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Synthesis and characterization of biopolymer based mixed matrix membranes for pervaporative dehydration

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ABSTRACT

Several blend membranes were prepared from different weight ratios of polyvinyl alcohol (PVA) and hydroxyethyl cellulose (HEC) and these unfilled membranes were crosslinked with maleic acid. In a similar way mixed matrix blend membranes were also prepared by varying weight ratio of PVA and HEC with micro and nano bentonite filler in each of these blends. These membranes were used for pervaporative dehydration of 89 wt% tetrahydrofuran (THF). Three membranes designated as UF (unfilled), MF2 (containing 2 wt% micro filler) and NF2 (containing 2 wt% nano filler) showing the best results for flux and selectivity were identified. These membranes were characterized by FTIR, UV, XRD and DTA-TG and used for separation of 80–99 wt% THF from water by pervaporation. The NF2 membrane was found to show the best results in terms of flux and separation factor.

1. Introduction

Pervaporation (PV) membranes of high separation potentials may be obtained by blending natural and synthetic polymers. Natural polymers are biocompatible and abundant in nature. Hence, these polymers are not expensive. However, it is difficult to make membrane from a pure natural polymer since most of these polymers are not soluble in common solvents and melt processing of natural polymers is also difficult because of degradation of its native structure on application of heat. On the other hand synthetic polymers possess better mechanical and thermal properties than natural polymers and these polymers can be processed to a wide range of products by melt processing or solution casting (Sionkowska, 2011). However, synthetic or man made polymers are expensive and the residual monomer, crosslinker or initiator of a synthetic polymer may also affect the separation performance of a PV membrane (Suh & Matthew, 2000). Blending of these two kinds of polymers may eliminate their respective shortcomings. Presently, PV membranes made by blending a synthetic polymer with a natural or semi synthetic polymers have been attempted by many researchers.

Cellulose or polysaccharide is natural polymer but not soluble in any solvent. Several semi synthetic polymers such as chitosan, sodium alginate, carboxymethyl cellulose, hydroxyethyl cellulose, etc., are made by chemical modification of polysaccharide or cellulose. These semi synthetic polymers may be processed to a suitable product. Blend and filled membranes of chitosan (Chanachai et al., 2000; Smitha, Dhanuja, & Sridhar, 2006; Sun, Lu, Chen, & Jiang, 2008), sodium alginate (Gao et al., 2014; Kalyani, Smitha, Sridhar, & Krishnaiah, 2006; Kuila & Ray, 2014), carboxymethyl cellulose (Chapman, Tan, Livingston, Li, & Oliveira, 2006; Wang et al., 2014; Das & Ray, 2013) hydroxyethyl cellulose (Chanachai et al., 2000; Kalyani et al., 2006; Naidu & Aminabhavi, 2005; Naidu, Sairam, Raju, & Aminabahvi, 2005) with different synthetic polymers have been reported for pervaporative separation. Thus, in the present work several membranes have been synthesized by blending polyvinyl alcohol (PVA) and hydroxyethyl cellulose (HEC). PVA has already been commercialized as hydrophilic membrane. HEC is cellulose ether soluble in water. It is compatible with wide range of water soluble polymers (Naidu, Sairam, et al., 2005; Rao et al., 2006). HEC with several hydroxy groups (—OH) in its structure is expected to improve hydrophilicity of PVA. Further, hydrophilic bentonite filler of micro and nano size was incorporated in the blend membrane. The inorganic filler not only improves the mechanical strength of the membranes but it also improves its separation potential. The incorporation of adsorptive fillers improves separation performance due to synergestic effects of molecular sieving effects, preferential adsorption and difference in rate of diffusion through organic polymer and inorganic filler (Bastani, Esmaeili, & Asadollahi, 2013). The objective of the present work was to improve hydrophilicity and mechanical strength of the PVA membrane by blending it with a hydrophilic polymer and incorporating

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inorganic fillers. In our previous works (Kuila & Ray, 2014; Das & Ray, 2013) several blend membranes were prepared and the unfilled blend showing the best results for flux and selectivity was filled with varied concentrations of micro or nano fillers. In these works composition of the polymer blends were not varied in presence of filler. However, blend composition showing the optimum results may also vary in presence of a fixed amount of filler because of polymer–filler interaction. Thus, in the present work several unfilled membranes were prepared by blending different concentrations of PVA and HEC. Similarly, several filled blend membranes with varied amounts of PVA and HEC were also prepared in presence of 2 wt% micro and 2 wt% nano fillers. The concentration of filler was kept constant at 2 wt% since in one of our previous works blend membranes containing 2 wt% filler showed the best results for flux and selectivity. In the present work these unfilled and filled blend membranes were used for pervaporative separation of THF–water mixtures. THF is an important and expensive organic solvent. It is frequently utilized in many pharmaceutical synthetic procedures because of its broad solvency for polar and nonpolar compounds. However, it is miscible with water in all proportion and it also forms an azeotrope with water. Thus, pervaporative separation of THF–water would be a better candidate since PV may be carried out at low temperature and unlike distillation no azeotrope is formed during PV separation of aqueous THF. In the present work a systematic method has been employed to find out optimum blend compositions for maleic acid crosslinked unfilled and filled blend membranes and these membranes were used for dehydration of 80–99 wt% THF.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) of analytical grade used for this study was purchased from E. Merck (India) Ltd., Mumbai. Polyvinyl alcohol (PVA) of number average molecular weight 125,000 and degree of hydrolysis of 98–99% was obtained from S.D. Fine Chemicals, Mumbai. Hydroxyethyl cellulose (HEC, viscosity average molecular weight 150,000) and maleic acid were purchased from Loba Chemie Pvt. Ltd., Mumbai and E. Merck, Mumbai, respectively and were used as obtained. Hydrophilic bentonite micro filler (API grade, residue of diameter > 75 μm or 200 mesh is 3.5%) and hydrophilic bentonite nano filler (sodium montmorilonite Na + MMT, polymer grade containing 98% montmorilonite, particle size 30–90 nm, aspect ratio 300–500, mineral's thickness 1 nm, cation exchange capacity 120 mequiv./100 g) was kindly given by Amrfeo pte. Ltd., Kolkata. These fillers were used after drying in a hot oven at 110 °C for 2 h. Deionized water, having a conductivity of 20 μS/cm was produced in the laboratory from a reverse osmosis module.

2.2. Preparation, crosslinking and casting of blend membranes

2.2.1. Preparation of blend solution

At first 5 wt% PVA solutions were made in deionized water 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 clear PVA solution. In a similar way 3 wt% HEC solution was made in deionized water. The clear and homogeneous HEC solution was then mixed with aqueous solution of PVA for making unfilled membranes from this mixture. For filled membranes (micro and nano), required amounts of the filler were added and stirred with magnetic stirrer for 8 h to get filler incorporated polymer dispersion.

2.2.2. Preparation of membrane

The aqueous blend solutions of PVA and HEC were mixed with required amounts of maleic acid (2 wt% of polymer blend) and stirred for 3 h at room temperature. These solutions were then cast on a clean and smooth glass plate covered with polyethylene sheet, dried at ambient temperature for 24 h and then peeled off. The membranes were then cured at 110 °C for 3 h in a hot air oven for crosslinking reaction (Singha, Parya & Ray, 2009). The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

2.3. Membrane characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the membrane samples were recorded on a Perkin Elmer, model-Spectrum-2, (Singapore) spectrophotometer using a thin film (~10 μm) of the polymer.

2.3.2. UV spectroscopy

UV spectra of the membrane samples were recorded on a UV–vis spectrophotometer (Perkin Elmer, model lamda25, USA) by inserting the membrane samples in the cuvette to record their absorbance in the wavelength range of 190–250 nm.

2.3.3. X-ray diffraction (XRD)

Wide angle X-ray diffraction profile of unfilled and filled blend membranes were studied at room temperature with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu K_α radiation (λ = 1.5418 Å) and a scanning rate of 2° (2θ/s).

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 in nitrogen atmosphere at the scanning rate of 10 °C/min in the temperature range of 60–600 °C.

2.3.5. Mechanical strength

The tensile strength and elongation at fracture of the unfilled and filled blend membranes were determined in a Lloyd-Tensile tester (Lloyd instruments, England). The experiment was performed according to ASTM D 882-97.

2.4. Sorption and permeation by pervaporation (PV)

The transport of solutes through membranes is governed by preferential sorption and diffusion due to concentration gradient from bulk feed to downstream side of the membranes. The relative performances of the membranes were evaluated by pervaporation (PV) experiments. However, PV is a dynamic process combining both sorption and diffusion. The evaluation of the membranes by sorption is important to find out the operating condition for pervaporation (Xiao, Feng, & Huang, 2007).

2.4.1. Total and partial sorption

For sorption experiments the membrane samples of known weights were immersed in THF–water mixtures of known concentration (~99–80 wt% THF in water) and allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. These membranes were taken out from the solution and weighed after the superfluous liquid was wiped out with tissue paper. Total sorption % (S_t) of water and THF mixtures by the membranes (%) is obtained as

$$S_t = \frac{w_i - w_d}{w_d} \times 100 \quad (1)$$

where w_d and w_i are weight of membranes before and after immersion in THF–water mixtures.

2.4.2. Membrane phase composition and partial sorption

The membrane phase composition of THF and water was determined by analyzing the sorbed liquid from the swollen membrane. In this experiment the swollen membranes are taken in a conical flask which is connected to a vacuum pump through a cold trap immersed in liquid nitrogen. By applying vacuum, the liquid, i.e., total amount of THF and water sorped by the swollen membrane is collected in the cold trap and analyzed by a digital refractometer (Anton Paar, model – Abbemat-HP, precision up to 5 decimal). The partial sorption of water and THF is obtained by multiplying total sorption with membrane phase weight fraction of water and THF.

2.5. Permeation studies

Permeation studies of THF–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. Downstream pressure was maintained at ~1 mmHg by a vacuum pump. The THF–water 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. Two types of experiments were carried out in PV. Firstly, membranes with (i) varied blend compositions, (ii) varied blend composition with 2 wt% micro filler (MF2) for each blend and (iii) varied blend compositions with 2 wt% nano filler for each blend (NF2) were used for separation of 89 wt% THF in water at 30 °C. One UF, one MF2 and one NF2 membranes showing the best results for flux and selectivity among all the membranes were identified and further used for separation of 80–99 wt% THF in water at the same temperature (30 °C). For studying the effect of temperature, PV experiment for 89 wt% THF in water was also carried out at four different temperatures, i.e., 30 °C, 40 °C, 50 °C and 60 °C. At steady state permeates was collected in traps immersed in liquid nitrogen. The results for pervaporation separation of THF–water mixtures were reproducible, and the errors inherent in the PV measurements were less than 1.0%. The permeate weight was determined by a digital electronic balance.

2.5.1. Permeation flux and separation factor

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 as

$$J = \frac{W}{At} \tag{2}$$

The amount of water present in the permeate was determined in a similar way as in the case of membrane phase composition for sorption experiment by a Abbey type digital refractometer (Anton Paar, model – Abbemat-HP). The separation factor (α_{PV}) of water was expressed as

$$\alpha_{PV} = \frac{y_{Water}/y_{THF}}{x_{Water}/x_{THF}} \tag{3}$$

Here y_i and x_i are weight fraction of component i (water) in permeate and feed, respectively.

2.5.2. Permeability and intrinsic membrane selectivity

The driving force normalized flux or permeability of component i is obtained from thickness (L) of the membrane and vapor pressure differential using the following Eq. (4) (Baker, Wijmans, & Huang, 2010)

$$P_i = \frac{J_i L}{(x_{fi}\gamma_i p_{fi}^{sat} - y_{pi}p_p)} \tag{4}$$

where x_{fi} and y_{pi} are mole fraction of component i on the 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 permeate pressure in PV process. Ignoring the very low pressure on permeate side, Eq. (4) reduces to

$$P_i = \frac{J_i L}{f} \tag{4a}$$

where fugacity, $f = x_{fi}\gamma_i p_{fi}^{sat}$.

Intrinsic membrane selectivity (α_s) is defined as the ratio of partial permeability

$$\alpha_s = \frac{P_i}{P_j} \tag{4b}$$

3. Results and discussion

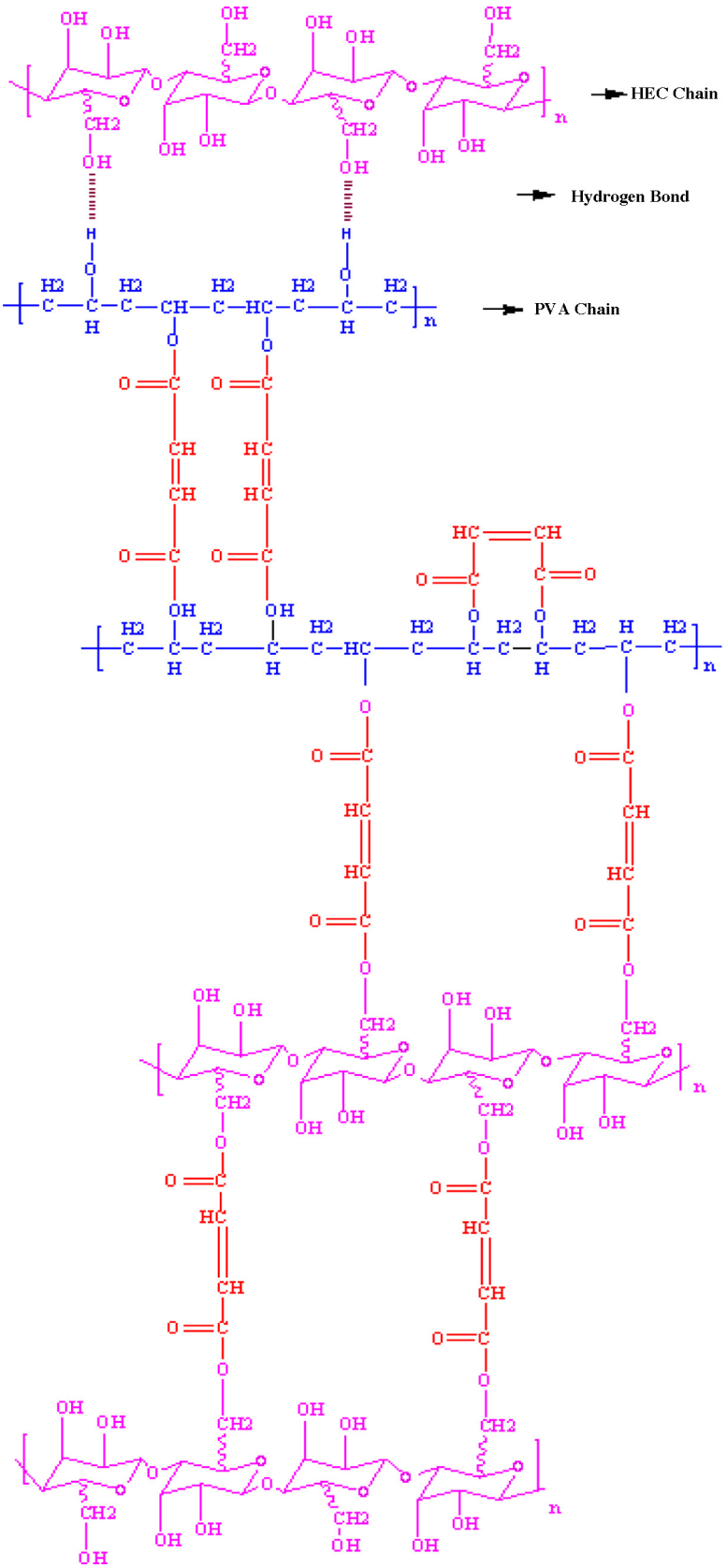
3.1. Synthesis and characterization of the membranes

3.1.1. Synthesis of blend membranes

The blend membranes of PVA and HEC were made by solution blending in water. PVA and HEC were chosen as membrane material since both are high molecular weight hydrophilic polymer and soluble in water. Because of close solubility parameter values (PVA 21.2, cellulose-21.7, Brandrup, Immergut, & Grulke, 1999) and similar polarity this polymer pair is expected to give a thermodynamically compatible blend with strong polymer–polymer interaction and interfacial adhesion by solution blending using a common and easily available solvent, i.e., water. In all of the blends PVA was the major component because of its excellent film forming property, hydrophilicity and mechanical integrity. HEC was added to further increase the hydrophilicity of PVA membrane. HEC can be crosslinked using maleic acid but HEC alone cannot give a stable hydrophilic membrane in spite of its high water absorption properties. However, blending of HEC with PVA followed by crosslinking with an aldehyde or acid gives a stable water resistant membrane. Thus, in the present work membranes were prepared from different compositions of PVA–HEC blend and used for dehydration of THF. For making pure polymer solutions 5 wt% PVA and 3 wt% HEC in water were made since above this concentration the respective polymer solutions become too viscous to make a stable solution blend. Among various crosslinkers 2 wt% (of total polymer) maleic acid was considered since in one of our previous works 2 wt% maleic acid crosslinked PVA membrane was found to give optimum flux and selectivity for water–organic binary mixtures (Singha et al., 2009). The possible structure of this blend polymer is shown in Scheme 1. Apart from formation of chemical bond or crosslinking between hydroxyl groups of the polymers, i.e., PVA or HEC with carboxyl groups of maleic acid, hydrogen bonding also forms among hydroxyl and carboxyl groups of PVA and HEC (Sin, Rahman, Rahmat, & Samad, 2010). Inorganic bentonite filler was used as hydrophilic filler since in our previous works this filler was found to increase water selectivity of PVA–carboxymethyl cellulose blend membranes (Das & Ray, 2013) and also copolymer (Samanta, Ray, Das & Singha, 2012) membranes.

3.1.2. Characterization of the membranes by FTIR

The FTIR spectra of the unfilled UF and filled MF2 and NF2 membranes are shown in Fig. 1a. For comparison, spectra of crosslinked PVA and HEC is also shown in the same figure. In Fig. 1a crosslinked



Scheme 1. Formation of crosslink blend.

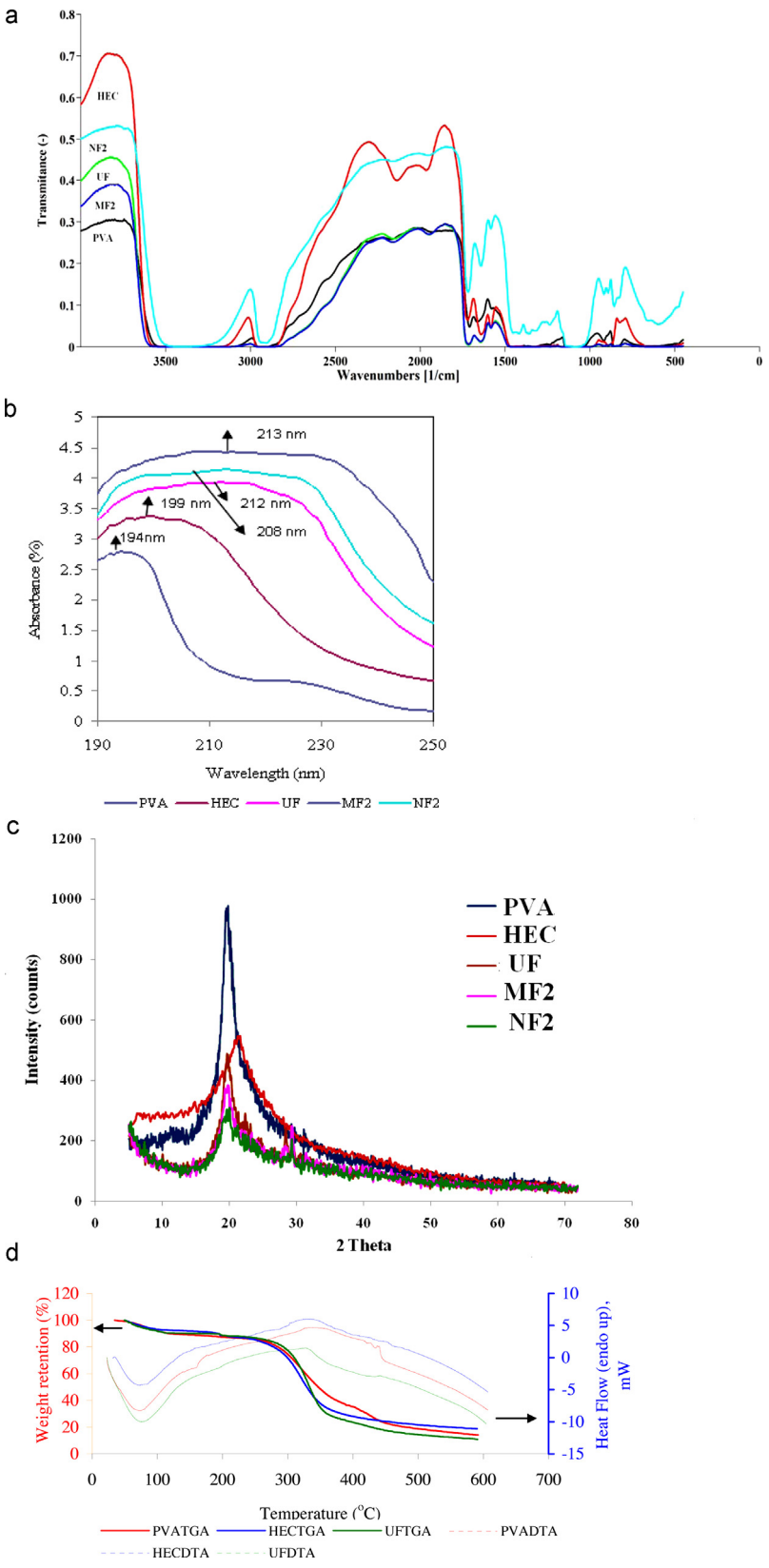


Fig. 1. (a) FTIR of the polymer. (b) UV spectroscopy of the polymers. (c) XRD of the polymer. (d) DTA and TGA of the polymer.

HEC is observed to show a broad band at 3324 cm^{-1} corresponding to its —OH stretching, intermolecular hydrogen bonding and also crosslinking (Dai, Yan, Yang, & Cheng, 2010; Wang, Wang, Kang, & Wang, 2011). This absorption band is observed at 3317 cm^{-1} in crosslinked PVA. In the blend of HEC and PVA both of these absorption bands are overlapped in one single broad peak, i.e., at 3331 cm^{-1} in UF, 3333 cm^{-1} in MF2 and 3352 cm^{-1} in NF2. Similarly, absorption band at 2903 cm^{-1} in HEC and 2925 cm^{-1} in PVA

due to asymmetric and symmetric stretching vibration of —CH_2 groups of HEC or PVA is shifted to 2907, 2907 and 2909 cm^{-1} in UF, MF2 and NF2, respectively (Abdel-Halim, 2014; Kalyani et al., 2006). The crosslinking reaction between PVA or HEC with unsaturated bi carboxylic maleic acid results in the formation of unsaturated ester which is evident by 1642 cm^{-1} band in HEC and 1664 cm^{-1} band in PVA due to —CO—CH=CH stretching (Nakanishi & Solomon, 1977). These two absorption bands of PVA and HEC also overlap to a single absorption band at 1644, 1644 and 1642 cm^{-1} in the UF, MF2 and NF2, respectively. The carbonyl (—C=O) stretching due to maleic acid at 1709 cm^{-1} in PVA and 1719 cm^{-1} in HEC is shifted to 1715, 1715 and 1719 cm^{-1} in the UF, MF2 and NF2, respectively. Similarly, 826 cm^{-1} band of HEC due to C—O—C stretching of its β-1,4 glucosidic linkages and 852 cm^{-1} band of PVA due to its —CH alkane group is also shifted and overlapped to 859 cm^{-1} in the UF, 860 cm^{-1} in the MF2 and 852 cm^{-1} in the NF2 membrane. The 1096 cm^{-1} absorption band of PVA due to bending vibration of its —OH groups is shifted and overlapped with absorption due to Si—O—Si to 1084, 1085 and 1085 cm^{-1} in the UF, MF2 and NF2, respectively. Similarly, the —CH stretching of 1316 cm^{-1} of crosslinked HEC is shifted to 1338 cm^{-1} in the UF, 1341 cm^{-1} in the MF2 and 1320 cm^{-1} in the NF2 blend. The CH_2 symmetric bending vibration at 1417 cm^{-1} of crosslinked HEC is observed to shift to 1452 cm^{-1} in MF2 and 1452 cm^{-1} in NF2 while 1584 cm^{-1} peak of HEC due to absorbed water shows minor shifting to 1582, 1583 and 1583 cm^{-1} in the UF, MF2 and NF2 blend. The MF2 and NF2 membranes are similar to UF membrane, i.e., blend of HEC and PVA and thus, their spectral absorbance appears to be similar. However, presence of micro (MF2) and nano (NF2) filler in these membranes are also evident by characteristic absorption bands at 916 cm^{-1} in MF and 917 cm^{-1} in NF due to vibration of SiO—H, 1604 cm^{-1} in MF2 and 596 cm^{-1} in NF2 due to vibration of Si—O—Al (Zheng, Xu, Peng, Wang, & Peng, 2007). All of these absorbance and its shifting and overlapping clearly indicate crosslinking and strong electrostatic interaction in the crosslinked, blend and filled blend membranes (Das & Ray, 2013; Kuila & Ray, 2014).

3.1.3. UV spectroscopy

The UV absorption of PVA, HEC, unfilled and filled blend membranes are shown in Fig. 1b. PVA is observed to show strong absorption in the 200–400 nm regions. Accordingly, the crosslinked PVA, HEC, UF, MF2 and NF2 membranes show shoulder like band at 194, 199, 212, 208 and 213 nm, respectively. These bands are due to presence of conjugated double bond as a result of isolated carbonyl groups associated with unsaturated ethylene group, i.e., $(CH{=}CH)_2C{=}O$ (Rao, 1967). The shoulder like band of PVA or HEC is broadened and shifted to higher wavelength in the blend and also in the filled membranes because of polymer–polymer and polymer–filler interaction as also reported elsewhere (Abdelaziz & Abdelrazek, 2007). The optical absorption of the membranes were evaluated in terms of absorption coefficient, $\alpha(\nu)$ using the following Eq. (5) (El-Sayed, Mahmoud, Fatah, & Hassen, 2011)

$$\alpha(\nu) = \frac{a}{L} \tag{5}$$

Here 'a' is absorbance of the membrane of thickness L. The absorption edge values of the membranes (ΔE) were determined by exponential regression of photon energy ($h\nu$) against $\alpha(\nu)$ using Urbach equation (Eq. (5a)) (El-Sayed et al., 2011)

$$\alpha(\nu) = \alpha_0 \ \exp\left(\frac{h\nu}{\Delta E}\right) \tag{5a}$$

The values of Urbach energy or absorption edge (ΔE) for PVA, HEC, UF, MF2 and NF2 membranes were (5.80, 5.86, 4.73, 4.45 and 4.25 eV, respectively). Blending or filler incorporation increases defect in the structure and thus blend and filled samples show lower absorption edge values. This signifies the induced change in number of available final states. The lower the values of E, the higher are the carrier concentration in the localized levels as per the blend composition. Similar values of E was observed for filled PVA and blend of uncrosslinked PVA and CMC (El-Sayed et al., 2011).

3.1.4. XRD analysis

The XRD of the PVA, HEC, UF, MF2 and NF2 blend membranes are shown in Fig. 1c. The crystallinity of PVA and HEC arises from intermolecular hydrogen bonding between polymer chains of PVA and HEC. The diffraction peak of the PVA at around 2θ of 20° as shown in Fig. 1c is due to diffraction from mixtures of its (1 0 1) and $(1\,0\,\bar{1})$ planes (Bhat, Nate, Kurup, Bambole & Sabharwal, 2005). Similarly, HEC is observed to show a diffraction peak at 21.6°. The peak intensity is reduced significantly and 2θ is also shifted in the blend and filled membranes. Thus, in the blend and filled membranes the PVA peak at around 20° is observed with much reduced intensity while the 21.6° peak is shifted to around 28°. It clearly indicates reduction in crystallinity in these membranes.

The loss in crystallinity of the blend and filled membranes may be attributed to electrostatic interaction and intermolecular hydrogen bonding between PVA and HEC in the blend which reduces hydrogen bonding of the respective polymer (PVA–PVA and HEC–HEC) molecules.

3.1.5. DTA–TGA

The DTA curves of polymers give information about loss of water at different temperatures as well as transition temperatures. However, it is difficult to clearly detect glass transition (T_g) because of the change of heat capacity of crosslink polymer over a wide range of temperature (Russo, Abbate, Malinconico, & Santagata, 2010). Crosslinking imposes restriction in segmental motion of polymer chain. Thus, the T_g of the polymer increases. Accordingly, uncrosslinked PVA shows a T_g of 80–85 °C (Finch, 1973) and uncrosslinked HEC shows a T_g of 65 °C (Naidu, Sairam, et al., 2005). From Fig. 1d it is observed that crosslinked HEC shows an exothermic peak at 155 °C corresponding to its T_g while crosslinked PVA shows its T_g at 162 °C as also reported elsewhere (Kuila & Ray, 2014). Because of electrostatic interaction between HEC and PVA, the T_g is shifted to around 198 °C in the UF blend. The crosslinked and blend polymers also show exothermic peaks due to thermal degradation at around 330–340 °C (Kuila & Ray, 2014; Wang et al., 2011). The TGA of the polymers are shown in the same figure. The crosslinked and blend polymers show three temperature regions of degradation – (i) around 5–20% degradation in the temperature range of 70–285 °C, (ii) 20–75% degradation in the temperature range of 290–360 °C and (iii) 80–90% degradation up to 600 °C. These degradation regimes are due to loss of water, breaking of hydrogen bond and thermal degradation of the main chain of the polymers (Kuila & Ray, 2014).

3.1.6. Mechanical properties

The tensile strength and elongation at fracture of the membranes were determined for evaluating its strength. To study the solvent resistance of the membranes, tensile strength and elongation at fracture of the membranes were also determined after immersion in pure solvent (THF and water) for 1 week. Accordingly, the tensile strength of the dry UF, MF2 and NF2 membranes were found to be 9.31, 18.76 and 22.48 MPa, respectively which reduced to 7.58, 17.0 and 19.5 MPa, respectively in water and 8.61, 17.95 and 21.01, respectively in THF. Similarly, elongation at fracture of these dry membranes were 37.4, 31.8 and 33.2%, respectively which increased to 43, 34 and 37% in water and 41, 32.3 and 34.2% in THF. The filled blend membranes were found to show higher tensile strength but lower elongation at fracture than unfilled blend membranes which may be due to increase in stiffness

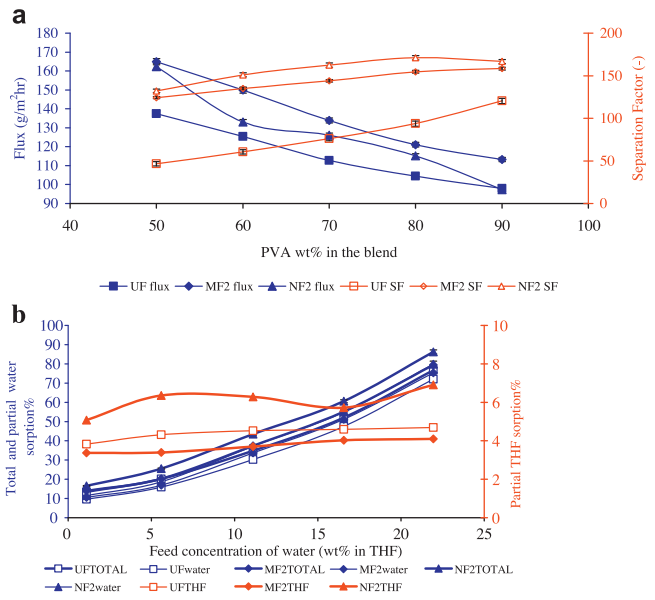


Fig. 2. (a) Optimization of blend composition for unfilled (UF), 2 wt% micro particle filled (MF2) and 2 wt% nano particle filled (NF2) membranes. (b) Feed conc. vs. total and partial sorption for UF, MF2 and NF2 membranes.

of the membranes in presence of inorganic fillers. From the above tensile data it is observed that the solvent-swollen membranes show somewhat lower tensile strength but higher elongation at fracture than the dry (not immersed in water or THF) membranes. Further, the change in tensile strength and elongation at fracture of the water swollen membranes are observed to be higher than those of the THF-swollen membranes which signify water selectivity of the hydrophilic blend membranes. For sorption and pervaporation experiments 80–99 wt% THF in water was used. In these solvent mixtures the mechanical properties of these unfilled and filled blend membranes are expected to be intermediate between the mechanical properties of the dry (and unused) membranes and wet membranes swollen in pure water and pure THF.

3.2. Selection of membranes

In Fig. 2a the flux and separation factor for 89 wt% water in feed were plotted against wt% of PVA in the blend for unfilled (UF), micro particle filled (MF2) and nano particle filled (NF2) membranes to find out the blend compositions giving the optimum results with respect to both flux and separation factor. In general flux and separation factor bears a trade off relation, i.e. for the same feed concentration, flux increases at the cost of selectivity as also observed in Fig. 2a. It is observed that with increase in wt% of PVA in the blend flux decreases while separation factor increases. PVA is a linear polymer with one —OH group in its repeating unit and thus it is flexible. However, the repeating unit of HEC is hexagonal ring structure containing three —OH groups (Scheme 1) and thus it is more hydrophilic but less flexible than PVA. Consequently, with decrease in HEC content or increase in PVA content, the membranes become increasingly flexible and flux decreases because of decreased hydrophilicity. In Fig. 2a the point of intersection of the curves corresponding to flux and curves corresponding to separation factor were considered as optimum blend composition for these three set of membranes, i.e., UF, MF2 and NF2. Accordingly, one UF, one MF2 and one NF2 membrane with 64, 67 and 56 wt% PVA, respectively (Fig. 2a), were found to give optimum flux and selectivity as shown in Fig. 2a. These three membranes were further used for sorption and pervaporation of 80–99 wt% THF in water.

3.3. Sorption

3.3.1. Effect of feed concentration on sorption

The variation of total sorption and partial sorption with feed concentration of water at 30 °C is shown in Fig. 2b. From this figure it is observed that total sorption (shown with thick blue lines) increases almost linearly with feed concentration for these three membranes, i.e., UF, MF2 and NF2. Similarly, these membranes also show high water sorption and partial water sorption (shown with thin blue lines) also follows the same trend, viz. it also increases linearly, with feed concentration. It is also observed that the membranes show much higher water sorption than THF sorption (shown with red lines). As the feed water concentration is increased from 5 wt% to around 19.5 wt% partial water sorption by the membranes is observed to increase from 16, 17 and 19 wt% to 72, 75 and 80 wt% for UF, MF2 and NF2 membrane, respectively. On the other hand for the same feed concentration range THF sorption is observed to increase marginally from 4.3, 3.3 and 6.3 wt% to only 4.6, 4.1 and 6.3 wt% for UF, MF2 and NF2, respectively. Xiao et al. (2007) reported around 12.5 wt% water and 6 wt% IPA in trimesoyl chloride crosslinked PVA membrane for sorption of IPA–water mixture containing19.5 wt% water in feed. Kuila and Ray reported (Kuila & Ray, 2014) around 25 wt% water in a blend membrane of PVA and sodium alginate containing 25 wt% PVA and 2 wt% nano sodium montmorilonite filler for sorption of dioxane–water mixtures with same feed concentration. In the present work the high water sorption may be ascribed to hydrophilic nature of the blend and filled membranes. Both PVA and HEC are hydrophilic because of the presence of large number of —OH groups in its structure which form hydrogen bonds with water. In fact, both PVA and HEC are soluble in water. However, crosslinking with maleic acid results in crosslinked structures of the blend membranes (Scheme 1) which is not soluble in water but can absorbs a large amount of water. Further, blending and crosslinking of the membranes results in reduction in crystallinity as also evident from XRD (Fig. 1d). With increase in water content in feed, crystallinity of the membranes further reduces (Hodge, Edward, & Simon, 1996) and hence water sorption also increases. On the other hand THF is a nonsolvent for PVA or HEC and thus, it shows poor sorption in the membranes.

3.4. Pervaporation (PV)

3.4.1. Flux and separation factor

The results of thickness normalized flux for the three membranes at 30 °C are shown in Fig. 3a for varied feed concentrations. Like sorption the thickness normalized flux of the membranes are also observed to increase almost linearly with feed water concentration while separation factor for water decreases almost exponentially with feed concentration. The high flux of the unfilled and filled blend membranes may also be ascribed to hydrophilicity of the membranes. At higher feed water concentration flux is also observed to increases at a much higher rates viz. as the feed water concentration is increased from 5 to 10 wt%, the flux of NF2 membrane increases from around 5 to 7 kgmμ/m^2 h while from 10 to 20 wt% water in feed flux increases from around 7 to 14 kgmμ/m^2 h. Similar rate of increase of flux is also observed for the other two membranes. In fact, hydrophilicity of the membranes increases further with increase in feed water concentration. Hodge et al. (1996) found that water swollen PVA membrane losses its crystallinity and above 62 wt% water in membrane, it becomes completely amorphous. From sorption experiments carried out with similar feed concentration it is observed that at around 20 wt% water in feed, the water% in the membranes are above 60 wt%. Thus, at higher

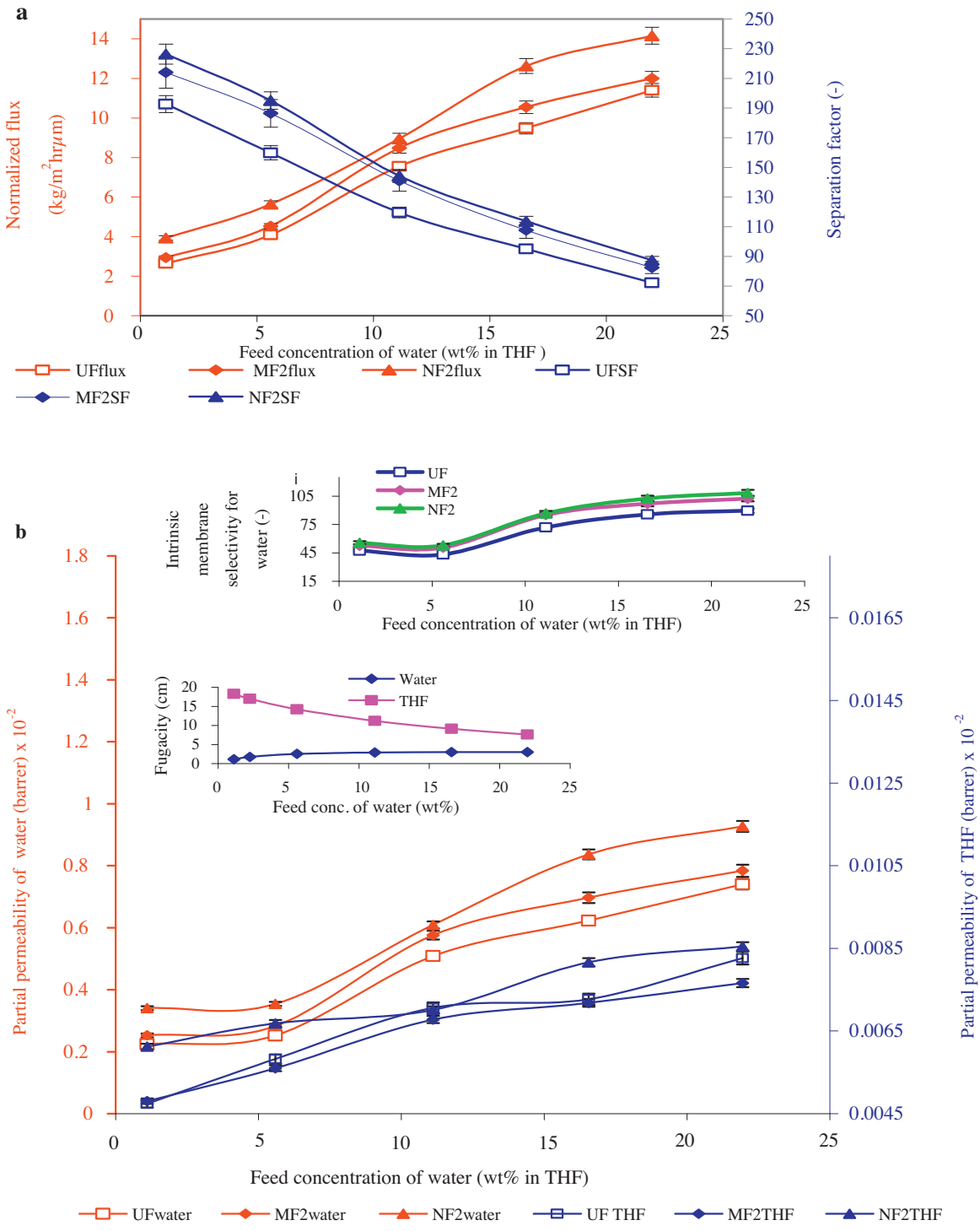


Fig. 3. Variation of (a) normalized flux and separation factor, (b) partial permeability, fugacity and intrinsic membrane selectivity with feed conc. at 30 °C temperature.

feed water concentration, the blend and filled membranes remain in the amorphous state and its polymer chains become more flexible resulting in increased free volume and hence increase in water flux. It is also observed from Fig. 3a that the membranes show very high selectivity even for diluted feed. Thus, the water selectivity of NF membrane is observed to be 226 at ~99 wt% THF in feed but it also shows a good selectivity of around 90 at ~78 wt% THF in feed. Similar trend is observed for the other two membranes. This may be because of low THF flux over the entire feed concentration range. THF being a nonsolvent for these blend membranes show low flux over the entire feed concentration range.

3.4.2. *Partial permeability and intrinsic membrane selectivity*

The variation of driving force normalized partial flux or partial permeability of water and THF is shown in Fig. 3b. From this figure it is observed that over the entire feed concentration range water permeability is much higher than THF permeability. Further, similar to flux, filled membranes viz., MF2 or NF2 also shows

higher permeability than unfilled UF2 membrane. Permeability and flux show different trend for most of the solvent dehydrations, i.e., unlike flux permeability decreases with feed concentration (Baker et al., 2010). In the present case an opposite trend of permeability is observed, i.e., like flux permeability also increases almost linearly with feed concentration. The partial permeability is the ratio of partial flux and fugacity ($x_{fi}\gamma_i p_{fi}^{sat}$, Eq. (4a)). In the present case the rate of increase of partial flux with concentration more than offset the rate of increase of fugacity with concentration and thus like flux, permeability also increases with concentration. It is also observed from the inset of Fig. 3b that change in fugacity of water with feed concentration is marginal while THF fugacity decreases drastically above around 10 wt% water in feed. This variation of fugacity is reflected in the results of permeability, i.e., partial permeability of the solvents also increase significantly above around 10 wt% water in feed. From the inset of Fig. 3b it is also observed that intrinsic membrane selectivity also increases with feed concentration. Similar trend of permeability or intrinsic membrane selectivity was also reported for pervaorative dehydration of THF by IPN type blend membrane of PVA and acrylic copolymer (Kuila & Ray, 2012).

3.4.3. Diffusive flux and diffusion coefficient

The diffusion coefficient of solvents through PV membranes may be determined by various methods based on solution diffusion models as reported elsewhere (Naidu, Shetty, & Aminabhavi, 2004; Shao & Huang, 2007). However, solvent concentration varies across the thickness of the membrane. The concentration average diffusion coefficients through the present unfilled and filled membranes were obtained as (Lue, Ou, Kuo, Chen, &Yang, 2010)

$$D_1 = \frac{J_{1diff} \times L}{m_1 \times \rho_p} \tag{6}$$

Here m_1 is membrane phase concentration of component 1 which is obtained from sorption experiment. J_{1diff} is diffusive flux of component 1 which is related to its mass flux i.e. J_1. Diffusive flux of component i and j may be expressed by the following Eqs. (6a) and (6b), respectively (Lue et al., 2010).

$$J_{idiff} = \frac{m_i[1+r^{-1}]}{\ln[1-m_i(1+r^{-1})]^{-1}} J_i \tag{6a}$$

$$J_{jdiff} = \frac{m_j[1+r]}{\ln[1-m_j(1+r)]^{-1}} J_j \tag{6b}$$

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

The effect of feed water concentration on the ratio of diffusive to partial flux (J_{diff}/J) of water and THF is shown in Fig. 4a. It is observed that diffusive flux of water contributes to around 50–95% of its partial flux while diffusive flux of THF is found to be around 15–85% of its partial flux. It indicates that permeation of the solvents through the membranes is dominated by diffusion. From Fig. 4a it is also observed that diffusive flux of the solvents decreases almost exponentially with feed concentration. It signifies plasticization of the hydrophilic membranes by water at higher feed water concentration. From Fig. 4b it is observed that at any feed concentration diffusion coefficient of water is higher than diffusion coefficient of THF. Further, filled membranes show higher diffusion coefficient than unfilled membrane. The kinetic diameter of water molecule (0.265 nm) is smaller than kinetic diameter of THF (0.490 nm) (Tuan, Li, Falconer, & Noble, 2002). Thus, smaller water molecules can easily diffuse through the membranes and consequently diffusive flux and diffusion coefficient of water is observed to be higher than diffusive flux or diffusion coefficient of THF.

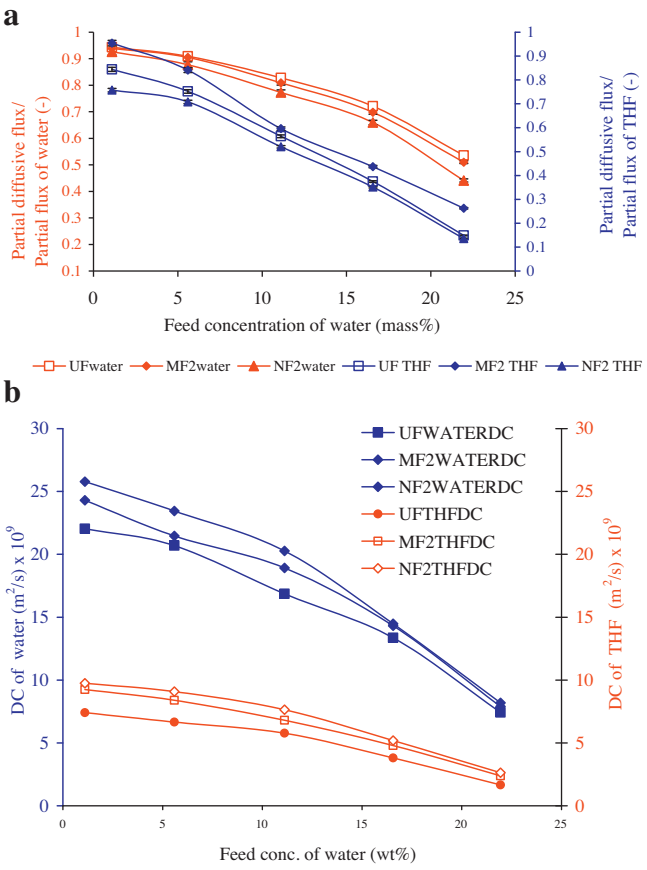


Fig. 4. (a)Variation of ratio of partial diffusive flux to partial flux with feed concentration, (b) Diffusion coefficient (DC) with feed conc. at 30 °C.

3.4.4. Effect of temperature

The effect of temperature on flux and separation factor is shown in Fig. 5i while variation of partial permeability and intrinsic membrane selectivity with temperature is shown in Fig. 5ii and iii, respectively. With increase in temperature flux increases because of increase in vapor pressure of solvents and also increases in frequency and amplitude of segmental motion of polymeric chain of the blend and filled membranes. In contrast partial permeability is observed to decrease with temperature. In this case rate of increase of fugacity with temperature more than offset rate of increase of flux with temperature. The separation factor or intrinsic membrane selectivity of the membranes are also observed to decrease with temperature which may be due to increase in THF flux at higher temperatures. The apparent activation energy (E_p) of solvent permeation was obtained from the slope of the linear plot of logarithmic of partial flux against inverse of absolute temperature ($1/T$). In each of these linear regressions the value of regression coefficients (r^2) was much above 0.9. E_{pwater} for UF, MF2 and NF2 membranes were found to be 18.3, 14.3 and14.1 kJ/deg mol, respectively while E_{pTHF} for these membranes were found to be 26.4, 19.6 and 17.9 kJ/deg mol, respectively. The lower activation energy for water also explains high water selectivity of the membranes (Naidu, Krishna Rao, & Aminabhavi, 2005). These values of activation energy are similar to those reported for water and THF with other membranes (Kuila & Ray, 2012; Naidu, Krishna Rao, et al., 2005).

3.4.5. Comparison of present work with reported data

In Table 1 the performance of the present unfilled and filled blend membranes were compared in terms of its flux and selectivity with other membranes reported for pervaporative dehydration of

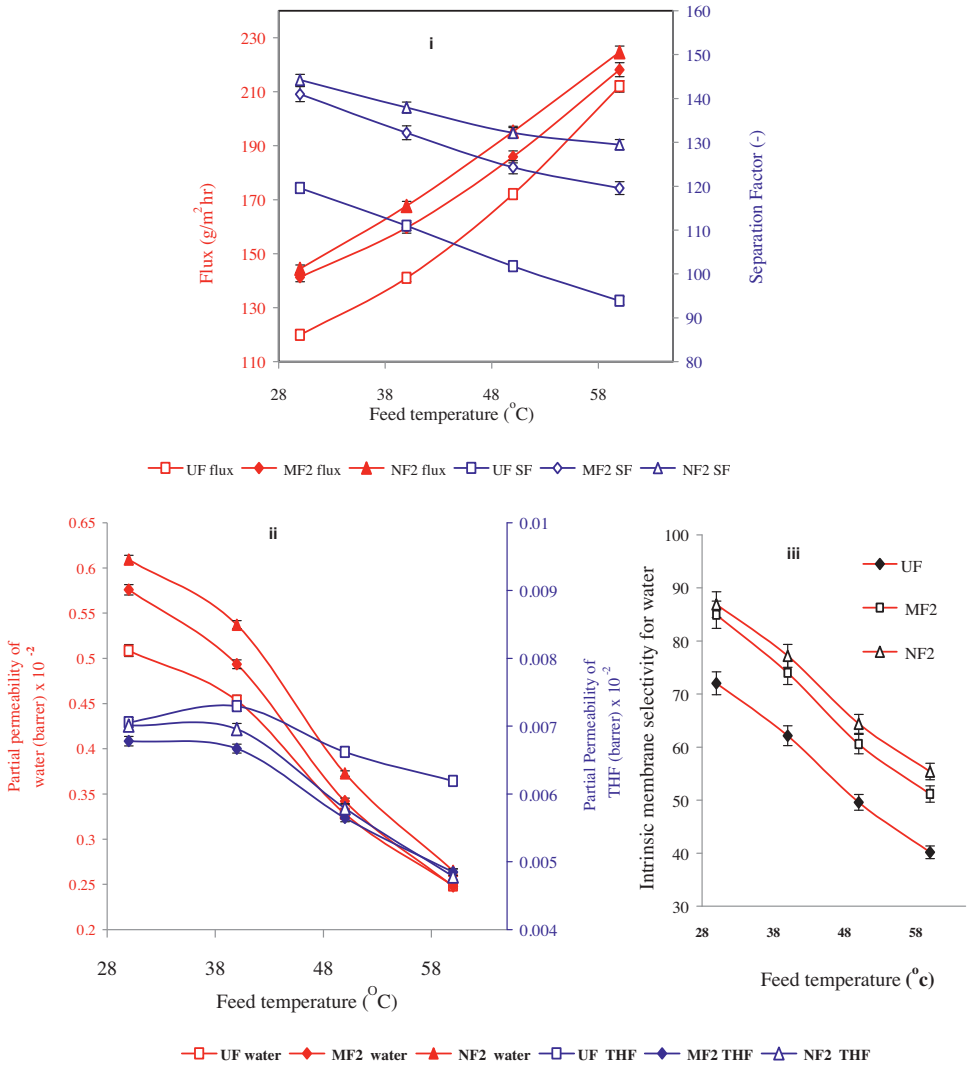


Fig. 5. (i) Variation of flux and separation factor (SF), (ii) partial permeability and (iii) intrinsic membrane selectivity with temperature for 89 wt% THF in feed.

Table 1
Comparison of pervaporation results of the present membranes with other publishes data for separation of THF–water mixtures.

Membrane	Feed conc. (wt% THF in water)	Temp (°C)/mem. thickness (μm)	Flux (kg/m^2 h)	Water selectivity	Ref.
NaAlg.HEC20	90	30/40	0.192	508	Naidu et al. (2005)
Celfa CMCcom	96	55/–	1	480	Chapman et al. (2006)
PVP-CS	94.31	35/40	0.0995	1025	Devi, Smitha, Sridhar, and Aminabhavi (2006)
PVA-Iron	90	30/40	0.079	470	Sairam, Naidu, Nataraj, Sreedhar, and Aminabhavi (2006)
PANHEMA-3	99.46	30/50	0.052	176.5	Ray and Ray (2007)
Polyaniline-AS	96	55/100	0.622	34	Chapman, Loha, Livingston, Lia, and Oliveira (2008)
PAMHEMA-1	99.7	30/50	0.57	216	Ray and Ray (2008)
FIPN50	94.3	30/50	0.069	79.34	Kuila and Ray (2012)
UF	94.5	30/50	0.082	160	Present work
MF2	94.5	30/50	0.090	186	Present work
NF2	94.5	30/50	0.112	195	Present work

THF. It is observed that the present membranes show much higher flux and selectivity than most of the reported membranes under similar operating conditions.

4. Conclusion

Unfilled and filled blend membranes of PVA and HEC were prepared by varying blend compositions. The unfilled and filled blend membranes were characterized by FTIR and UV spectroscopy, XRD, DTA-TG and mechanical properties. These membranes were used for sorption and pervaporation of THF–water mixtures. It was observed that with increase in wt% of PVA in the blend the flux and permeability of the membranes decreased while water selectivity increased. Among all the membranes the filled membrane containing 2 wt% nano filler showed the highest flux and separation factor for water over the entire feed concentration range of 80–99 wt% THF

in water. These hydrophilic blend and filled membranes may also be used for pervaporative dehydration of other similar solvents.

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