Indian Journal of Chemical Technology
Vol. 26, January 2019, pp. 44-51

Swelling and sorption behaviour of PVA and PVA/silica nanocomposite membrane at different silica loadings

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Received 13 January 2018; accepted 12 September 2018

Intercalation of nanomaterial with a polymer is an intriguing approach for modifying the microstructure of polymer to improve the swelling property, performance, and selectivity of the membrane. The effect of sorption and swelling on membrane selectivity of organic-inorganic polyvinyl alcohol/silica (PVA/SiO_2) membranes with a different weight percentage of silica has been investigated using propanol/water, isopropanol/water, and butanol/water mixture. The PVA composite membrane is prepared using solution casting method, and sol-gel derived route using tetraethoxysilane (TEOS) as the precursor material for silica and PVA as a polymer. Swelling experiment results show an inverse relationship between the degree of swelling and the silica concentration due to the formation of a rigid structure with increase in weight of the nanomaterial. Dense structure results in less free volume and decreases the amount of absorbed liquid in the polymer at a lower concentration of nanoparticles. The result is also modeled using Flory Huggins parameter, and the similar trend was observed as for the experimental value for the degree of swelling.

Keywords: Composite, Nanomaterial, Polymer, Sorption, Swelling.

Variation in the application field of membrane technology, e.g., separation of water from organic mixtures as water is an essential and precious resource for human beings[1], separation of chemical mixtures in the electronics industry[2], promotes the development of polymeric and composite membrane material. In recent years biodegradable polymer is widely used as membrane material as they are environmentally friendly[3], but these suffer from poor water resistant property. The biodegradable polymer membrane, when used in the separation of an aqueous-organic mixture, is characterized by a slow rate of water uptake. This behaviour is due to the interaction between membrane and solvents that restrain both permeability and selectivity[4, 5].

Swelling is an important parameter that ultimately changes the physical and chemical structure of the membrane and hence affects the transport of molecules through the membrane. Swelling of the membrane is due to the effect of the chemical potential gradient when solvent (liquid phase) enters the membrane (polymeric phase)[6]. This transfer leads to distortion of the polymeric network[7]. Swelling in membrane increases free volume allowing more liquid to pass, thus affecting the separation and efficacy of the membrane. Research has been done to investigate the swelling behaviour of membrane using different species. Praptowido[8] reported swelling values of PVA membranes for ethanol-water mixtures and reported a decrease in selectivity due to increase in the degree of swelling. Yeom *et al.*[9] carried out swelling measurements in water and acetic acid and concluded that the swelling behaviour was dependent on crosslinking density and chemical functional groups. Researchers have also reported that swelling of the membrane can be reduced by the development of the organic, inorganic membrane or by introducing a cross-linking[10] or a combination of both.

Swelling in membrane influences rejection parameter of the membrane. Rejection through membrane is governed by three different mechanisms[11]:

- Size exclusion: size of transporting molecule is important because size will determine whether the molecule should enter the transport region within the membrane.
- Surface repulsion: a molecule is rejected by the surface due to the repelling force exerted by the hydrophilic/hydrophobic membrane material with the molecule.
- Sorption: selective sorption of one or more molecule by the membrane material.

The biodegradable, nontoxic synthetic polymer polyvinyl alcohol (PVA) is mostly used polymer because it has the good film-forming ability and is inexpensive, but it has poor stability in aqueous solution. Filler additives to polymer will modify the structure of a polymeric material and enhance its physical and chemical stability. This modification has a direct effect on the performance and stability of the membrane. The focus of this paper is to evaluate the swelling degree, sorption behavior and solvent-polymer interaction at different silica/PVA ratios and their combined effect on the performance of membranes. This analysis was carried out using simple swelling experiments for the different binary mixture of an alcohol-water solution.

Experimental Section

Materials

PVA (hydrolyzed 99%, weight average molecular weight = 86000–98000) was obtained from Sigma-Aldrich (India). Maleic Acid (MA), Tetraethoxysilane (TEOS) and hydrochloric acid (HCl, 37wt %) were purchased from Merck Chemicals. All the chemicals used and purchased were of analytical grade. Distilled water was utilized in all the membrane preparation experiments. All alcohols including propanol, isopropanol (IPA), and butanol were obtained from Merck chemicals.

Methodology

PVA solution was prepared by dissolving 6 g of PVA in 100 mL of distilled water and was continuously heated and stirred for 2 h at 90°C to obtain the clear solution. The 6 wt% PVA solution was left to cool to room temperature (26-27°C). Maleic acid (1.2 g), as crosslinker, was added at room temperature (26-27°C) to the PVA solution and was stirred at room temperature till it fully dissolved. For the preparation of composite membrane, a definite amount of TEOS was added to above solution followed by dropwise addition of 0.1 M of 0.5 µL HCl. This mixture was stirred for 4 h. The amount of TEOS added was in the SiO_2 weight percentage with respect to the amount of PVA, i.e., amount of silica with respect to PVA is 0.5 to 2 wt%. Casting solution with different weight % of silica to polymer (PVA) were prepared and named as P1 (pure PVA), P2 (PVA+MA), P3 (silica/PVA, 0.5 wt %), P4 (silica/PVA, 1wt%) and P5 (silica/PVA, 2 wt%). After the continuous stirring solution was sonicated for 30 min then kept still overnight at an ambient temperature for degassing process to remove bubble present. The membrane of PVA/MA/Silica was prepared by casting solution on the glass plate. It was kept for drying at room temperature for 2-3 days to allow the solvent (water) to evaporate to form the thin film. After casting the dry film formed was peeled off away from the glass plate. Pristine PVA and PVA/MA membrane were also synthesized by the similar process for reference. The membrane thickness was measured at a different location across the membrane using a micrometer, and an average value of 80 µm was observed. The simple block diagram for membrane synthesis is shown in Fig. 1.

Membrane characterization

SEM (Scanning Electron Microscope) analysis is carried out using High-Resolution Scanning Electron Microscope (SUPRA 40, Zeiss) to study the surface morphology of different PVA membranes.

FTIR (Fourier Transform Infra-Red Spectroscopy) analysis is used to characterize the groups present in PVA and PVA/silica. This study was conducted using NICOLET- 5700 spectrometer (Thermo Electron Corporation) operating at the resolution of 6 and 32 scans and wave number range from 800 to 4000 cm^{-1}.

Swelling measurements

The swelling experiment was conducted using pre-weighed dry membrane (W_d). A pre-weighed membrane sample of dimension (1cm × 1cm) was immersed in 30% propanol/water, 30% IPA/water, 30% butanol/water for a day at ambient temperature. The sample was taken after a fixed interval of time, blotted with filter paper and is weighed again. This procedure is repeated until the weight of swollen membrane becomes constant (W_s). Swelling degree is (SD) expressed as

$$SD = (W_s - W_d) / W_d * 100 \quad \text{... (1)}$$

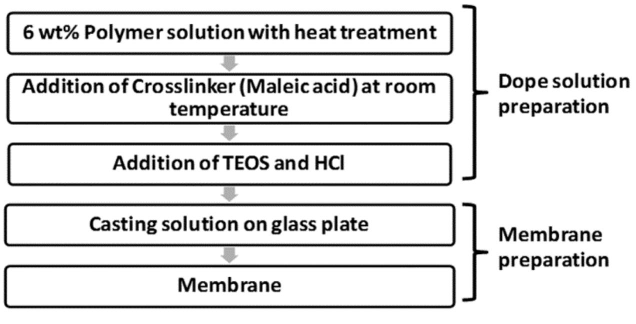

Fig. 1 — Block diagram of membrane synthesis

W_d is the weight of dry membrane, W_s is the weight of the swollen membrane.

Polymer solvent interaction parameter was determined using Flory-Huggins interaction parameter χ[2,8] For Flory-Huggins theory, fraction of polymer volume in swelled membrane is determined as

$$\varphi = 1/(1+\rho_2/ \rho_1 .\ \Delta W) \quad \text{... (2)}$$

ρ_1 and ρ_2 are solvent and polymer density (g/cm^3), $\Delta W = (W_s - W_d)/ W_d$

Then equation 3 was used to calculate interaction parameter assuming ideal solvent approximation ($a_1=1$, $\ln a_1 = 0$)

$$\ln a_1 = \ln (1- \varphi) + \varphi + \chi \varphi^2 \quad \text{... (3)}$$

for $\ln a_1 = 0$

$$\chi = -[\ln (1- \varphi) + \varphi]/ \varphi^2 \quad \text{... (4)}$$

χ parameter reveals interaction between polymer and solvent.

Selectivity can be related to solubility coefficient. The solubility coefficient can be defined as

$$Si = W_i^M / W_i^F \quad \text{... (5)}$$

where W_i^M is weight fraction of compound i inside the membrane, W_i^F is the weight fraction of compound i in the feed.

Sorption experiments

Batch experiments were carried out for sorption analysis where solvent concentration was determined using NUCON GC analyzer (Model 5765) equipped with the porapack column and TCD detector. The oven temperature was programmed at 180°C while injector and detector temperature were maintained at 220°C and 240°C respectively pure hydrogen at 2 kg/cm^2 was used as carrier gas. The calibration curves were prepared for mass balance calculation. Membrane sample was immersed in alcohol/ water mixture and is removed when the weight of swelled membrane becomes constant as described in swelling measurement analysis. Solvent concentration after removal of membrane sample in the remaining aqueous solution was measured from the calibration curve whereas in the swollen polymer it was calculated using mass balance.

Pervaporation experiments

The membranes performance was analyzed using a constructed pervaporation cell. The components of the cell include stainless steel cell housing providing an effective area of 122.6 cm^2 consisting of the base plate to hold the membrane and the upper retaining plate. A glass beaker equipped with a stirrer and heating device was used to collect feed sample at the desired temperature before passing through membrane cell. The downstream side of the membrane was evacuated to a vacuum pressure of 12 mm Hg with the help of FUJI 2-stage vacuum pump. The test was carried out for 1.5 h with the alcohol-water mixture before starting an experiment to achieve equilibrium. After equilibrium is reached, vapors after passing through membrane were condensed by using chiller and permeate was collected.

The permeate samples collected were analyzed using gas chromatographic technique GC NUCOM analyzer (Model 5765) equipped with the porapack column and TCD detector. Schematic representation of the experimental setup is given in Fig. 2.

Performance of membrane

Steps for transport of molecule in pervaporation are - a) transport from the bulk liquid to the feed side of the interface, b) sorption of the molecule at feed-membrane interface, c) diffusion through the membrane and iv) desorption at the membrane-permeate interface[12,13]. Solubility and diffusivity a thermodynamic quantity and a mass transfer quantity respectively play an important role in selectivity of the membrane. The performance of membrane was measured in terms of flux and selectivity of diffusing component.

The flux (J), selectivity (α), pervaporation index (PSI), is described by equation 6,7 and 8 respectively [13]

$$J = Wp/At \quad \text{... (6)}$$

Here J is permeate flow rate per unit area and time (kg/m^{2}h), W_p is the permeate mass (kg), A is the effective membrane area (m^2), and t is the time (h). The selectivity or separation factor (α) is calculated using equation 7:

$$\alpha = \left(\frac{y_a}{1-y_a}\right)\left(\frac{1-x_a}{x_a}\right) \quad \text{... (7)}$$

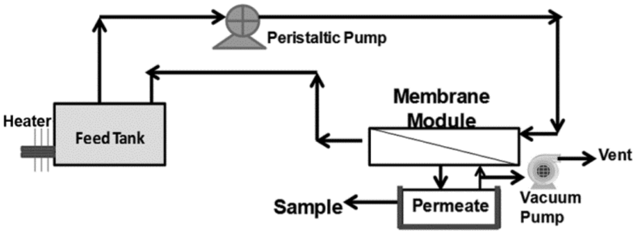

Fig. 2 — Schematic representation of pervaporation setup

Here y_a is the mass percentage of water in permeate; x_a is the mass percent of water in the feed, respectively.

The overall performance of the membrane is defined by polymer swelling index (PSI) and is calculated using equation 8:

$$PSI = J\alpha \qquad \text{... (8)}$$

Results and Discussion

SEM

The SEM images of PVA and PVA composite with different silica content is shown in Fig. 3. It is visible that silica is dispersed within polymer matrix below 2 wt% of silica/PVA while no silica was observed in pristine PVA (Fig. 3.(a) pure PVA, (b) and (c) silica/ PVA is 0.5 wt % and 1wt% respectively) but when silica content increase to 2 wt% particle gets agglomerated due to high concentration and defects becomes clearly visible (Fig. 3 (d)).

FTIR characterization

A FTIR spectrum of PVA was compared with PVA/MA and PVA/MA/silica (1 wt %) as shown in Fig. 4. Spectra confirm network linking between PVA/MA and PVA/MA/Silica because of the presence of additional peaks in the range of 1800 to 900 cm^{-1} which was not found in pristine PVA, the major FTIR bands are summarized in (Table 1).

An absorption peak at 1095cm^{-1} is assigned to Si-O-Si bond in PVA/MA/Silica spectra which were not observed in PVA and PVA/MA membranes. This bond formation is due to condensation reaction between Si-OH group of TEOS and CH-OH group of PVA. A new peak was also observed at 1726 cm^{-1} which is due to ester group in the hybrid membrane of PVA/MA/Silica. In the preparation of PVA/silica membranes, hydrolysis of TEOS when carried in the presence of acid catalyst produces silanol group which was condensed to form silicon oxide network[16]. During fabrication of PVA/silica membranes, the repeating unit of PVA, -OH group creates strong interaction with silanol group to form covalent bonds. Thus peak obtained in the range of 1088-1220 cm^{-1} is due to Si-O-Si bond formation, the similar peak was obtained for FTIR spectra of pure silica nanoparticle[17]. It

Table 1 — Assignment of FTIR bands for PVA, PVA/MA, and PVA /MA/ Silica membranes [14]

Wavenumber (cm^{-1})	Assignment
2800–3000 cm^{-1}	C–H
3200–3570 cm^{-1}	hydrogen bonded hydroxyl band
1000–1100 cm^{-1}	C–O stretching vibration of the secondary alcohol (–CH–OH) of PVA
1095 cm^{-1}	Si-O-Si [15]
1726 cm^{-1}	–CO–O–

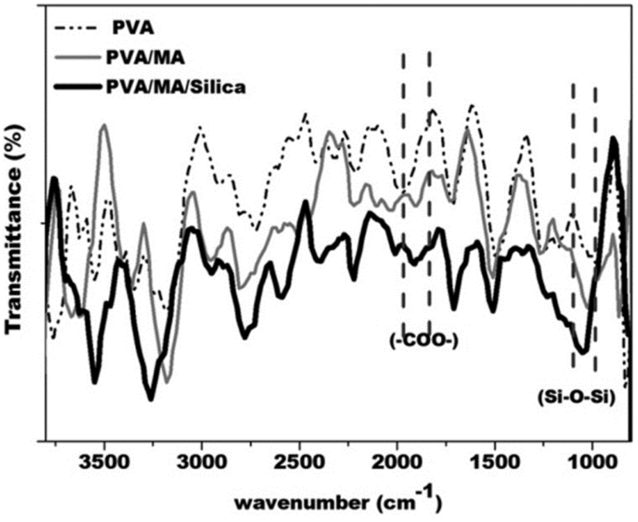

Fig. 4 — FTIR spectra of PVA, PVA/MA and PVA/MA/Silica (1 wt%)

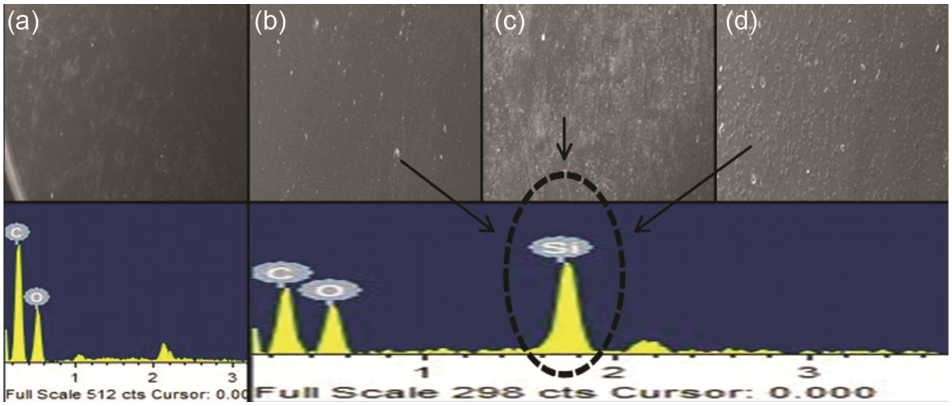

Fig. 3 — SEM image of (a) pure PVA, (b) silica/ PVA 0.5 wt % (c) silica/ PVA 1wt% (d) silica/PVA 2 wt%

indicates that hydrolysis and condensation reaction in the sol-gel reaction was completed[18].

In the synthesis of PVA/MA/Silica membrane strong covalent bond formation between TEOS and OH group of polymer and–COOH group of MA (difunctional acid) respectively results in the emergence of intermolecular and intramolecular type ester group in the hybrid membrane and forms a dense, rigid polymeric structure.

Swelling behaviour

The existence of hydroxyl group in PVA leads to high degree of swelling of the PVA membrane in aqueous solution due to strong hydrogen bonds[19]. The swelling in the polymeric membrane is a function of the diffusion coefficient of solvent, degree of crystallinity of polymer and relaxation rate of the amorphous region[19]. The pure PVA and different ratio PVA/silica based membrane of the known cross-section area were dipped into a solution of 35 wt % of alcohol to water mixture.

Figure 5, reveals a decline in swelling degree as the content of silica is increased. This data indicates polymer structure becomes rigid after introducing silica. It can also be said that silica generated during hydrolysis and condensation reaction crosslink with –OH group of PVA and –COOH group of MA, therefore water sorption capability of PVA is greatly suppressed, similar results were also reported by Kotoky and Dolui[20]. It can also be explained as the incorporation of silica from TEOS with increasing amount decreases chain length between crosslinks. So shorter the chains between crosslinks, stronger will be the elastic resistance (elastic modulus increases with the amount of crosslinker due to the formation of a tighter network) to swelling stress hence lower will be the swelling degree of the membrane[21]. Thus the addition of silica derived from TEOS to polymer network results in a reduction in free volume in the polymer matrix, which ultimately affects polymer property by reducing its ability to absorb water or alcohol from solution[4]. Amount of silica added also affects the hydrophilicity of polymer that has a direct impact on sorption of alcohol/water mixture by the membrane.

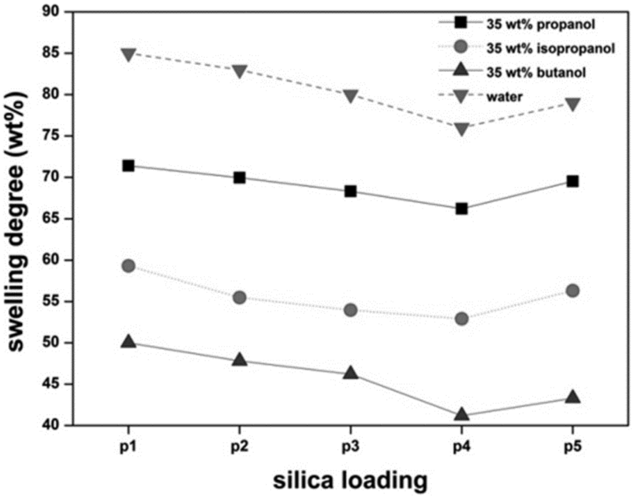

Fig. 5 — Swelling degree of PVA in water and alcohol/water at different PVA/silica loading

Effect of silica content on alcohol sorption

To determine the alcohol concentration within the swollen polymer, swelling equilibrium studies were developed. PVA membrane of different silica content was immersed in the flask containing 35% of alcohol in water. Solvent concentration in remaining liquid when the membrane is removed was calculated from a calibration curve and with the help of mass balance solvent concentration in the swollen polymer was evaluated. Table 2 shows variation in equilibrium composition as PVA/silica ratio changes.

The results presented in Table 2 indicate that for each alcohol, their concentration within swollen polymer decreases with increasing silica content. It is expected because polymer network becomes more rigid on adding crosslinker MA which reduces further on the addition of silica and has a less free volume within polymer results in the decrease in sorption of propanol, IPA, and butanol and it also reduces the hydrophilicity of membrane.

Table 2— Propanol and water, IPA and water, Butanol and water concentration in swollen polymer

Sample name		Concentration in swollen membrane					
		Propanol	water	IPA	Water	Butanol	Water
p1	PVA	3.08	7.88	2.84	9.69	1.74	13.08
P2	PVA+MA	2.54	6.64	2.20	7.61	1.35	10.51
P3	PVA+MA+Si (.5)	2.27	6.00	2.06	7.34	1.02	9.01
P4	PVA+MA+Si (1)	1.78	5.02	1.54	7.10	0.75	8.20
P5	PVA+MA+Si (2)	2.05	5.28	1.86	7.51	1.48	12.01

Figure 6 indicates that as the silica loading increases from 0 to 1.0 wt%, the concentration within the swollen membrane decrease from 28.10 to 26.3 % for propanol, 22.6 to 17.80 % for isopropanol and 11.74 to 8.38 % for butanol. Trends are found similar in all three cases. It was also observed that beyond 1 wt % of silica loading, the degree of swelling increases, this could be due to the higher concentration of nanoparticle which causes agglomeration and results in non-homogeneous distribution within the polymer, thus providing –OH group of PVA to form the bond with aqueous alcohol mixture and this agglomeration creates interfacial defects that damage membrane property adversely[22] and can be seen from SEM images in Fig. 3d. Results also predict the higher concentration of propanol in membrane and least for butanol due to the difference in molecular size explained in later section.

Sorption analysis

Sorption properties of the polymer are measured in two ways i) polymer exposure to the pure compound in vapor phase ii) immersion of polymer in the solution[23]. These measurements lead to the development of some models that include UNIQUAC (Universal Quasi-Chemical) by Abrams and Prausnitz [24], ENSIC (Engaged species Induced clustering) and iii) Flory–Huggins theory[25]. Flory–Huggins theory was originally developed for the binary system then further applied to the ternary system also and is the simplest mathematical model. This model is used in this article to study the polymer-solvent interaction parameter which is determined using Flory-Huggins interaction parameter χ. This parameter characterizes the polymer solubility in given solvent fluid. If the interaction between polymer and penetrants increases, the amount of penetrates within polymer also increases and hence the value of χ decreases and vice versa. Therefore the large value of χ is the indication of lower sorption. Table 3 presents the Flory Huggins parameter (χ) for propanol, isopropanol, and butanol at different ratio PVA/silica. Increase in the content of silica decreases free volume size hence component with smaller molecular size can easily penetrate or sorbed through the membrane.

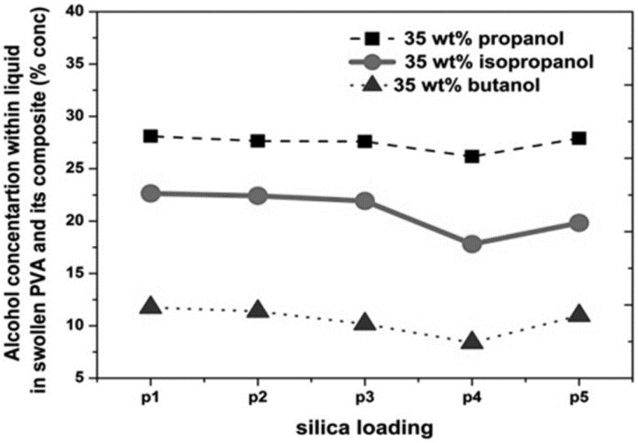

Fig. 6 — Effect of silica loading on a concentration within the liquid in swollen PVA and its composite.

These results show that the inclusion of silica into polymer interaction parameter χ increases with increase in silica loading. Hence lower sorption of alcohol at high silica loading occurs. This result is found to be as expected and similar to that reported by Polotskaya *et al.* [2].

Swelling experiment and its analysis also help in the possibility to study the sorption properties of polymer alcohol-water mixture. However, sorption of alcohol appears to be dependent on molecular size[23]. The molecular size of the different alcohol-water mixture is water <propanol < isopropanol< butanol and inverse relation exist between sorption and molecular size. As the silica loading is increased, a small free volume will be available for penetration so smaller size molecule will occupy space more than the larger molecule. Similar results were also observed for Flurry Huggins interaction parameter, the value increases with increase in silica loading indication hence low sorption at high loading, but at the same time it was observed that interaction parameter value increases for each silica loading

Table 3 — Flory Huggins parameter for propanol, isopropanol, and butanol at different ratio of PVA/silica in membrane

Membrane composition		Flory Huggins parameter (χ)		
		Propanol	IPA	Butanol
p1	PVA	0.5024	0.515	0.521
P2	PVA+MA	0.5430	0.565	0.578
P3	PVA+MA+Si (.5)	0.629	0.6321	0.641
P4	PVA+MA+Si (1)	0.635	0.6414	0.691
P5	PVA+MA+Si (2)	0.683	0.6954	0.725

when molecular size increases in the order (propanol < isopropanol< butanol) thus indicating less interaction for high molecular size.

Effect of shape and size

The variation in selectivity between alcohols is different due to the difference in molecular size; this difference is due to the difference in a number of carbon atom and their structure. With the increase in a number of carbon atom in alcohols selectivity of the membrane towards alcohol decreases[4]. The effect of shape and size of permeant was also studied by Huang and Jarvis[26]. They reported that with an increase in the molecular weight in given homologous series, the decrease in the permeation rate and increases in the selectivity of water.

The solubility coefficient provides the knowledge related to the selectivity of membrane polymer[23]. The solubility coefficient of the membrane for alcohol in different alcohol/water mixture was calculated using equation 5 and results are plotted as shown in see Fig. 7.

This graph depicts a decrease in solubility coefficient with increasing concentration silica in PVA. It was also concluded that coefficient value is high for propanol compared to other alcohol; hence affinity for propanol is higher as confirmed by the swelling degree results also. As stated earlier in this section that an increase in molecular weight of compound and increase in a number of a carbon atom results in the decrease in selectivity, the present investigation follows the same trend for homologous series n propanol, isopropanol, n butanol for PVA composite membrane.

Performance evaluation

Based on the analysis explained above, the effects of sorption and swelling on the performance of membrane are investigated, and results are presented here. Figure 8 concluded that with an increase in silica loading there is an enhancement in total flux and selectivity of the membranes up to 1 wt% of SiO_2. However further increase results in decline of selectivity. The result was expected, and similar findings were also observed and reported in other literature[13].

Huang and Jarvis[26] reported that there is an increase in selectivity with an increase in a number of carbon atom, the present study also holds the same relation (Fig. 7). As explained earlier, with increasing molecular size, selectivity toward water molecule will

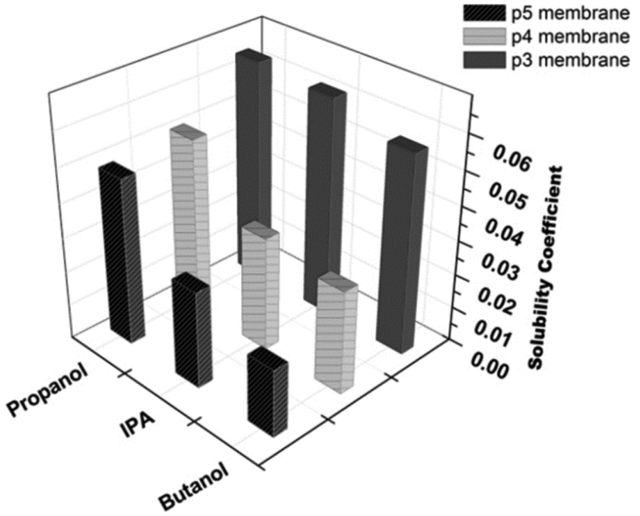

Fig. 7 — Solubility coefficient for alcohols in alcohol/water at different PVA composite membranes.

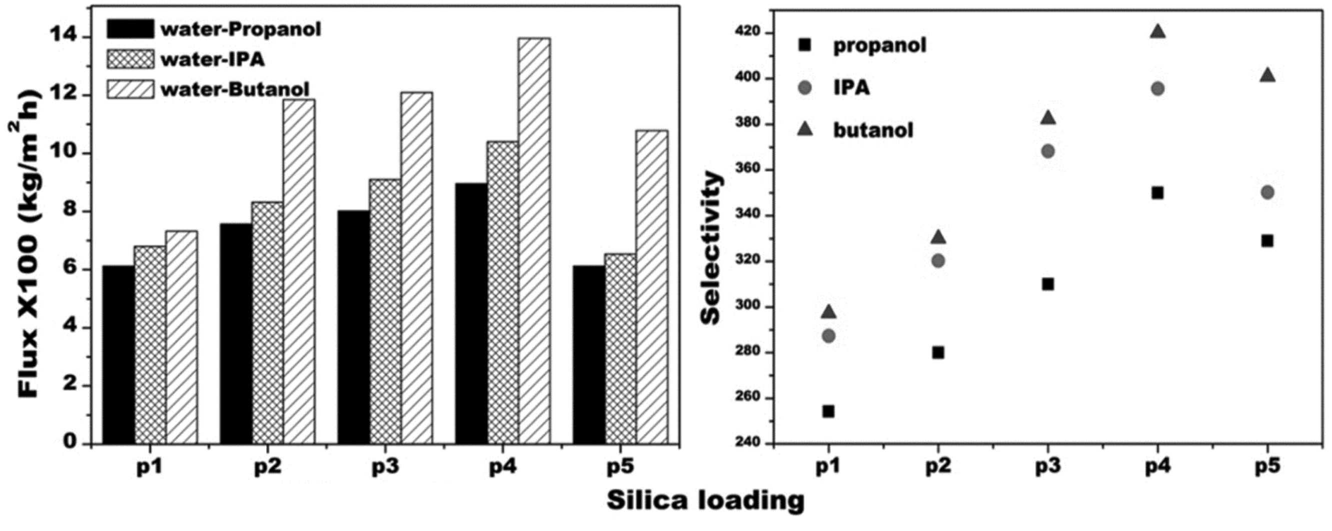

Fig. 8 — Variation in Flux and selectivity with a number of carbon atoms of permeating species for 10% of water in the feed.

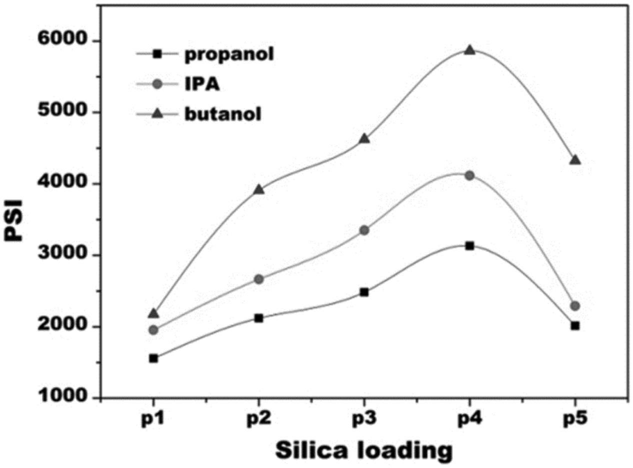

Fig. 9 — Effect of silica loading on PSI for 10% mass of water in different alcohol feed mixture.

increase, as the interaction parameter for different alcohol increases with increase in a number of carbon atom, hence large volume will be available for water molecules to occupy compared to a molecule with the highest number of carbon atom. Selectivity of water is higher in butanol-water aqueous solution. It was also concluded that for a similar number of carbon atom as in case of *n*- propanol and iso-propanol, selectivity is higher for IPA. This may be explained as the diffusive cross section of IPA is large compared to propanol, the expected diffusion coefficient will be lower compared to *n*-propanol[27].

The separation index (PSI) characterizes the performance of pervaporation membranes. Figure 9 depicts the effect of silica loading and number of carbon atom on PSI for 10 % water in the feed. It was observed that value increases with increase in silica loading and number of carbon atom as expected due to increase in selectivity.

Conclusion

A systematic study of swelling and sorption property of PVA and its composite membrane has been carried out for aqueous homologous alcohol series. It is concluded that increase in silica loading decreases the swelling degree. Alcohol sorption within the membrane is affected by the silica loading because the addition of silica will provide less free volume through which molecule is absorbed. The interaction of PVA composites with aqueous alcohol is studied by the measurements of Flory Huggins parameter. A small value of interaction parameter indicates high sorption. These data are found to follow the same trend as observed in swelling degree. It is concluded that increase of silica loading is beneficial for membrane performance.

Acknowledgement

Financial support from MHRD (Ministry of Human Resource Development) for their research grant support and Central Instrument Facility Center (CIFC), of IIT (BHU), are gratefully acknowledged.

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