Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.999131

57 (2016) 4920–4934
March

Taylor & Francis
Taylor & Francis Group

Performance enhancement of the poly (vinyl alcohol) (PVA) by activated natural clay clinoptilolite for pervaporation separation of aqueous–organic mixtures

Sakey Ravindra[a,*], V. Rajinikanth[a], Antoine F. Mulaba-Bafubiandi[b], Vijaya Srinivasu Vallabhapurapu[a]

[a]*Department of Physics, College of Science, Engineering and Technology, University of South Africa, Johannesburg 1709, South Africa, Tel. +27 749778041; email: ravisakey@gmail.com (S. Ravindra), Tel. +27 843430820; email: rajineekanth@gmail.com (V. Rajinikanth), Tel. +27 722601037; email: Vallavs@unisa.ac.za (V.S. Vallabhapurapu)*
[b]*Faculty of Engineering and the Built Environment, Department of Metallurgy, University of Johannesburg, Johannesburg 2028, South Africa, Tel. +27 11 559 6635; Fax: +27 (0)11 559 6194; email: amulaba@uj.ac.za*

Received 31 July 2013; Accepted 10 December 2014

ABSTRACT

The pervaporation (PV) performance of poly (vinyl alcohol) (PVA) is enhanced by the addition of natural clay clinoptilolite into it. Nanocomposites of glutaraldehyde cross-linked (*in situ*) PVA/clinoptilolite membranes were prepared by solution casting technique to investigate the water flux, selectivity, perm selectivity and enrichment factor. PV experiments using clay incorporated membrane matrix (CIMM) have been performed at 30, 40 and 50˚C to separate water–isopropanol/ethanol feed mixtures containing 10–40 wt. % of water. These membranes were characterized by universal testing machine to understand the mechanical strength. The morphological analysis has been studied using scanning electron microscopy. The high content (5 and 10%) of clay in the CIMM extracts water efficiently on the permeate side with high selectivity. The hydrophilic nature of clay and the formation of CIMM are responsible to offer such increased separation of water over the organic components of the feed mixtures.

Keywords: Mixed matrix membranes; Pervaporation; Azeotropic mixtures; Clay

1. Introduction

Membrane separation process has become one of the emerging technologies that underwent a rapid growth in the past few decades. Pervaporation (PV) is a widely employed membrane-based separation method used to separate azeotropic mixtures and organic–organic mixtures [1–3]. Interest in PV is significantly increasing in the chemical industry as an effective and energy-efficient technology to carry out separations. The advantage of this method is environmentally benign as it does not require entrainer such as carcinogenic benzene to break the azeotrope and it provides efficient separation at normal operating conditions without using any external chemical separating agent [4].

The sorption–diffusion process is well-known mechanism for pervaporative separation. Firstly, a sorption into the membrane has to take place at the upstream side, secondly, diffusion through the

---

*Corresponding author.

membrane, and then, desorption into the vapour phase at the downstream side [5]. Hydrophilic membranes are more suitable to separate water from water/organic mixtures. Even if hydrophilic polymeric membranes showed a high selectivity, they were known to be very sensitive to the operational condition such as the feed concentration and the temperature. Mixed matrix membranes (MMM) are eventually a right choice to use for water separation, since they show not only molecular sieve effects but also good thermal, chemical and mechanical stabilities [6,7].

In view of selecting an organic-based polymer matrix, poly (vinyl alcohol) (PVA) is a suitable synthetic polymer due to nontoxic, environmentally safe, water soluble, biocompatible and biodegradable properties. PVA attracts the attention of the research community because of the good film forming ability, high tensile strength, flexibility and barrier properties [8,9,13]. However, the semicrystalline property of PVA limits its application as PVA membranes have satisfactory permeation flux but not PV dehydration. Several researchers reported about incorporation of fillers, clay, etc. to improve the swelling property, increase flux and separation factor [10,11] of PVA. It has been proved that the hydroxyl groups on PVA can also serve to adsorb heavy metal ions, anionic and cationic dyes [12,13].

Oh et al. [1] prepared the MMM using both nanosized NaA zeolite particles and micro-sized NaA zeolite particles dispersed in the PVA matrix. Increase in the % of the NaA zeolite particles (0–5 wt. %) in PVA membrane increases the flux of water through the MMM by a factor of 2.5 compared to the pure PVA membrane at the typical operation condition. When the nanosized particles were dispersed in the MMM instead of the micro-sized particles, the flux of water increased by 20% and separation factor by 5% as compared to the MMM containing the micro-sized NaA particles. Gao et al. [14] have fabricated hydrophilic composite membranes consisting of micro-sized NaA zeolites and PVA for the PV of ethanol/water PV. They observed that the flux and separation factor were 172 ml/m^2/h and 36.6 at 50˚C. Adoor et al. [15] have reported the use of the MMM of PVA containing sodium montmorillonite clay for PV of water–isopropanol mixtures. Their MMM showed the water flux range between 151 g/m^2/h and 184 g/m^2/h at 10 wt. % of water in a feed solution and the temperature range of 40–50˚C. On the other hand, the separation factors were in the range of 217–1,314. Teli et al. [16] published their results on MMM of PVA loaded with phosphomolybdic heteropolyacid (HPA) for the PV separation of water-isopropanol mixtures. In this study, they concluded that by increasing the amount of HPA in MMM, the performance of PVA membrane has improved. The PVA membrane containing 7 wt. % HPA exhibited a water selectivity to of 89,991 as compared to the pristine cross-linked PVA membrane when tested for 10 wt. % water in the feed. Such a considerable increase in selectivity (compared to a value of 77 for pristine PVA) at higher concentration of HPA is due to increased hydrophilicity of the MMMs, thereby attracting more of water molecules than isopropanol.

Hu et al. [17] reported that the impact of the MWCNTs in PVA membrane on the separation performance was particularly significant at low feed water concentrations (1 wt.% at 70˚C), a permeation flux of 146 g/(m^2 h) and a separation factor of 1,160 were achieved using a PVAm-PVA/CNT composite membrane containing 2 wt. % MWCNTs. Similar result has been observed by Xia et al. [18]. A simultaneous increase in both flux and separation factor occurs with increase in the temperature (from 50 to 70˚C) in the PV process. When the operation temperature was 60˚C, the feed was 5.1 wt. % and the feed flow rate was 252 mL/min, the membrane exhibited excellent PV performance with the water permeance of 1.45 × 10^{-5} kg/m^{2}s kPa and selectivity (water to EAC) of 129. So this particular property of the membrane is good to the PV process. Flynn et al. [19] have suggested inexpensive mesoporous synthesis routes as well as chemical functionalization treatments that are very useful in the PV separation process. In this work, they observed the significant increases in both flux and selectivity. Huang et al. [20] used multilayer PVA membrane with and without 4A zeolite membrane for separation of water from highly concentrated ethanol aqueous solution, they found interested results show that the addition of zeolites has increased separation factor and significantly boosted the overall flux, indicating that incorporated zeolite 4A can promote water transport and at the same time limit ethanol permeation. For a feed of 76.3 wt.% ethanol aqueous solution at 60˚C, the zeolite 4A-filled membranes exhibit a total flux of 936 g/m^2 h and a separation factor of 710, whereas the unfilled one possesses a total flux of 538 g/m^2 h and a separation factor of 658.

Anjali Devi et al. [21] reported the limitation of the PVA/PAAc blend membrane for separation of dimethylformamide/water mixture. Increasing the PAAc content of the blend membrane decreased the selectivity from 275 to 15.54 along with an improvement in flux from 0.012 to 0.56 kg/m^2 h. This is attributed to excessive membrane swelling due to plasticization effect. Kim et al. [22] studied the effect of organoclay in PV separation performance of PVA/PSSA-MA membranes, with a series of hybrid membranes incorporating different clay particles (clay Na^+, clay 15A and clay 30B). The prepared clay Na^+ (2.86 g/cm^3) showed the highest methanol permeability while the membrane with clay 15A (1.66 g/cm^3) showed the lowest methanol permeability. The water swelling and proton conductivity of the hybrid membrane with clay 30B was affected by organic modifier of clay 30B. The membrane with clay 30B showed the highest water swelling and proton conductivity.

Choudhari et al. [23] investigation upon the development of new composite hybrid membranes by dispersing different mass% of Na^+-MMT clay in the quaternized chitosan. They published interesting results the membrane containing 10 mass% of Na^+-MMT clay exhibited the highest separation selectivity of 14,992 and with a permeation flux of 14.23×10^{-2} kg/m^2 h at 30°C for 10 mass% of water in the feed. With regard to increase in temperature the permeation rate was increased while suppressing the selectivity. But beyond 10% mass, they found drastic decrease in flux accounted for the lower degree of swelling at higher % mass of clay due to lower free volume in polymer matrix.

In the literature, innumerable PV membranes have been developed for the separation of organic–water mixtures. Different PVA membranes have been widely used, and to improve its membrane separation performance, particularly for dehydrating alcohols, many inorganic filler particles have been added into the base polymers. The commercial success of composite membranes of PVA with poly (acrylonitrile), popularly called as GFT membranes, has been commercialized by Germans. Many studies have dealt with different types of blends or grafts of PVA to enhance their separation characteristics [16,24–27]. However, the zeolite-filled PVA MMMs are the recent trends in the PV separation of aqueous–organic mixtures [28,29].

In the present investigation, the natural clay-loaded PVA MMMs have been prepared to enhance PV performance in terms of flux and selectivity over that of pristine PVA membrane. This paper deals with the development of nanocomposite membranes of PVA by incorporating activated clinoptilolite natural clay in different concentrations for the PV separation of water–isopropanol and water–ethanol mixtures at various temperatures and feed water compositions. The developed nanocomposite membrane is used to study the flux and separation factors in terms of membrane-permeant and membrane-filler interactions.

2. Experimental

2.1. Materials

PVA ($\overline{M_w}$ = 1,20,000) is purchased from s.d. fine Chemicals, Mumbai, India. We used clinoptilolite clay in this study, and we obtained this clay sample as a gift from Zuka's group (Department of Physics, University of Kinshasa, DRC). Isopropanol, ethanol, glutaraldehyde (GA), acetone and HCl were purchased from Merck (Pty) Ltd Chemical Division Johannesburg, South Africa. Deionized water was produced in the laboratory.

2.2. Modification of clay

Acid activation method was used for the activation of clay. 50 g of natural clay having particle size of 2.0 μm was activated by refluxing with 250 mL of 1 mol/L of H_2SO_4 at 80°C in a round-bottom flask for 2 h. The slurry was air-cooled and filtered. The filter cake was repeatedly washed with distilled water until the filtrate was neutral. Finally, it was dried in an oven at 110°C before use.

2.3. Membrane fabrication

MMMs of pure PVA, PVA-Clay5 and PVA-Clay10 have been prepared by solution casting method using light hot water (around 40°C) as solvent, by incorporation of 5wt. % (PVA-Clay5) and 10 wt. % (PVA-Clay10) of clay with respect to the weight of the polymer. 4 gm of PVA was dissolved in 80 mL of water with constant stirring. Separately, activated clay particles were weighed for 5 and 10%, i.e. 0.2 and 0.4 g, respectively, and dispersed in 20 mL of distilled water. This solution was sonicated for 120 min and then added to the previously prepared PVA solution. These mixed solutions were stirred for a further period of 24 h. *In situ* cross-linking was done by adding 0.3 mL of glutaraldehyde and 0.3 mL of concentrated hydrochloric acid to the polymer solution and further stirred for about 10–15 min. Now, these polymer solutions were then poured on a clean dust-free glass plate to cast uniform thickness membranes. These polymer membranes were peeled off from the glass plate before they became thicker. Pristine PVA membrane was prepared in the same manner except clay particles were not added to the solution. The thicknesses of the PVA and PVA/clay membranes measured by micrometer screw gauze was around 50 ± 1.0 μm. Hybrid composite membranes considered for the study were slightly cloudy ash in colour and semitransparent.

2.4. Characterization

Surface micrographs of pristine PVA, PVA-Clay5 and PVA-Clay10 were obtained under a high resolution scanning electron microscope (Make: TESCANVEGA3, Bruno in Check Republic).

Differential scanning calorimetry (DSC) thermograms of pristine PVA, PVA-Clay5 and PVA-Clay10, membranes were recorded on a Rheometric Scientific (Model DSC-SP, Ashtead, Surrey, United Kingdom) instrument with a variation of temperature from 25 to 400˚C at a heating rate of 10˚C/min in nitrogen atmosphere.

Tensile strength and elongation at break of the pristine PVA, PVA-Clay5 and PVA-Clay10 filled matrix membranes were measured using a universal testing machine (UTM) (Model H 25KS, Hounsfield, Surrey, United Kingdom). Test specimens were prepared in the form of dumbbell shape as per ASTM D-638 standards. Films of gauge length 50 mm and width 10 mm were stretched at the crosshead speed of 10 mm/min.

Thermogravimetric analysis (TGA) thermograms of unfilled PVA, PVA/Clay5 and PVA/Clay10, MMMs were recorded on a TGA/SDTA (Model STA 1500, Ashtead, Surrey, United Kingdom) instrument at the heating rate of 10˚C/min in nitrogen atmosphere.

FTIR spectra were taken for monomers as well as cross-linked IPN membranes. Measurements were done on a Nicolet-740, Perkin-Elmer-283B FTIR spectrometer, Milwaukee, WI, USA. Membrane samples were ground well with KBr, and pellets were prepared by applying a hydraulic pressure of 400–450 kg/cm^2. Spectra were scanned in the range of 450–4,000 cm^{-1}.

2.5. PV experiments

The detail of PV experimental setup is described earlier in our report [30]. Before starting the PV experiment, the test membrane was equilibrated for about 2 h with the feed mixture. After establishment of a steady state, permeate vapours were collected in cold traps immersed in liquid nitrogen up to 2 h. Weight of permeate collected was measured to determine flux, J (kg/m^2 h) using the weight of liquids permeated, W (kg), effective membrane area, A (m^2) and measurement time, t (h) as:

$$J = \frac{W}{At} \tag{1}$$

The analysis of feed and permeate samples was analysed using a MAPL Gas Chromatograph (Model 1100, Bangalore, India) equipped with a thermal conductivity detector on a DEGS packed column of 1/800 ID having 2 m length by maintaining the oven temperature at 70˚C (isothermal). The injector and detector were kept at 150˚C using a sample injection volume of 1 μL. Pure hydrogen was used as a carrier gas at 0.75 kg/cm^2 pressure. The GC response was calibrated for the column and for known compositions of water + isopropanol/ethanol mixtures. Separation factor (α), PV separation index (PSI) and enrichment factor (β) were calculated using the equations:

$$\alpha = \left(\frac{P_{\mathrm{W}}}{P_{org}}\right)\left(\frac{F_{org}}{F_{\mathrm{W}}}\right) \tag{2}$$

$$\mathrm{PSI} = J(\alpha - 1) \tag{3}$$

$$\beta = \mathrm{C}_w^P/\mathrm{C}_w^F \tag{4}$$

Here, P_W and P_{org} are wt. % of water and organic components, respectively, in permeate; F_W and F_{org} are wt. % of water and organic components, respectively, in the feed. A minimum of three independent measurements of flux and separation factor were taken under similar conditions of temperature and feed compositions to confirm the steady-state PV. Subscript w stands for water, J is water flux, and C is concentration in wt. %.

2.6. Degree of swelling

Gravimetry was used to measure the sorption capacity of the membranes [31] in 10–40 wt. % water-containing feed mixtures at 30˚C. To do this, dry weight of the circularly cut (diameter = 2.5 cm) pure PVA, PVA-Clay5 and PVA-Clay10 membranes was measured on a micro balance sensitive to ± 0.01 mg, and then, samples were taken inside the specially designed air tight test bottles of 20 cm^3 test media capacity. The bottles were then transferred to oven, kept at the desired constant temperature. Dry membranes were equilibrated by soaking in different compositions of feed mixtures in a sealed vessel at 30˚C for 48 h to measure the weight of the sorbed membrane to calculate % sorption using:

$$\%\mathrm{Sorption} = \frac{\mathrm{W}_\infty - \mathrm{W}_0}{\mathrm{W}_0} \times 100 \tag{5}$$

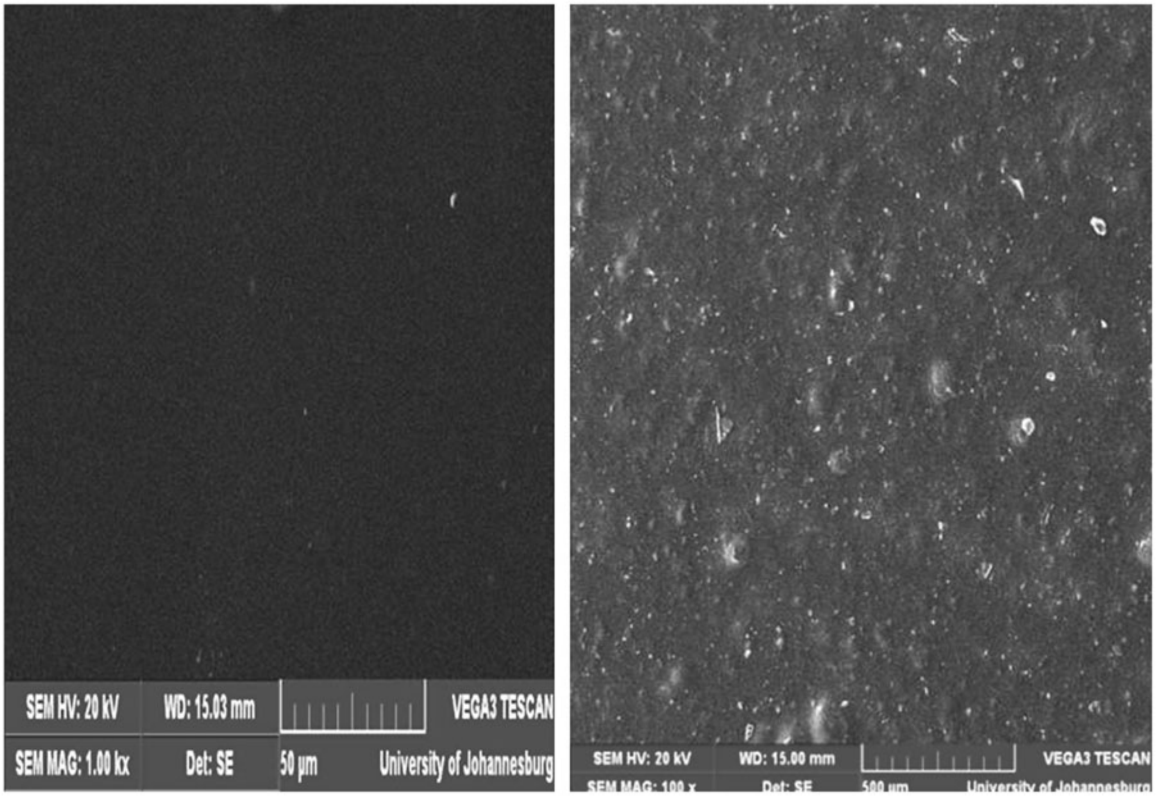

Fig. 1. SEM images of MMM.

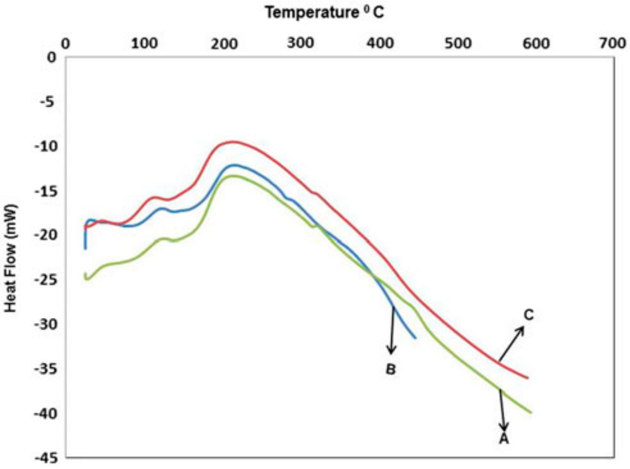

Fig. 2. DSC thermograms of (A) unfilled PVA, (B) PVA-Clay5 and (C) PVA-Clay10 membranes.

where W_∞ and W_0 are weights (g) of the swelled and dry membranes, respectively.

3. Results and discussion

3.1. Scanning electron microscopic studies (SEM)

Fig. 1 shows the surface morphology of PVA-Clay5, PVA-Clay10 clay incorporated MMM, in which clay particles are distributed homogeneously. The uniform distribution of clay throughout the PVA matrix facilitates the easy transport of water molecules.

3.2. DSC measurements

DSC thermograms of the unfilled and MMMs are depicted in Fig. 2. The melting point of unfilled PVA and PVA-Clay10 membranes are 210.3 and 223.66˚C, respectively. The melting point of MMM has shifted to higher value than pristine PVA which illustrates the importance of clay in the membrane.

3.3. Universal testing machine (UTM)

The elongation % of virgin PVA was 271 with a maximum tensile strength of 31 N/mm^2. However, for PVA-5 and PVA-10 membranes, the elongation %

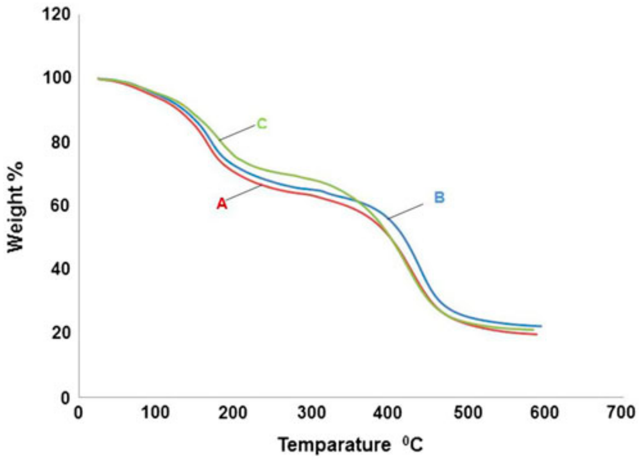

Fig. 3. TGA thermograms of (A) unfilled PVA, (B) PVA-Clay5 and (C) PVA-Clay10 membranes.

were 179 and 153, respectively, with tensile strengths 36 and 41 N/mm^2, respectively. The mechanical strengths of the MMMs are enhanced than those of the pure membranes, signifying their physical toughness.

3.4. Thermogravimetric analysis (TGA)

The thermograms obtained from TGA analysis of unfilled PVA, PVA/Clay5 and PVA/Clay10 membranes are shown in Fig. 3. Major weight losses are observed between 125 and 475°C. However, single stage degradation is observed for unfilled PVA with an onset of degradation at 191.24°C with a major weight loss occurring between 125 and 379°C. Thermal decomposition curve for PVA/Clay5 was observed within temperature of 130.25 and 390.11°C, and onset degradation is increased to 202°C. However, the first thermal decomposition of PVA/Clay10 is between 130.25 and 390°C, and the second thermal decomposition is seen between 405 and 475.06°C. The onset decomposition temperature increased further for the PVA/Clay10 MMM with 137.45°C. The decomposition temperatures of clay incorporated membrane matrices (CIMMs) have shifted to higher temperatures due to the existence of clay particles. Two-step decomposition is observed for PVA/Clay5 MMM. This confirms the increase in thermal stability of the MMMs due to the incorporation of clay in to PVA segments.

3.5. Membrane performance

Membrane performances of pristine PVA, PVA-Clay5 and PVA-Clay10 have been studied by calculating flux, separation factor, permeation separation index and enrichment factor. Mass transfer in binary feed mixtures through mixed matrix dense membrane has been described by the solution–diffusion mechanism [5]. In PV, molecular transport occurs due to the concentration gradient that exists between feed and permeate sides of the membrane. This process is generally explained by the solution–diffusion mechanism. According to this principle, permeating molecules first dissolve in the membrane and then diffuse out as a consequence of the concentration gradient. However, the overall separation can be explained on the basis of physical nature of the solvents, their affinity towards membrane as well as the morphological arrangement of the membrane. It is well known that alcohols can diffuse into the PVA matrix due to hydrophilic–hydrophilic interactions. However, after adding clay, swelling of PVA is controlled, which will give a decrease in the diffusive transport of organic molecules. The selectivity to water increases depending upon the clay content in the MMM and performance will change accordingly. PVA has many hydroxyl groups and is a very tight membrane due to the high degree of inter and intramolecular hydrogen bonding effects. For the separation of water–alcohol mixtures, numerous attempts have been made to improve the separation capabilities of PVA membranes [15]. The PV properties of PVA membrane can be improved by incorporation of clays [32]. Such membranes are quite selective to water molecules than alcohol. In the present study, increase of flux with PVA MMM increased its selectivity to water. However, at lower water concentration of the feed, the permeation flux is small. Virtually, no reports are available in the earlier literature on the membranes of PVA incorporated activated natural clinoptilolite clay used in PV dehydration of isopropanol or ethanol. PV separation results of water + isopropanol and water + ethanol mixtures obtained at 30, 40 and 50°C are presented in Tables 3 and 4, respectively. In the earlier literature, PVA is reported to have the most outstanding membrane performance properties for dehydrating alcohols [33], but it exhibited a serious decline in selectivity due to relaxation of PVA chains during the PV experiments. In a flexible polymer chain such as PVA, the chain segments are in a continuous random motion by allowing permeating water (hydrophilic) molecules to diffuse into the transient gaps created due to fluctuations in void spaces of the PVA matrix. The consequence of this phenomenon leads to macroscopic swelling of the membrane for which relatively a fast diffusion could occur within the loosened polymer segments. The observed water selectivity of feed mixtures of water + isopropanol

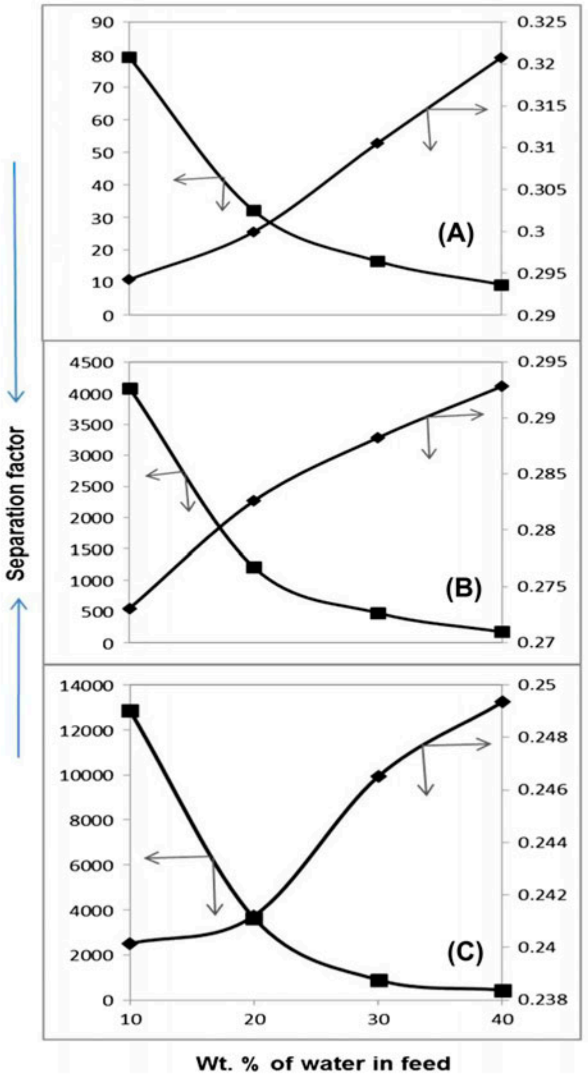

Fig. 4. Water flux and separation factor vs. wt. % of water for (a) unfilled PVA, (b) PVA-Clay5 and (c) PVA-Clay10 membranes for water–isopropanol feed mixtures at 30˚C. Symbols: (♦) flux and (■) separation factor.

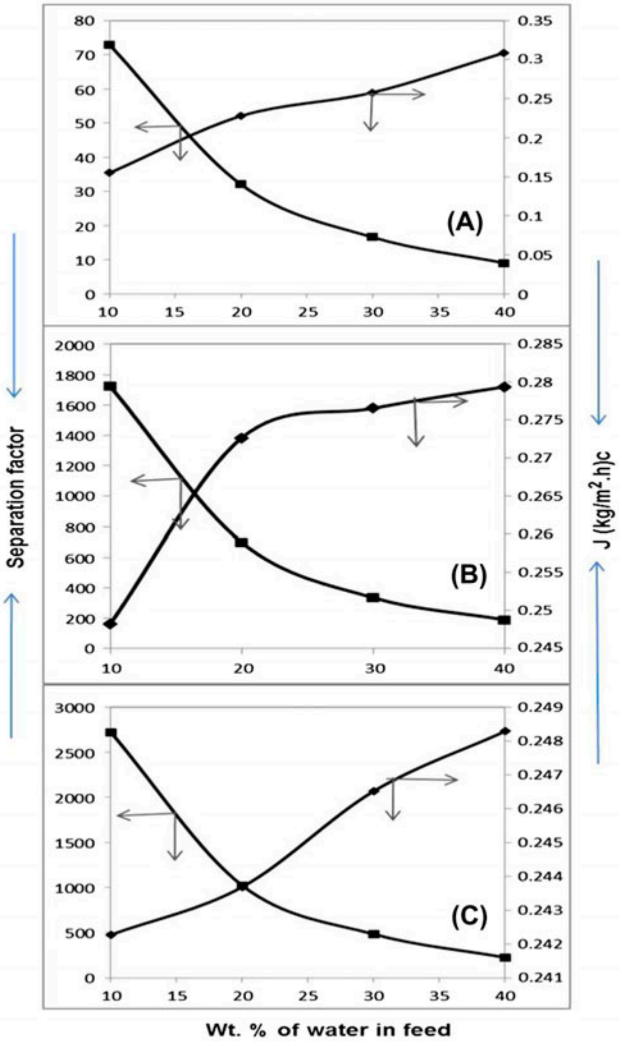

Fig. 5. Water flux and separation factor vs. wt. % of water for (a) unfilled PVA, (b) PVA-Clay5 and (c) PVA-Clay10 membranes for water–ethanol feed mixtures at 30˚C. Symbols: (♦) flux and (■) separation factor.

containing 10 wt. % water is 79 at 30˚C, which is higher than water selectivity for water + ethanol feed mixture. However, selectivity of both the feed mixtures tends to decrease with increasing concentration of water in the feed, and conversely, flux values have increased. The observed higher selectivity of water + isopropanol feed mixture than that of water + ethanol mixture is because of more water molecules enter into the membrane matrix through the void spaces, leading to an increase in the mobility of PVA chains (plasticization effect). This indicates that the interaction of ethanol with water is stronger than isopropanol (IPA) [10]. Higher concentration of water in the membrane (i.e. membrane with a higher solubility coefficient) would result in a higher permeability (see Figs. 4 and 5). The pristine cross-linked PVA membrane shows selectivity data of 72 and 79 for Water–ethanol, water–isopropanol feed mixtures, respectively, at 10% feed water compositions. However, with increasing clay content of the PVA MMMs, water selectivity values increased to 2,718 and 12,848, respectively, for the same 10% feed water compositions. These values are very high when compare with pure membrane. In pristine PVA membrane, the permeating water molecules first get absorb into the micro voids and then diffuse out on the permeate side due to the existence of concentration gradient. In case

Table 1
PV data for pure and CIM membranes for different water + isopropanol feed mixture at 30˚C

Water in feed (wt. %)	Water in permeate (wt. %)	Water flux (*J*) (kg/m^2 h)	Separation factor (*α*)	PSI
Pure PVA				
10	89.81	0.264	79.32	19
20	88.95	0.266	32.19	7.5
30	87.69	0.272	16.62	3.5
40	86.25	0.276	9.40	1.6
PVA-Clay5				
10	99.78	0.251	4,081	1,024
20	99.67	0.253	1,208	305
30	99.51	0.255	473	119
40	99.12	0.258	168	42
PVA-Clay10				
10	99.93	0.222	12,848	2,855
20	99.89	0.223	3,632	810
30	99.74	0.228	895	203
40	99.66	0.230	439	100

Table 2
PV data for pure and CIM membranes for different water + ethanol feed mixtures at 30˚C

Water in feed (wt. %)	Water in permeate (wt. %)	Water flux (*J*) (kg/m^2 h)	Separation factor (*α*)	PSI
Pure PVA				
10	89.01	0.137	72.89	9.05
20	88.94	0.202	32.03	5.48
30	87.68	0.226	16.60	2.75
40	85.8	0.264	9.06	1.40
PVA-Clay5				
10	99.48	0.246	1,721	424
20	99.43	0.271	697	188
30	99.31	0.274	335	91
40	99.22	0.277	190	51
PVA-Clay10				
10	99.67	0.218	2,718	594
20	99.61	0.222	1,021	226
30	99.52	0.228	483	109
40	99.34	0.237	225	52

of filled matrix membranes, the overall separation can be explained by the hydrophilic interactions between clay layers and the PVA matrix. The clay layers may be distributed throughout the PVA matrix, thus, forming a strong intercalation. However, majority of water molecules are adsorbed in the hydrophilic clay region, which in turn will get adsorbed by the hydrophilic regions of the PVA matrix for an easy diffusion through the barrier membrane. It is noticed that flux of the clay-filled PVA membrane is slightly lower than the pristine PVA membrane (see Figs. 4 and 5). Therefore, separation takes place due to the selective adsorption of water molecules onto the hydrophilic sites of the clay particles, which will then diffuse through the hydrophilic PVA membrane by inhibiting the transport of organic components (isopropanol or ethanol) from the feed mixtures. This further promotes for an increased flux due to increase in driving force [15]. It may be noted that molecular transport occurs due to the faster desorption rate of water molecules on the permeate side. This effect is more beneficial for water transport, since water molecules will occupy most of the channels in the hydrophilic regions of the MMMs. This also justifies a marked increase in water separation factor with a recovery of higher amount of water on the permeate side by sacrificing the (minuet) flux. In any case, the complimentary effects of clay on water transport will help to attain the best progress of the membrane performance, thereby offering a high separation factor to water. However, with the increasing concentration of water in the feed, selectivity of MMM for both the feed mixtures declined drastically, possibly due to the plasticization effect. This is further supported by the permeation separation index (PSI) and enrichment factor (β) (given in Tables 1 and 2).

3.6. Effect of feed water composition

The effect of feed water composition on PV performance of both pristine and CIMMs was investigated, and results are presented in Tables 1 and 2. Clay-loaded PVA membranes swell to a larger extent in the presence of water as compared to pristine PVA membrane. The flux data of CIMMs are higher than those of the pristine PVA membrane. For CIMMs, flux increased with increasing water composition from 10 to 40 wt. % of the feed mixture. At 10 wt. % water in the feed mixture, a strong adsorptive effect of water molecules onto hybrid composite membranes is obtained, which would facilitate to increase the transport of water from the feed side [34]. For PVA-Clay10 membrane, the observed selectivity for water–isopropanol is 12,848 at 10 wt. % of water in the feed, which decreased with increasing concentration of water in the feed (see Fig. 4). At higher concentration of water in the feed mixture, PVA-Clay10 membrane could absorb more amounts of water molecules when compared to Pristine and PVA-Clay5 membrane due to plasticization effect of the polymer. However, selectivity has increased, but flux decreased considerably for the 10 wt. % clay containing PVA membrane. For 40 wt. % water-containing feed mixture, selectivity increased to 439, but flux is enhanced to 0.230 kg/m^2 h for the PVA-Clay 10 membrane. In case of pristine PVA and PVA-Clay5 membrane, the respective values are much lower, i.e. 9.40, 0.276 and 168, 0.258 kg/m^2 h. In all cases, flux and selectivity of PVA-Clay membranes are higher than that of plain PVA membrane. The present study demonstrates the positive role played by clay upon incorporation into PVA to enhance the membrane performance over that of pristine cross-linked PVA membrane.

3.7. Effect of clay on membrane performance

The variations of flux and separation factor are studied as a function of different wt. % of clay particles into PVA matrix. Pristine PVA membrane exhibits a separation factor of 72.89 with a flux of 0.137 kg/m^2 h at 10 wt. % of water in the feed mixture of isopropanol. Separation factor of PVA increases after the incorporation of clay particles. For PVA-Clay5 membrane, the separation factor and flux are increased to 1,721 and 0.246 kg/m^2 h, respectively, while that for PVA-Clay10, the values are 2,718 and 0.241 kg/m^2 h at the same content of water in the water–ethanol feed mixture. For water–isopropanol, the flux and separation values are 0.251 kg/m^{2}h, 4,081 and 0.222 kg/m^2 h, 12,848. However, this favours the molecular level interaction between the polymer and the clay, resulting in decreased free volume. In addition, a high aspect ratio of layered silicates caused them to act as a barrier and offers more resistance to diffusion by creating tortuosity to the diffusion pathway. This has suppressed the diffusion of both water and IPA molecules. However, the diffusion of IPA molecule is affected significantly, as the kinetic diameter of IPA molecule is almost four times bigger than that of water molecule [35]. Obviously, transports of IPA molecules are less preferred as compared to water molecules for which it results high selectivity and low permeation flux. On further increase of the amount of clay beyond 10 wt. %, flux is decreased. The decrease in flux accounted for the lower degree of swelling at higher wt. % of clay. The PV separation index (PSI) is the product of total permeation flux and separation factor, which characterizes the membrane separation ability. This index can be used as a relative guideline for the design of new membranes for PV separation processes and also to select a membrane with an optimal combination of flux and selectivity. Tables 1 and 2 show the variation of PSI as a function of wt. % of clay loading at 30°C for 10 weight % of water in the feed. It is observed that there is a dramatic increase in PSI values with increase in the clay from 0 to 10 wt. %, but further addition of clay (more than 10 mass %) decreases the PSI value [23]. These increased values with increasing loading of clay compared to the pristine PVA membrane can be attributed to the fact that clay provides higher hydrophilicity and higher strength to the PVA. The simultaneous increase of separation factor and flux is a difficult problem in PV separation, even though several studies have demonstrated this effect [16,36]. From the plot of separation factor and flux vs. clay loading (Fig. 6), it is observed that separation and flux increased with filler loading, suggesting suitability of the composite membrane for interchanging phenomena.

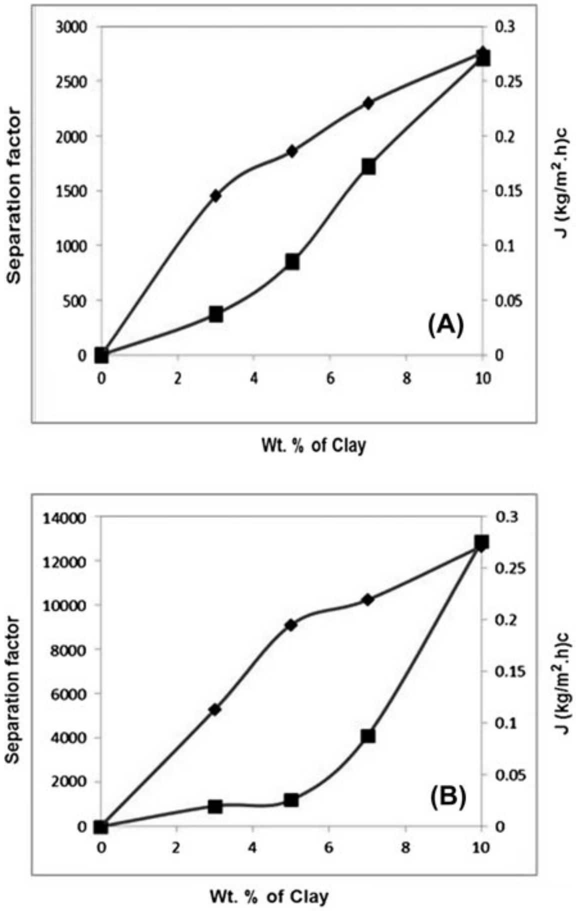

Fig. 6. Water flux and separation factor vs. wt. % of clay loading for (a) water–ethanol and (b) water–isopropanol mixtures for 10 wt. % of water in the feed at 30˚C. Symbols: (♦) flux and (■) separation factor.

Since both PVA polymer and clay particles are hydrophilic in nature, and therefore, membrane performance can be explained on the basis of solution–diffusion theory [15] in addition to adsorption–diffusion–desorption concepts [37]. In pristine PVA membrane, the permeating water molecules first get absorbed into the micro voids and then diffuse out on the permeate side due to the existence of concentration gradient. In case of filled matrix membranes, the overall separation can be explained by the hydrophilic interactions between clay particles and the PVA matrix. The clay particles may be distributed throughout the PVA matrix, thus, forming a strong intercalation. However, majority of water molecules are adsorbed in the hydrophilic clay region, which in turn will get absorbed by the hydrophilic regions of the PVA matrix for an easy diffusion through the barrier membrane. Notice that after 5 wt. % of clay the flux of clay-filled PVA membrane is slightly lower than the PVA-Clay5 membrane (see Figs. 4 and 5). Therefore, separation takes place due to the selective adsorption of water molecules on to the hydrophilic sites of the clay particles, which will then diffuse through the hydrophilic PVA membrane, by inhibiting the transport of organic components (isopropanol or ethanol) from the feed mixtures. This further promotes for an increased flux due to increase in driving force. It may be noted that molecular transport occurs due to the faster desorption rate of water molecules on the permeate side. This effect is more beneficial for water transport, since water molecules will occupy most of the channels in the hydrophilic regions of the MMMs. This also justifies a marked increase in water separation factor with a recovery of higher amount of water on the permeate side by sacrificing the flux. In any case, the complimentary effects of activated clay on water transport will help to improve the membrane performance, thereby offering a high separation factor to water. The selection of clay as a filler is helpful to achieve good enhancement of separation factor and flux to water in the present work.

3.8. Effect of temperature on membrane performance

The membrane performance was studied at higher temperatures, viz., 30, 40 and 50˚C for 10 wt. % water-containing feed solutions of isopropanol as well as ethanol. The present membranes are quite stable at higher temperatures under the PV conditions. Results

Table 3
PV data for water + isopropanol feed mixture at 10 wt. % of water in the feed mixture at different temperature for different membranes

Temperature (˚C)	Water flux (*J*) (kg/m^2 h)	α	PSI
Pure PVA			
30	0.26	79	19
40	0.27	61	15
50	0.29	51	14
PVA-Clay5			
30	0.272	4,081	1,111
40	0.302	595	178
50	0.328	523	171
Pva-Clay10			
30	0.239	12,848	3,082
40	0.344	678	232
50	0.383	583	222

Table 4
PV data for water + ethanol feed mixture at 10 wt. % of water in the feed mixture at different temperature for different membranes

Temperature (°C)	Water flux (J) (kg/m^2 h)	α	PSI
Pure PVA			
30	0.25	72.8	17.5
40	0.30	49.06	13.4
50	0.37	34.3	11.9
PVA-Clay5			
30	0.24	1,721	424
40	0.29	443	131
50	0.32	248	79
PVA-Clay10			
30	0.21	2,718	594
40	0.34	629	215
50	0.38	459	177

of flux and separation factors for 10 wt. % of water in the feed solutions of isopropanol and ethanol at 30, 40 and 50°C are presented in Tables 3 and 4. As expected, flux has increased with increasing temperature, but separation factor decreased. The temperature dependency of flux is analysed by Arrhenius equation of the type:

$$J_p = J_{po} \exp\left(\frac{-Ep}{RT}\right) \tag{6}$$

where J_p is the permeation flux of water, J_{po} the permeation rate constant, E_p the activation energy for permeation, R the molar gas constant and T is the temperature in Kelvin. If activation energy is positive, permeation flux increases with increasing temperature, which is indeed observed in most PV separation experiments [38,39]. The driving force represents the concentration gradient, resulting from a difference in partial vapour pressure of the permeants between feed and permeate mixtures. As the feed temperature increases, vapour pressure in the feed compartment also increases, but vapour pressure at the permeate side is not affected. This results in an increase of driving force with increasing temperature of the PV experiment. Pristine PVA membrane shows the highest *Ep* compared to CIMMs, while PVA-Clay10 membrane has the lowest values, signifying that *Ep* values decrease with increasing concentration of clay, thus, smoothening the easy passage of water molecules from the feed to permeate side.

3.9. FTIR

Fig. 7 shows the IR spectra of PVA-Clay10 membranes and pure PVA. The pure PVA had some similar bands with O–H stretching at 3,285 cm^{-1} and CH stretching and bending at 2,922 and 1,344 cm^{-1}[40]. The peak observed in the pure PVA at 1,713 cm^{-1} is most likely due to residual acetate groups still present in the partially hydrolysed form. In addition to that

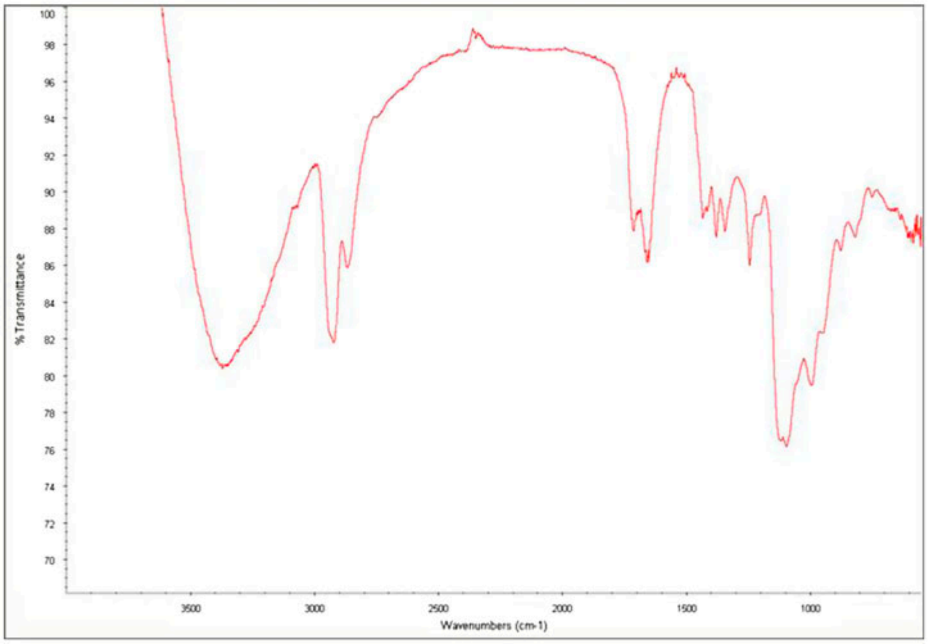

Fig. 7. IR spectra of PVA-Clay10 membrane.

the 1,096 cm^{-1} band arises from asymmetric stretching vibration modes of internal S–O bonds in TO4 tetrahedral (T = Si and Al). The 995 and 585 cm^{-1} bands are assigned to the stretching vibration modes of O–Si–O groups and the bending vibration modes of S–O bonds, respectively [41].

3.10. Swelling studies

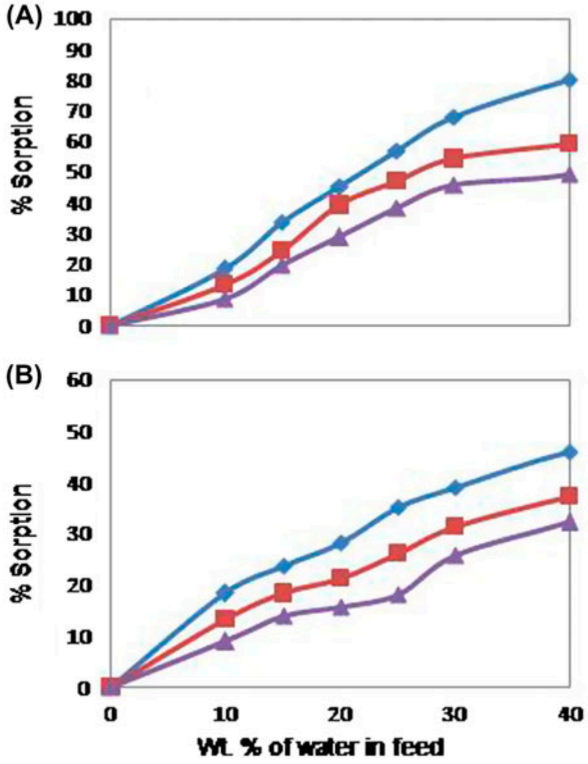

Fig. 8. % Sorption curves of pure PVA (♦), PVA-Clay 5 (■) and PVA-Clay10 (▲) mixed membranes for (A) water + isopropanol and (B) water + ethanol feed mixtures at 30˚C.

Fig. 8 displays the results of % sorption of pristine PVA and PVA/clay-filled matrix membranes at 30˚C for 10–40 wt. % water-containing feed mixtures. The efficiency of a membrane lies in its selective nature towards the preferred liquid component of the feed mixture, which depends upon the extent of sorption of the membrane. It is observed that PVA membrane adsorbs to a larger extent in water + isopropanol feed mixture, due to higher level interactions of isopropanol with the PVA membrane. Sorption of PVA/clay-filled matrix membranes in both the feed mixtures is smaller than observed for pristine PVA membrane. When 10 wt. % of clay particles are added to PVA to obtain the filled matrix membrane, an increase in membrane sorption is observed due to the presence of excess of hydrophilic clay particles as compared to 5 wt. % clay-loaded PVA. However, sorption for clay–PVA membrane is smaller than pristine PVA membrane, as clay is less hydrophilic than the pristine

Table 5
Comparison of present PV performance with literature values for water + isopropanol mixtures 10 wt. % of water in feed at 30˚C

Membrane	wt. %Water	Water flux (J) (kg/m^2 h)	α	References
PVA/PMMA	10	0.075	400	[4]
(PVA–TiO$_2$)	10	0.180	∞	[6]
PVA/PANI	10	0.069	564	[27]
NaAlg/PVA75:25)	10	0.125	195	[34]
PVA/HPA-1	10	0.105	337	[32]
PVA/HPA-7	10	0.032	89,991	
PVA-Fe(c)-4.5	10	0.079	470	[42]
PVA/Clay	10	0.222	12,848	Present work

Table 6
Comparison of PV performance of the present membranes with literature for water + ethanol mixtures at 10 wt. % of water in feed at 30˚C

Membrane	wt. % Water	Flux (J) (kg/m^2 h)	α	References
PVA/PVP (M-4)	10	0.23	3,324	[7]
PVA/PVS	6.2	0.50	700	[43]
PVA/Clay	10	0.218	2,718	Present work

PVA. Such a decrease in membrane sorption is attributed to the insertion of PVA chain segments into layered structure of clay galleries, thus, causing an intercalation between PVA and clay particles. This will further decrease solvent uptake capacity of the membrane from the feed mixture. Therefore, an increase in separation factor of the filled matrix membranes in comparison to pristine PVA membrane is related to the decrease in solvent uptake capacity of the MMMs.

3.11. Comparison of present work with literature

Present results are compared with published data in literature and are shown in Tables 5 and 6. In effect clay incorporated membrane results are found to be better than pure PVA membranes as well as compared to the literature data for dehydration of isopropanol and ethanol. For example, the highest separation factor of 12,848 is observed for PVA-Clay10 membrane with a flux of 0.222 kg/m^2 h10μm, which is higher than the reported values as presented in the Tables 5 and 6. The minimum value of separation factor of 79.32 of pure PVA membrane with a flux value of 0.264 kg/m^2 h10μm distinctly indicates the water-selective nature of the hybrid composite membranes compared to pure PVA membrane. Thus, due to the addition of clay into PVA, a tremendous increase in membrane separation factor to water occurs, signifying that the composite hybrid membranes of this study are more advantageous for PV dehydration of isopropanol and ethanol than pure PVA membrane as well as other membranes reported in the literature.

4. Conclusions

We successfully synthesized nanocomposites of glutaraldehyde cross-linked (*in situ*) PVA/clinoptilolite membranes by solution casting technique. We showed that incorporation of activated clay particles improves the separation characteristics of the PVA MMMs and therefore are better than the pristine PVA membrane. This is because of reduction of their swelling in the presence of mixed feed water and isopropanol/ethanol. The flux and separation factor of the MMMs were much higher than the pristine PVA membranes due to induced hydrophilicity of PVA matrices. Moreover, the present membranes are also mechanically tough. We compared the performance of these membranes with those reported in the literature in detailed way and found that our membranes have better separation characteristics.

Acknowledgements

Authors immensely thank Department of metallurgy, University of Johannesburg, South Africa for making available some of the experimental facilities. Karnataka University, Dharwad, India is acknowledged for the facilities and hospitality provided. Also, NRF South Africa is acknowledged for partial financial support in the form of rated researcher's incentive fund.

References

[1] D. Oh, S. Lee, Y.t. Lee, Mixed-matrix membrane prepared from crosslinked PVA with NaA zeolite for pervaporative separation of water–butanol mixtures, Desalin. Water Treat. 51 (2013) 5362–5370.

[2] H. Abdallah, A. El-Gendi, E. El-Zanati, T. Matsuura, Pervaporation of methanol from methylacetate mixture using polyamide-6 membrane, Desalin. Water Treat. 51 (2013) 7807–7814.

[3] D.P. Suhas, A.V. Raghu, H.M. Jeong, T.M. Aminabhavi, Graphene-loaded sodium alginate nanocomposite membranes with enhanced isopropanol dehydration performance via a pervaporation technique, RSC Adv. 3 (2013) 17120–17130.

[4] S.G. Adoor, B. Prathab, L.S. Manjeshwar, T.M. Aminabhavi, Mixed matrix membranes of sodium alginate and poly(vinyl alcohol) for pervaporation dehydration of isopropanol at different temperatures, Polymer 48 (2007) 5417–5430.

[5] S.G. Adoor, L.S. Manjeshwar, B.V.K. Naidu, M. Sairam, T.M. Aminabhavi, Poly (vinyl alcohol)/poly (methyl methacrylate) blend membranes for Pervaporation separation of water + isopropanol and water + 1,4-dioxane mixtures, J. Membr. Sci. 280 (2006) 594–602.

[6] M. Sairam, M.B. Patil, R.S. Veerapur, S.A. Patil, T.M. Aminabhavi, Novel dense poly (vinyl alcohol)-TiO$_2$ mixed matrix membranes for pervaporation separation of water–isopropanol mixtures at 300°C, J. Membr. Sci. 281 (2006) 95–102.

[7] V.T. Magalad, G.S. Gokavi, K.V.S.N. Raju, T.M. Aminabhavi, Mixed matrix blend membranes of poly (vinyl alcohol)–poly(vinyl pyrrolidone) loaded with phosphomolybdic acid used in pervaporation dehydration of ethanol, J. Membr. Sci. 354 (2010) 150–161.

[8] R. Schellekens, C.J. Bastiaansen, A drawing behavior of polyvinylalcohol fibers, J. Appl. Polym. Sci. 43 (1991) 2311–2315.

[9] H. Zheng, Y. Du, J. Yu, R. Huang, L. Zhang, Preparation and characterization of chitosan/poly(vinyl alcohol) blend fibers, J. Appl. Polym. Sci. 80 (2001) 2558–2565.

[10] D.P. Suhas, T.M. Aminabhavi, A.V. Raghu, Mixed matrix membranes of H-ZSM5-loaded poly (vinyl alcohol) used in pervaporation dehydration of

alcohols: Influence of silica/alumina ratio, Polym. Eng. Sci. 54(8) (2013) 1774–1782.

[11] S. Amnuaypanich, J. Patthana, P. Phinyocheep, Mixed matrix membranes prepared from natural rubber/poly(vinyl alcohol) semi-interpenetrating polymer network (NR/PVA semi-IPN) incorporating with zeolite 4A for the pervaporation dehydration of water–ethanol mixtures, Chem. Eng. Sci. 64 (2009) 4908–4918.

[12] S. Wu, F. Li, H. Wang, L. Fu, B. Zhang, G. Li, Effects of poly (vinyl alcohol) (PVA) content on preparation of novel thiol functionalized mesoporous PVA/SiO_2 composite nanofiber membranes and their application for adsorption of heavy metal ions from aqueous solution, Polymer 51 (2010) 6203–6211.

[13] A. Rashidzadeh, A. Olad, Novel polyaniline/poly (vinyl alcohol)/clinoptilolite nanocomposite: Dye removal, kinetic, and isotherm studies, Desalin. Water Treat. 51 (2013) 7057–7066.

[14] Z. Gao, Y. Yue, W. Li, Application of zeolite-filled pervaporation membrane, Zeolites 16 (1996) 70–74.

[15] S.G. Adoor, M. Sairam, L.S. Manjeshwar, K.V.S.N. Raju, T.M. Aminabhavi, Sodium montmorillonite clay loaded novel mixed matrix membranes of poly(vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane, J. Membr. Sci. 285 (2006) 182–195.

[16] S.B. Teli, G.S. Gokavi, M. Sairam, T.M. Aminabhavi, Mixed matrix membranes of poly(vinyl alcohol) loaded with phosphomolybdic heteropolyacid for the pervaporation separation of water–isopropanol mixtures, Colloids Surf., A 301 (2007) 55–62.

[17] S. YijieHuY. Zhang, D. Lawless, X. Feng, Composite membranes comprising of polyvinyl amine-poly (vinyl alcohol) incorporated with carbon nanotubes for dehydration of ethylene glycol by pervaporation, J. Membr. Sci. 417–418 (2012) 34–44.

[18] S. Xia, X. Dong, Y. Zhu, W. Wei, F. Xiangli, W. Jin, Dehydration of ethyl acetate–water mixtures using PVA/ceramic composite pervaporation membrane, Sep. Purif. Technol. 77 (2011) 53–59.

[19] E.J. Flynn, D.A. Keane, P.M. Tabari, M.A. Morris, Pervaporation performance enhancement through the incorporation of mesoporous silica spheres into PVA membranes, Sep. Purif. Technol. 118 (2013) 73–80.

[20] Z. Huang, Y. Shi, R. Wen, Y.H. Guo, J.F. Su, T. Matsuura, Multilayer poly(vinyl alcohol)–zeolite 4A composite membranes for ethanol dehydration by means of pervaporation, Sep. Purif. Technol. 51 (2006) 126–136.

[21] D. Anjali Devi, B. Smitha, S. Sridhar, T.M. Aminabhavi, Pervaporation separation of dimethylformamide/water mixtures through poly(vinyl alcohol)/poly(acrylic acid) blend membranes, Sep. Purif. Technol. 51 (2006) 104–111.

[22] D.S. Kim, I.C. Park, H.I. Cho, D.H. Kim, G.Y. Moon, H.K. Lee, J.W. Rhim, Effect of organo clay content on proton conductivity and methanol transport through crosslinked PVA hybrid membrane for direct methanol fuel cell, J. Ind. Eng. Chem., 15 (2009) 265–269.

[23] S.K. Choudhari, M.Y. Kariduraganavar, Development of novel composite membranes using quaternized chitosan and Na^+-MMT clay for the pervaporation dehydration of isopropanol, J. Colloid Interface Sci. 338 (2009) 111–120.

[24] T.M. Aminabhavi, H.G. Naik, Pervaporation separation of water/dimethylformamide mixtures using poly(vinyl alcohol)-g-polyacrylamide copolymeric membranes, J. Appl. Polym. Sci. 83 (2002) 273–282.

[25] S. Takegami, H. Yamada, S. Tsujii, Dehydration of water/ethanol mixtures by pervaporation using modified poly (vinyl alcohol) membrane, Polym. J. 24 (1992) 1239–1250.

[26] H. Zheng, Y. Du, J. Yu, R. Huang, L. Zhang, Preparation and characterization of chitosan/poly(vinyl alcohol) blend fibers, J. Appl. Polym. Sci. 80 (2001) 2558–2565.

[27] B.V.K. Naidu, M. Sairam, K.S.V.N. Raju, T.M. Aminabhavi, Pervaporation of water + IPA mixture using navel Nanocomposite membranes of poly(vinyl alcohol) and polyaniline, J. Membr. Sci. 260 (2005) 142–155.

[28] T. Zhu, Z. Li, Y. Luo, P. Yu, Pervaporation separation ofdimethyl carbonate/methanol azeotrope through cross-linked PVA–poly (vinyl Pyrrolidone)/PAN composite membranes, Desalin. Water Treat. 51 (2013) 28–30.

[29] Z. Huang, H.-m. GuanW.l. Tan, X.-Y. Qiao, S. Kulprathipanja, Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly(vinyl alcohol) membranes: Effect of zeolites, J. Membr. Sci. 276 (2006) 260–271.

[30] B.V.K. Naidu, S.D. Bhat, M. Sairam, A.C. Wali, D.P. Sawant, S.B. Halligudi, N.N. Mallikarjuna, T.M. Aminabhavi, Comparison of the pervaporation separation of a water-acetonitrile mixture with zeolite-filled sodium alginate and poly(vinyl alcohol)-polyaniline semi-interpenetrating polymer network membranes, J. Appl. Polym. Sci. 96 (2005) 1968–1978.

[31] S.G. Adoor, V. Rajineekanth, M.N. Nadagouda, K. Chowdoji Rao, D.D. Dionysiou, T.M. Aminabhavi, Exploration of nanocomposite membranes composed of phosphotungstic acid in sodium alginate for separation of aqueous-organic mixtures by pervaporation, Sep. Purif. Technol. 113 (2013) 64–74.

[32] Y.C. Wang, S.C. Fan, K.R. Lee, C.L. Li, S.H. Huang, H.A. Tsai, J.Y. Lai, Polyamide/SDS-clay hybrid nanocomposite membrane application to water-ethanol mixture pervaporation separation, J. Membr. Sci. 239 (2) (2004) 219–226.

[33] R.Y.M. Huang, Pervaporative Membrane Separation Processes, Elsevier, Amsterdam, 1991.

[34] M.D. Kurkuri, U.S. Toti, T.M. Aminabhavi, Syntheses and characterization of blend membranes of sodium alginate and poly(vinyl alcohol) for the pervaporation separation of water + isopropanol mixtures, J. Appl. Polym. Sci. 86 (2002) 3642–3651.

[35] X. Qiao, T.S. Chung, Fundamental characteristics of sorption, swelling, and permeation of P84 Co-polyimide membranes for pervaporation dehydration of alcohols, Ind. Eng. Chem. Res. 44 (2005) 8938–8943.

[36] S.B. Teli, G.S. Gokavi, T.M. Aminabhavi, Novel sodium alginate poly (N-isopropylacryl amide) semi-interpenetrating polymer network membranes for pervaporation separation of water + ethanol mixtures, Sep. Purif. Technol. 56 (2007) 150–157.

[37] J.G. Wijmans, R.W. Baker, The solution-diffusion model: A review, J. Membr. Sci. 107 (1995) 1–21.

[38] R.C. Binning, R.J. Lee, J.F. Jennings, E.C. Martin, Separation of liquid mixtures by permeation, Ind. Eng. Chem. Res. 53 (1961) 45–50.

[39] M.C. Burshe, S.A. Netke, S.B. Sawant, J.B. Joshi, V.G. Pangarkar, Pervaporative dehydration of organic solvents, Sep. Purif. Technol. 32 (1997) 1335–1349.

[40] K.M. Dean, M.D. Do, E. Petinakis, L. Yu, Key interactions in biodegradable thermoplastic starch/poly (vinyl alcohol)/montmorillonite micro- and nanocomposites, Compos. Sci. Technol. 68 (2008) 1453–1462.

[41] H. Tanaka, N. Yamasaki, M. Muratani, R. Hino, Structure and formation process of (K, Na)—Clinoptilolite, Mater. Res. Bull. 38 (2003) 713–722.

[42] M. Sairam, B.V.K. Naidu, S.K. Nataraj, B. Sreedhar, T.M. Aminabhavi, Poly(vinyl alcohol)-iron oxide nanocomposite membranes for pervaporation dehydration of isopropanol, 1,4-dioxane and tetrahydrofuran, J. Membr. Sci. 283 (2006) 65–73.

[43] A. Toutianoush, L. Krasemann, B. Tieke, Polyelectrolyte multilayer membranes for pervaporation separation of alcohol/water mixtures, Colloids Surf. A 198–200 (2002) 881–889.