$\chi_{ij} = \frac{1}{x_i v_j}\left[x_i \ln\left(\frac{x_i}{v_i}\right) + x_j \ln\left(\frac{x_j}{v_j}\right) + (x_i \ln\gamma_i + x_j \ln\gamma_j)\right] \tag{6}$$

Here $v_1$ and $x_1$ are volume and mole fraction, respectively of solvent 1. The activity coefficient of water ($\gamma_i$) and dioxane ($\gamma_j$) were determined from the two-parameter Wilson equation (Hirata, Ohe, & Nagahama, 1985). Interaction parameter between solvents in the membrane ($\chi_{ij}^m$) was determined from the feed interaction parameter and the feed and membrane phase volume fraction of water (Han, Zhao, Zhang, & Zhang, 2008).

*2.4.4.2. Interaction parameter between polymer and solvent ($\chi_{ip}$ or $\chi_{jp}$).* $\chi_{ip}$ or $\chi_{jp}$ was determined from the sorption data of pure (100 wt%) solvent in membrane using Eq. (7) (Mulder & Smolders, 1984)

$$\chi_{1p} = \frac{-\ln(1 - \varphi_p) - \varphi_p}{\varphi_p^2} \tag{7}$$

Here $\chi_{1p}$ is interaction parameter between component 1 and polymer (membrane) while $\varphi_p$ is volume fraction of membrane polymer in polymer–solvent binary mixture.

*2.5. Permeation studies*

Permeation studies of dioxane–water mixtures were carried out by pervaporation experiment in a batch cell with dead-end type flow. The membrane was inserted in the stainless-steel stirred cell. Effective membrane area (*A*) in contact with the feed solution was 19.6 $cm^2$ and the feed compartment volume was 150 $cm^3$. The downstream pressure was maintained at ~1 mm Hg by a vacuum pump. The feed mixtures in contact with the membrane were allowed to equilibrate for around 3 h for the first experiment and 1 h for the subsequent experiments with different feed compositions. The pervaporation experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the pervaporation cell for different feed compositions at four different temperatures, i.e., 35 °C, 40 °C, 50 °C and 60 °C. At steady state permeates were collected in traps immersed in liquid nitrogen. Pervaporation experiments of dioxane–water mixtures were reproducible and the errors inherent in the measurements were less than 1.0%.

*2.5.1. Permeation flux and separation factor for water*

Permeation flux (*J*) was calculated by dividing the amount of total permeate (*W*) by the time (*t*) of experiment and area (*A*) of the membrane using Eq. (8)

$$J = \frac{W}{At} \tag{8}$$

The amount of water and dioxane present in permeate was determined in a similar way as in the case of sorption experiment by a digital refractometer (Anton Paar, model – Abbemat-HP). The partial molar flux of solvent (water or dioxane) was obtained from Eq. (9)

$$J_1 = \frac{W}{At} \times \frac{w_1}{M_1} \tag{9}$$

Here $w_1$ and $M_1$ are weight fraction and molecular weight of solvent 1, respectively.

Separation factor ($\beta_{water}$) of water was expressed as the ratio of molar concentration of water in permeate ($Y_{water}$) and feed ($X_{water}$) by Eq. (10) (Luis, Degreve, & VanderBruggen, 2013)

$$\beta_{water} = \frac{Y_{water}/Y_{dioxane}}{X_{water}/X_{dioxane}} \tag{10}$$

Here $Y_i$ and $X_i$ are the molar fraction of component *i* (water) in permeate and feed, respectively.

*2.5.2. Partial permeability and intrinsic membrane selectivity*

Partial permeability ($P_i$) of solvents through the membranes was obtained from its partial molar flux ($J_i$), membrane thickness (*L*) and partial vapor pressure on feed and permeate side using Eq. (11) (Baker, Wijmans, & Huang, 2010).

$$P_i = L \times \frac{J_i}{x_{fi}\gamma_i p_{fi}^{sat} - y_{pi}p_p} \tag{11}$$

where $x_{fi}$ and $y_{pi}$ are the mole fraction of component *i* on feed (liquid phase) and permeate (vapor phase) side, $p_{fi}^{sat}$ is saturated vapor pressure of component *i* on the feed side obtained using Antoine's equation and $p_p$ is the permeate pressure in pervaporation process. Because of very low permeate pressure $y_{pi}p_p$ in Eq. (11) may be ignored. Hence, Eq. (11) may be simplified as

$$P_i = L \times \frac{J_i}{f_i} \tag{11a}$$

where

$$f_i = x_{fi}\gamma_i p_{fi}^{sat} \tag{11b}$$

$f_i$ is the fugacity of solvent *i*.

**Table 1**
Flux and selectivity of various blend membranes for 90 wt% dioxane in water and mechanical properties of the membranes.

| Membrane name | Membrane composition | % GLA | Total flux (g/(m$^2$ h))/SF$_{water}$ | TS/EAB of dry membranes (kgf/cm$^2$)/(%) | TS/EAB of water swollen membranes (kgf/cm$^2$)/(%) | TS/EAB of dioxane swollen membranes (kgf/cm$^2$)/(%) |
|---|---|---|---|---|---|---|
| PS1 | 75% PVA + 25% SA | 2 | 72.3/13.17 | 3.12/167 | 2.89/178 | 2.75/159 |
| | | 4 | 48.7/15.16 | 4.12/155 | 3.55/172 | 3.14/143 |
| | | 6 | 38.5/22.22 | 4.89/139 | 4.28/144 | 3.86/117 |
| PS2 | 50% PVA + 50% SA | 2 | 114.5/21.03 | 2.89/118 | 2.56/124 | 2.23/113 |
| | | 4 | 66.58/32.14 | 3.12/102 | 2.81/115 | 2.55/98 |
| | | 6 | 44.0/30.56 | 4.27/98 | 3.81/105 | 3.21/84 |
| PS3 | 25% PVA + 75% SA | 2 | **110.7/75.5** | 2.15/85 | 1.98/97 | 1.82/79 |
| | | 4 | 98.67/76.23 | 3.12/73 | 2.89/85 | 2.66/67 |
| | | 6 | 90.52/71.19 | 3.89/68 | 3.33/72 | 3.13/56 |
| PS4 | 20% PVA + 80% SA | 2 | Membranes were not | 1.25/21 | 0.89/24 | 0.67/16 |
| | | 4 | stable during PV | 1.85/18.3 | 1.65/22 | 1.57/15 |
| | | 6 | | 2.13/13.2 | 1.88/15 | 1.66/11 |
| PS5 | 10% PVA + 90% SA | 2 | Membranes were not | 0.75/18 | 0.64/21.3 | 0.59/15 |
| | | 4 | stable during PV | 1.10/14.5 | 0.88/16 | 0.73/10 |
| | | 6 | | 1.23/9.2 | 1.10/12 | 0.95/7 |

PVA, polyvinyl alcohol; SA, sodium alginate; GLA, glutaraldehyde; SF, water separation factor for water; TS, tensile strength; EAB, elongation at break.

Intrinsic membrane selectivity ($\alpha_{ms}$) was obtained as ratio of partial permeability, i.e.,

$$\alpha_{ms} = \frac{P_i}{P_j} \quad (12)$$

## 3. Results and discussion

### 3.1. Synthesis and selection of membranes

Several blend membranes were prepared by solution blending of PVA and sodium alginate in water using glutaraldehyde as a common crosslinker. The hydroxyl groups (—OH) of PVA and sodium alginate react with glutaraldehyde to form the crosslinked structures. Accordingly, full interpenetrating network (IPN) type crosslinked blend is formed (Kulkarni, Sreedhar, Mutalik, Setty, & Sa, 2010). It was observed that the blends containing sodium alginate above 75 wt%, viz. membranes made from PS4 and PS5 were not stable in dioxane–water mixtures during the pervaporation experiments. In fact, sodium alginate is more hydrophilic than PVA because of the presence of both hydroxyl and carboxylate functional groups in its structure (Kulkarni et al., 2010). However, PVA is a linear polymer with flexible carbon–carbon ($CH_2$-CHOH) repeating unit while the repeating unit of sodium alginate is rigid hexagonal. Thus, the hydrophilicity of blend increases with increase in % of the alginate but the membranes become increasingly brittle. As a result the membranes made from PS4 and PS5 containing 80 and 90 wt% alginate collapsed within the first 1 h of the pervaporation experiments. However, the membranes made from PS1, PS2 and PS3 were stable during pervaporation experiments. The flux and selectivity of these membranes for pervaporative separation of 90 wt% dioxane in water is shown in Table 1. Among these membranes PS3 blend crosslinked with 2 wt% glutaraldehyde is observed to show the best result for flux and selectivity. Thus, PS3 blend was further filled with 2, 4 and 6 wt% sodium montmorillonite filler to produce three filled membranes, i.e., F1PS3, F2PS3 and F3PS3, respectively. These membranes were crosslinked with 2 wt% glutaraldehyde and used for pervaporative separation of 80–99.5 wt% dioxane in water.

### 3.2. Characterization of membrane

Stability and performance of the blend membranes in pervaporation depend on blend composition, state of crystallization, interaction between functional groups of the constituent polymers as well as distribution of fillers in the polymer matrix. Stability of the membranes may be evaluated by its mechanical properties. Interaction between functional groups and crosslinking reaction can be evaluated by FTIR, state of crystallization can be evaluated by XRD, flexibility of polymer chains may be evaluated by $T_g$ while distribution of filler in membrane matrix and blend compatibility may be explained by SEM. Thus, the membranes were characterized by mechanical properties, FTIR, XRD, DTA–TGA and SEM as given below.

#### 3.2.1. Mechanical properties of the membranes

Mechanical properties viz. tensile strength and elongation at break of the dry membranes and the membranes after immersion for seven days in pure solvents (100 wt% water or dioxane) are also shown in Table 1. The mechanical properties of the membranes in different feed solutions will be intermediate in between its mechanical properties in pure water or pure dioxane (Kuila & Ray, 2011). It is observed that the tensile strength and elongation at break of the membranes decrease with increase in wt% of sodium alginate (SA) in the blends. It is also observed that for the same blend tensile strength increases with increase in wt% of crosslinker while elongation at break decreases. Similar trend is observed for solvent swollen membranes though these membranes show lower tensile strength than dry membranes. Further, elongation at break of the water swollen membranes are observed to be somewhat higher than the dry membranes while dioxane swollen membranes show even lower elongation at break than the dry membranes. Sodium alginate is a brittle polymer and thus, its tensile strength and elongation at break is lower than tensile strength and elongation at break of PVA (Kulkarni et al., 2010; Xie et al., 2012). Thus, tensile strength and elongation at break of the blend decreases with increase in wt% of SA in the blend. Further, stiffness of the membrane increases with increase in wt% of the crosslinker resulting in increase in tensile strength but decrease in elongation at break. For an ideal pervaporation membrane there should be a good balance between its tensile strength and elongation at break (Kuila & Ray, 2011). Tensile strength indicates its strength while elongation at break measures its flexibility. The mechanical properties, i.e., tensile strength and elongation at break of the membranes made from PS4 and PS5 blends are observed to be much lower than tensile strength and elongation at break of other membranes. This may be the reason for collapsing of the membranes

made from PS4 and PS5 blends during the pervaporation experiments.

### 3.2.2. Characterization of membranes by FTIR

As observed in Fig. 1a, sodium alginate shows absorption band at 1107 and 1022 $cm^{-1}$ corresponding to asymmetric and symmetric stretching vibration of its C—O—C group (Ionita, Pandele, & Iovu, 2013). The band at 1642 $cm^{-1}$ and 1402 $cm^{-1}$ corresponds to asymmetric and symmetrical stretching vibration, respectively, of its $COO^-$ groups (Islama & Karim, 2010). The absorption band at 3357 $cm^{-1}$ is due to its hydroxyl (OH) stretching. For crosslinked PVA the bands appearing near 3300 $cm^{-1}$ is assigned to O—H stretching due to strong intermolecular and intramolecular hydrogen bonding in PVA. The crosslinked PVA also shows carbonyl peak at 1709 $cm^{-1}$ (Islama & Karim, 2010; Shalumon, Anulekha, Nair, Chennazhi, & Jayakumar, 2011). In the blend of PVA and sodium alginate some of the characteristic peaks of PVA and alginate disappears while some peaks of alginate and PVA is shifted due to electrostatic interaction between these polymers. Thus, in the blend asymmetric and symmetric carboxylate stretching is shifted to 1717 and 1432 $cm^{-1}$, respectively, indicating interaction of sodium alginate and PVA through hydrogen bonding (Ionita et al., 2013). Intermolecular hydrogen bonding in the blend is also evident by broadening of hydroxyl peak at 3350 $cm^{-1}$ as observed in Fig. 1a (Shalumon et al., 2011).

### 3.2.3. XRD analysis

From Fig. 1b it is observed that sodium alginate shows three crystalline peaks at 14.3°, 21.3° and 37.1° as also reported elsewhere (Dong, Dong, Cao, Han, & Ding, 2011). The diffraction peak of PVA at $2\theta$ of 20.4° as observed in Fig. 1b is due to diffraction from mixtures of its (1 0 1) and (1 0 $\bar{1}$) planes (Bhat, Nate, Kurup, Bambole, & Sabharwal, 2005). It also shows diffraction peak at 12.1° and 40.9° (Shalumon et al., 2011). Since PVA is blended with sodium alginate, most of the characteristic peaks of PVA and sodium alginate disappears and some new peaks appears as observed in the blend with diffraction peaks at new $2\theta$ of 9.5° and

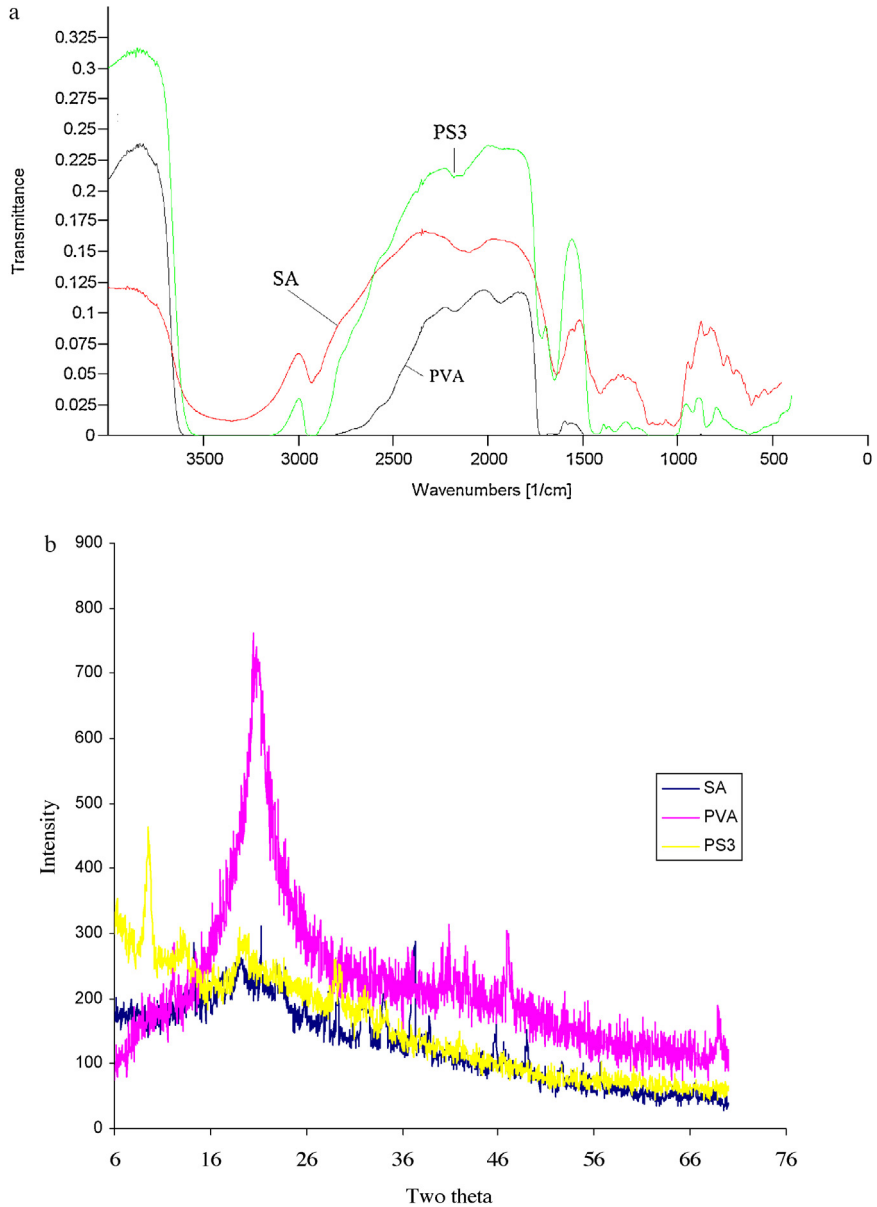


**Fig. 1.** (a) FTIR of the membranes. (b) XRD of sodium alginate (SA), polyvinyl alcohol (PVA) and unfilled blend (PS3). (c) (i) DTA and (ii) TGA of the polymers. (d) SEM of blend membranes: (i) PS3, (ii) F1PS3, (iii) F2PS3 and (iv) F3PS3.

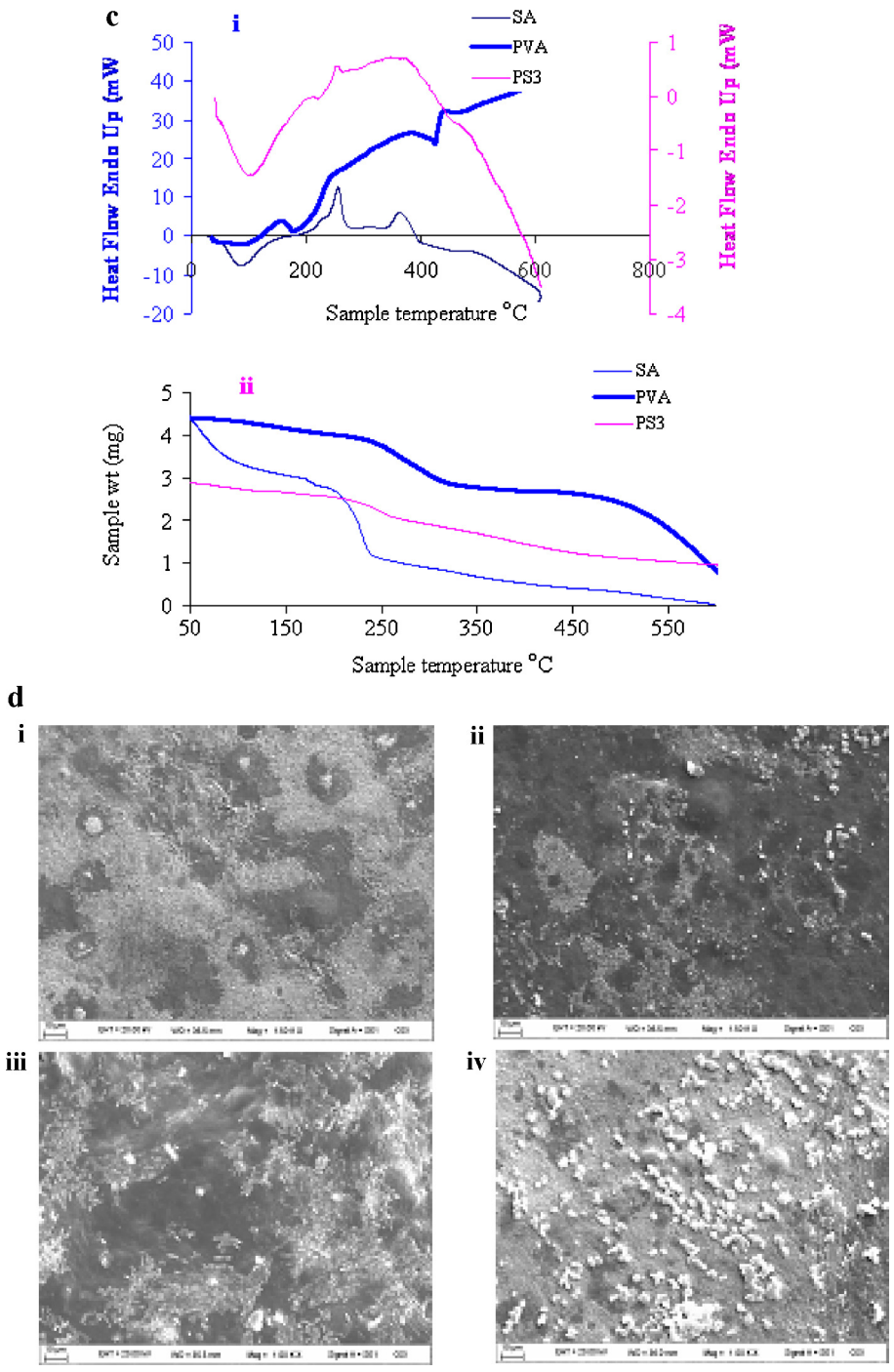


**Fig. 1.** (*Continued*).

19°. This shifting of *d* spacing also signifies strong interaction of PVA and alginate in its blend (Shalumon et al., 2011).

### 3.2.4. DTA and TGA

*3.2.4.1. DTA.* From Fig. 1c (i) it is observed that sodium alginate shows an endothermic peak at 86 °C corresponding to loss of water while the exothermic peak at 257 °C is due to its degradation. Similar thermal characteristic peaks were reported elsewhere (Davidovich & Bianco, 2011). For crosslinked PVA the exothermic peak at 165 °C corresponds to its $T_g$ while the sharp endothermic peak at around 190 °C is assigned to its melting ($T_m$). Similar $T_g$ (Das et al., 2011) and $T_m$ (Islama & Karim, 2010) were reported elsewhere. In the blend of PVA and alginate the endothermic peak of 86 °C corresponding to loss of water of alginate is shifted to around 110 °C. Similarly, exothermic peak at 165 °C corresponding to $T_g$ of PVA is shifted to 215 °C and endothermic melting peak of PVA at 190 °C is shifted to 230 °C in the blend indicating strong interaction between PVA and alginate through crosslinking and hydrogen bonding.

*3.2.4.2. TGA.* The TGA diagram of PVA, sodium alginate and its blend (PS3) is also shown in Fig. 1c (ii). Sodium alginate is observed to show an initial degradation at 196 °C while onset of degradation is observed at 240 °C for PVA. In fact, degradation of sodium alginate is associated with dehydration in three regimes, i.e., 40–60 °C for release of free water, breakage of hydrogen bond at 80–120 °C

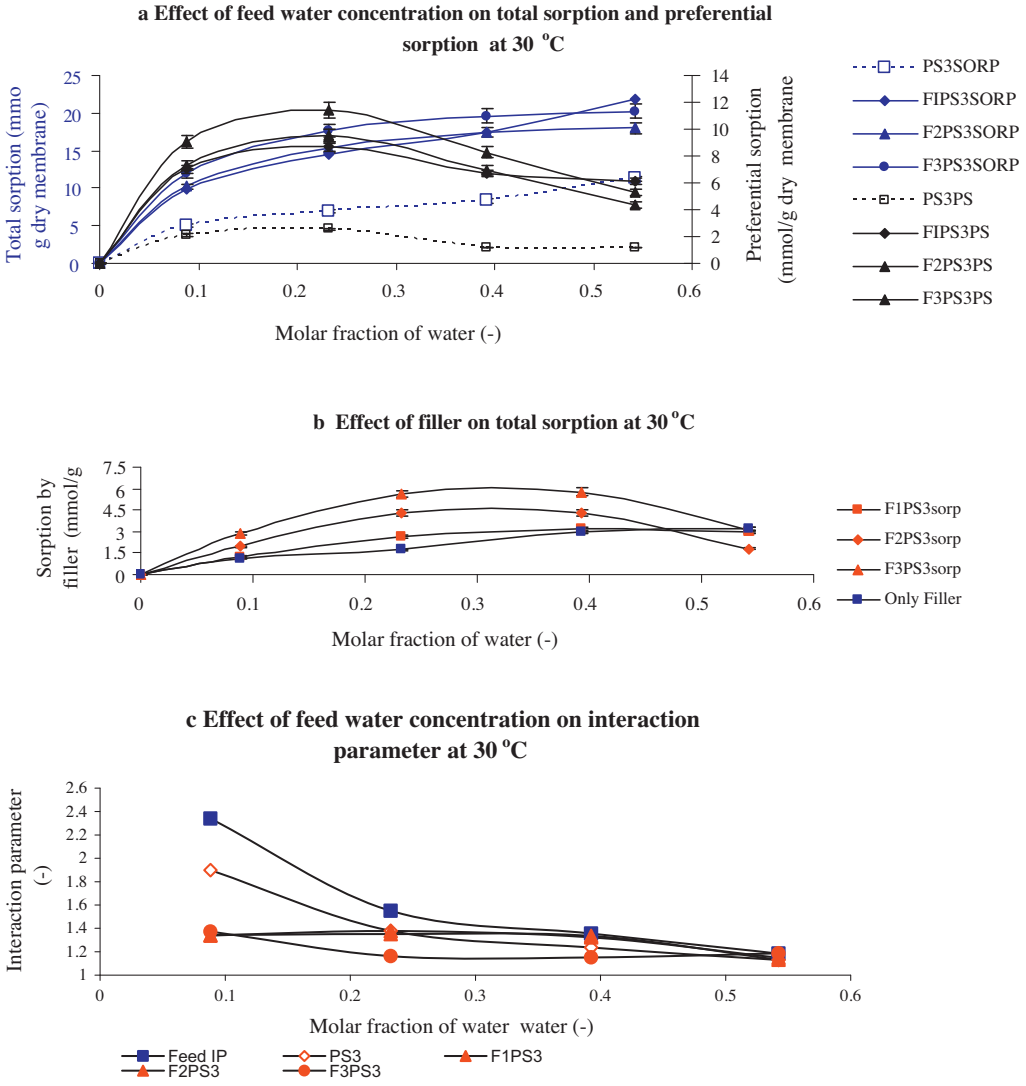


**Fig. 2.** (a) Effect of feed water concentration on total sorption and preferential sorption at 30 °C. (b) Effect of filler on total sorption at 30 °C. (c) Effect of feed water concentration on interaction parameter at 30 °C.

and loss of polar interaction with carboxylic groups up to 160 °C (Russo, Giuliani, Immirzi, Malinconico, & Romano, 2004). These three regions are not separately detected in TGA of sodium alginate in Fig. 1c (ii), but a weight loss of about 20% is observed up to 160 °C which is in agreement with reported value at this dehydration regime (Russo et al., 2004). In contrast to sodium alginate or PVA, the blend does not show any degradation regime and it is observed to degrade linearly at a much slower rate which also indicates increased thermal resistance. This may be due to crosslinking and hydrogen bonding among hydroxyl and carboxylate groups of PVA and sodium alginate in the blend which restrict chain movements during thermal treatment (Lin, Yu, & Yang, 2006).

### 3.2.5. SEM analysis

The SEM of unfilled PS3 blend and the three filled blend membranes, i.e., F1PS3, F2PS3 and F3PS3 are shown in Fig. 1d (i), (ii), (iii) and (iv), respectively. In the unfilled blend membrane the major component, i.e., sodium alginate forms the continuous phase while PVA is distributed as dispersed phase. Two different morphologies of sodium alginate and PVA are quite evident from this figure. The morphology of the blended membranes becomes coarser from F1PS3 to F3PS3 when the amount of nanofiller is increased. However, the distribution of filler in the blend matrix is observed to be uniform in all of these filled membranes.

## 3.3. Sorption

### 3.3.1. Effect of feed concentration on sorption isotherms

Variation of the total sorption of water and dioxane with feed concentration of water by unfilled PS3 and the three filled blend membranes (mole/g of dry membrane) is shown in Fig. 2a. Total sorption is observed to increase with feed water concentration and above around 0.25 mole fraction of water in feed there is no significant change in the total sorption for these membranes. In fact, these membranes show a dual mode type-II sorption which is a combination of Henry and Langmuir type, i.e., with increase in feed concentration the total sorption increases and at higher feed concentration the membrane becomes saturated and thus there is no significant increase in sorption. In this case sorption in the polymer matrix is governed by Henry's law while sorption in the filler occurs in accordance with Langmuir adsorption (Rogers, 1985). The preferential sorption of water is also observed to increase initially with feed mole fraction of water as shown in Fig. 2a. At around 0.25 mole fraction of water in feed the preferential sorption reaches its maximum value and then it goes down with further

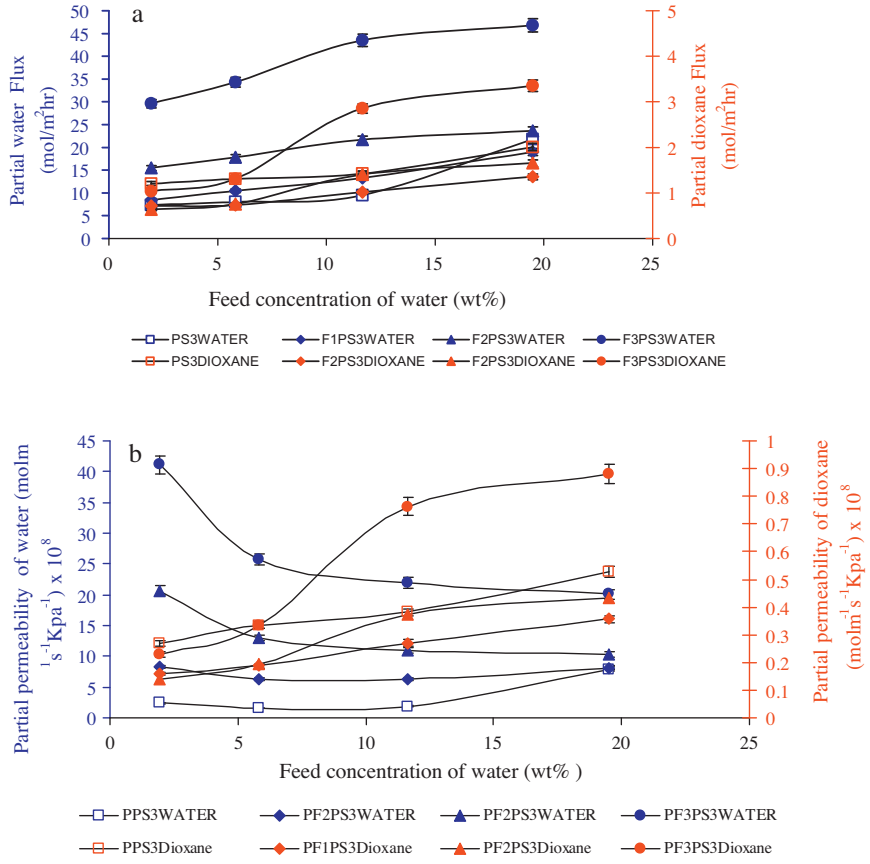


**Fig. 3.** Variation of (a) partial molar flux and (b) partial permeability with feed concentration of water at 30 °C.

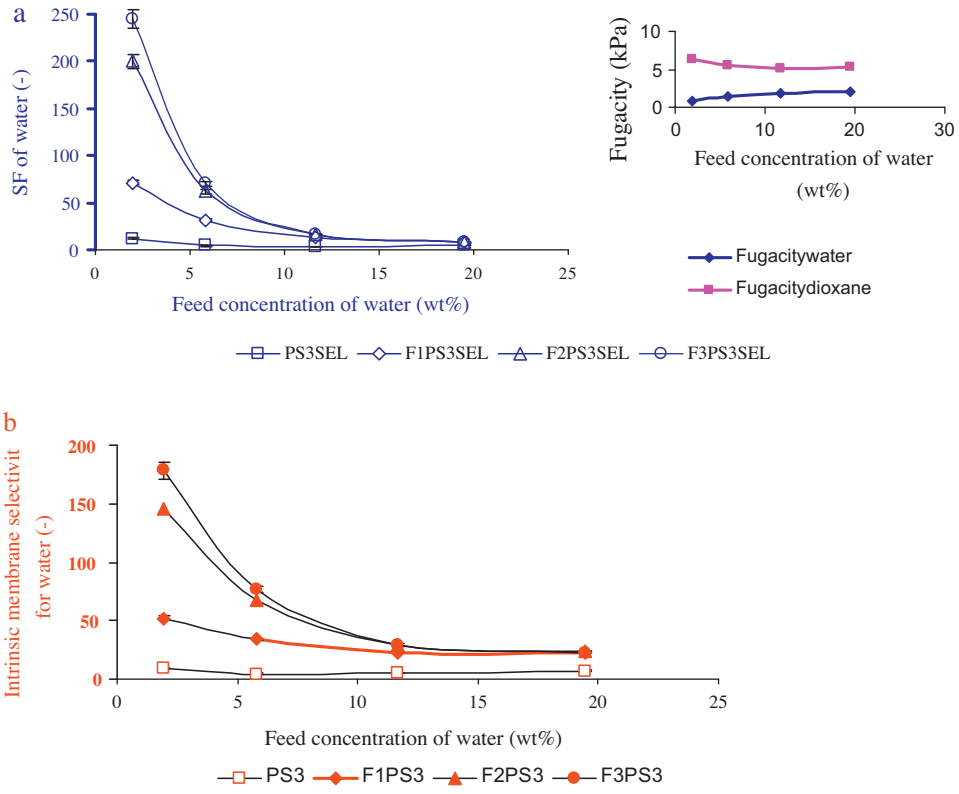


**Fig. 4.** Variation of (a) separation factor (SF) and fugacity and (b) intrinsic membrane selectivity with feed concentration of water at 30 °C.

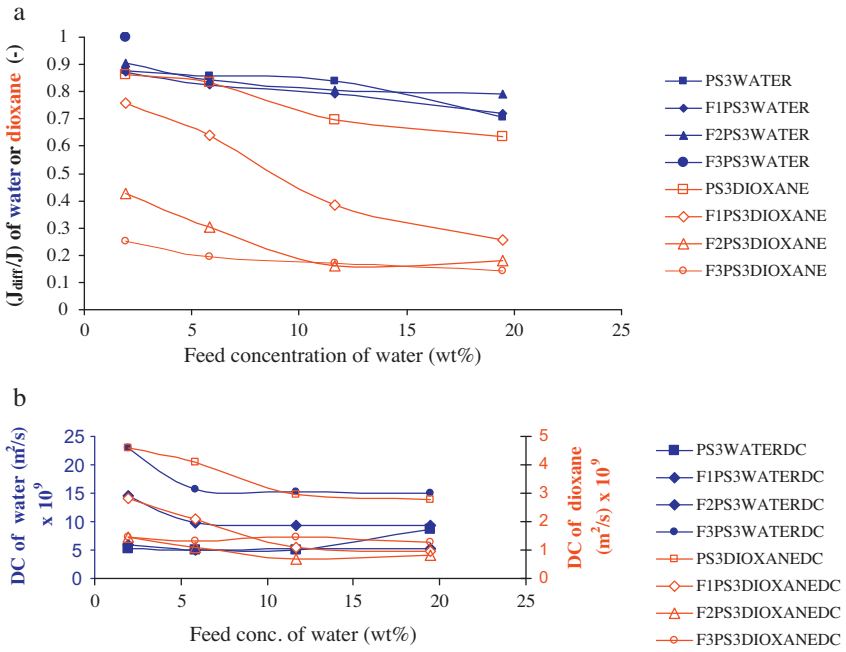


**Fig. 5.** Variation of (a) ratio of diffusive flux to partial flux ($J_{diff}/J$) and (b) diffusion coefficient (DC) with feed concentration of water at 30 °C.

increase in feed concentration of water. It is evident that sorption of these hydrophilic membranes is dominated by sorption of water. At higher feed water concentration change in the total sorption is marginal and hence the preferential sorption also decreases. A similar trend of preferential sorption of methanol was reported from methanol–benzene mixtures by a Nafion membrane (Randová et al., 2009) and toluene from toluene–heptane mixtures by an LDPE membrane (Friess et al., 2009).

### 3.3.2. Sorption by filler

From Fig. 2a it is also observed that for the same feed concentration the total sorption and the preferential sorption for water ($\Omega_i$) increases with increase in filler concentration from PS3 (0% filler) to F3PS3 (6% filler). Accordingly, for 0.09–0.54 molar fraction of water in feed PS3 membrane shows the total sorption of around 5–11.5 mmol/g dry membrane which increases up to 12–20 mmol for F3PS3 membrane. Similarly, for 0.23 molar fraction of water in feed the highest value of $\Omega_i$ is observed to increase from 2.4 mmol/g of unfilled PS3 membrane to 11.4 mmol/g for filled F3PS3 membrane. The total sorption by filler in the membrane at various feed water concentrations was obtained from Eq. (5). It is observed from Fig. 2b that the fillers in the membranes show much higher sorption than same amount of virgin filler (filler in absence of membrane polymer) indicating strong coupling effect of polymer on sorption by filler. This positive coupling effect also increases with increase in concentration of filler in membrane. However, at higher feed concentration sorption by filler in membrane decreases implying reduced coupling by polymer.

### 3.3.3. Sorption thermodynamics

The total sorption or preferential sorption of the membranes may be explained in terms of solvent–solvent ($\chi_{ij}$) and solvent–polymer ($\chi_{im}$ or $\chi_{jm}$) interaction parameter. The values of $\chi_{ij}$, $\chi_{im}$ and $\chi_{jm}$ were determined from feed concentration and sorption data using Eqs. (6) and (7). The lower the value of interaction parameter, the higher will be the interaction between solvents or solvent and polymer. From Fig. 2c it is observed that $\chi_{ij}$ in feed is much higher than $\chi_{ij}$ in membrane. Thus, the membrane shows high sorption. It is also observed that with increase in feed water concentration solvent–solvent interaction parameter in membrane decreases and hence total sorption also increases because of increased solvent–solvent interaction in membranes. Interaction parameter between water and membrane viz. $\chi_{im}$ for PS3, F1PS3, F2PS3 and F3PS3 membranes were found to be 0.561, 0.506, 0.504 and 0.502, respectively while interaction parameter between dioxane and membrane viz. $\chi_{jm}$ for these membranes were much higher, i.e., 1.131, 0.961, 0.946 and 0.918, respectively. Thus, the membranes show preferential water sorption because of lower water-membrane $\chi_{im}$ values. From these interaction parameter values it is also observed that with increase in concentration of filler membrane–solvent interaction parameter decreases and hence total sorption and preferential water sorption increases.

## 3.4. Pervaporation

### 3.4.1. Effect of feed concentration

*3.4.1.1. Partial molar flux and partial permeability.* Effect of feed concentration on partial molar flux and partial permeability of water and dioxane at 30 °C is shown in Fig. 3a and b, respectively. The partial molar flux of the solvent (i.e., water or dioxane) was obtained from flux data using Eq. (9). From Fig. 3a it is observed that partial molar flux of both water and dioxane increases almost linearly with feed concentration. However, the membranes show much higher water flux than dioxane flux over the entire feed concentration range. Partial solvent flux also increases with increase in filler concentration from PS3 (0% filler) to F3PS3 (6% filler). The partial permeability of solvents was determined from partial flux and vapor pressure data using Eq. (11). From Fig. 3b it is observed that partial permeability of water shows an opposite trend of partial water flux, i.e., partial water permeability decreases with feed concentration and above around 5 wt% water in feed the change of permeability with concentration is marginal. Partial permeability is the ratio of partial flux and fugacity ($x_{fi}\gamma_i p_{fi}^{sat}$, Eq. (11a)). From Fig. 4a it is observed that fugacity increases with feed concentration. Thus, permeability of water decreases with increase in feed concentration since rate of increase of its fugacity more than offset the rate of increase of its flux. At higher feed concentration water flux

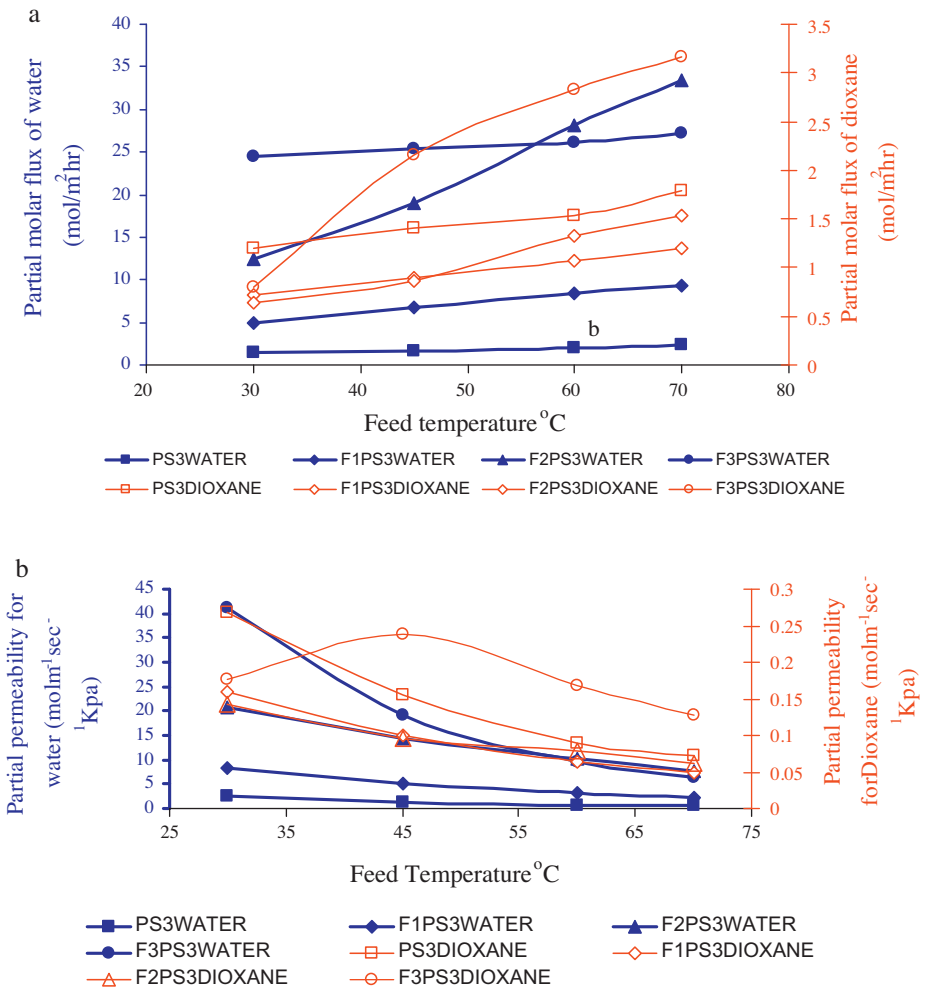


**Fig. 6.** Variation of partial (a) molar flux and (b) permeability with feed temperature. Feed concentration: 1.93 wt% water.

increases (Fig. 3a) but change of fugacity (Fig. 4a) is marginal. Thus, water permeability changes little at higher feed concentration as observed in Fig. 3b. In a similar way increase in partial permeability of dioxane with concentration may be ascribed to increase in flux (Fig. 3a) and decrease in fugacity of dioxane (Fig. 4a) with concentration. From Fig. 3a or b it is also observed that over the entire feed concentration partial flux or permeability of water is much higher than partial flux or permeability of dioxane indicating water selectivity of the membranes. It is also observed that like sorption or partial flux, permeability also increases with increase in filler concentration in membrane over the entire feed concentration of water.

*3.4.1.2. Separation factor and intrinsic membrane selectivity.* Separation factor for water was obtained from feed and permeate composition using Eq. (10) while intrinsic membrane selectivity for water was obtained from the ratio of partial permeability of water and dioxane using Eq. (12). From Fig. 4a and b it is observed that both separation factor and membrane selectivity show a similar trend, i.e., it decreases almost exponentially with feed concentration. At higher feed concentration, the membranes become plasticized and hence dioxane flux increases. Thus, the separation factor or permeability for water decreases. It is also observed that for the same feed concentration, separation factor and membrane selectivity of water increases with increase in filler concentration from PS3 to F3PS3. The hydrophilic adsorptive nano filler contributes to preferential water sorption and hence water selectivity increases.

*3.4.1.3. Diffusive flux and diffusion coefficient.* The concentration average diffusion coefficients through the various used membranes may be obtained from Eq. (13) (Lue, Ou, Kuo, Chen, & Yang, 2010)

$$D_1 = \frac{J_{1\text{diff}} \times L}{m_1 \times \rho_p} \tag{13}$$

Here $m_1$ is the membrane phase concentration of component 1 obtained from sorption experiment. $J_{1\text{diff}}$ is the diffusive flux of component 1 which is related to its mass flux, i.e., $J_1$. The diffusive flux of component $i$ and $j$ may be expressed by Eqs. (14) and (15), respectively (Lue et al., 2010).

$$J_{i\text{diff}} = \frac{m_i[1 + r^{-1}]}{\ln[1 - m_i(1 + r^{-1})]^{-1}} J_i \tag{14}$$

$$J_{j\text{diff}} = \frac{m_j[1 + r]}{\ln[1 - m_j(1 + r)]^{-1}} J_j \tag{15}$$

Here $r$ is the ratio of flux of component $i$ and component $j$, i.e., $r = J_i/J_j$.

Variation of ratio of diffusive to partial flux ($J_{\text{diff}}/J$) of water and dioxane with feed concentration of water is shown in Fig. 5a. It is observed that the diffusive flux of water contributes to around 50–90% of its partial flux while the diffusive flux of dioxane is found to be around 15–75% of its partial

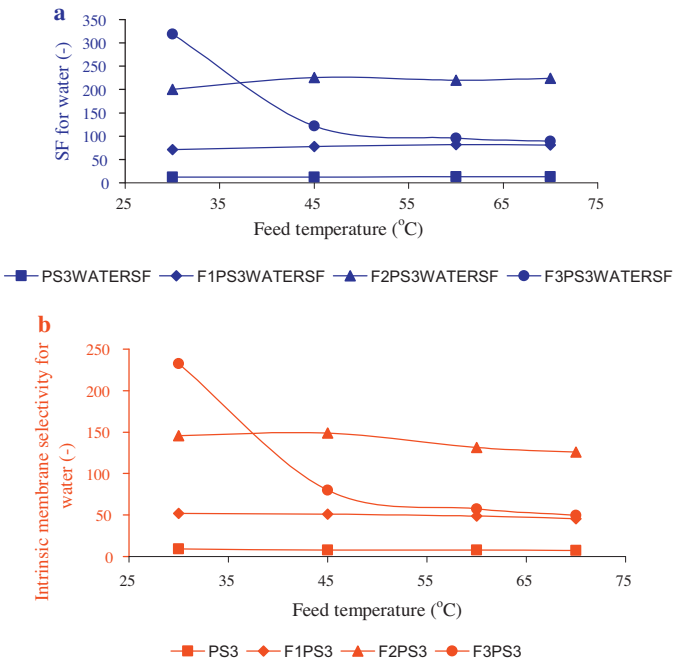


**Fig. 7.** Variation of (a) separation factor (SF) for water and (b) intrinsic membrane selectivity with temperature. Feed concentration: 1.93 wt% water.

flux. It indicates that the permeation of the solvents through the membranes is dominated by diffusion. From Fig. 5a it is also observed that the diffusive flux of both water and dioxane decreases almost exponentially with increase in feed concentration. It signifies plasticization of the hydrophilic membranes by water at higher feed water concentration. Effect of feed concentration on diffusion coefficient of water and dioxane is shown in Fig. 5b. It is observed from this figure that at any feed concentration diffusion coefficient of water is much higher than diffusion coefficient of dioxane. Further, with increase in filler concentration diffusion coefficient of water increases while diffusion coefficient of dioxane decreases. Kinetic diameter of water molecule (0.265 nm) is much smaller than dioxane (0.650 nm) (Piera, Coronas, Menéndez, & Santamaria, 1999). Thus, smaller water molecules can easily diffuse through the membranes. As a result diffusive flux and diffusion coefficient of water is observed to be higher than diffusive flux or diffusion coefficient of dioxane.

### 3.4.2. *Effect of temperature*

Variation of partial molar flux and partial permeability with temperature is shown in Fig. 6a and b, respectively, for 1.93 wt% water in feed. From Fig. 6a and b it is observed that partial molar flux of water and dioxane increases almost linearly with temperature (Fig. 6a) while partial permeability decreases with temperature (Fig. 6b). At higher temperature the segmental motion of the polymer chain increases. Further, vapor pressure of both water and dioxane increases significantly at higher temperatures. All of these effects lead to increase in flux but decrease in permeability at higher temperature. From Fig. 7 it is observed that the separation factor (Fig. 7a) or the intrinsic membrane selectivity (Fig. 7b) remains marginally constant with temperature.

*3.4.2.1. Activation energy.* Activation energy obtained from slope of the linear plot of logarithmic of partial flux against the inverse of absolute temperature ($1/T$) is apparent activation energy since it does not include heat of vaporization. On the other hand, gas based parameter like permeability ($P_i$) at different temperatures gives actual activation energy (Villegas, Vidaurre, Habert, & Gottifredi, 2011) from the following Arrhenius type equation

$$\ln P_i = P_{0,i} - \frac{E_{pi}}{RT} \tag{16}$$

Linear plotting of $\ln P_i$ against $1/T$ gives the value of activation energy for permeation ($E_{pi}$) and pre-exponential factor ($P_{0,i}$) from slope and intercept, respectively. Activation energy for permeation of water ($E_{pwater}$) and dioxane ($E_{pdioxane}$) was obtained from the slope of the linear plotting of $\ln P_i$ at 1.9 wt% feed water concentration (not shown). In each of these linear regressions the value of regression coefficients ($r^2$) was much above 0.9. $E_{pwater}$ for PS3, F1PS3, F2PS3 and F3PS3 membranes were found to be 32.4, 28.72, 20.6 and 40.4 kJ/deg mol while $E_{pdioxane}$ for these membranes were found to be 28.8, 25.9, 17.1 and 2 kJ/deg mol. These values of activation energy are similar to those reported for water and dioxane with other membranes (Baker et al., 2010; Bhat & Aminabhavi, 2006a; Bhat & Aminabhavi, 2006b).

## 4. Conclusion

Several blend membranes were made from PVA and sodium alginate with varied compositions of these two polymers. These membranes were crosslinked with 2, 4 and 6 wt% glutaraldehyde. The membranes made from the blends containing above75 wt% alginate were not stable during pervaporation experiments while the membrane containing 75 wt% sodium alginate and crosslinked with 2% glutaraldehyde showed the best results for flux and selectivity for pervaporative dehydration of 90 wt% dioxane in water. This blend membrane was further filled with 2, 4 and 6 wt% nano size sodium montmorillonite filler and used for pervaporative separation of 80–99.5% dioxane in water. The membranes were also characterized by mechanical properties, FTIR, XRD, SEM and DTA–TGA. The membrane containing 6 wt% nano filler was found to give the best results for flux and selectivity.

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