International Journal of Current Engineering and Technology
ISSN 2277 – 4106

Research Article

Pervaporation separation of water-dioxane mixtures through poly(vinyl alcohol)-silicone based hybrid membranes

A. A. Kittur[a], Jeevankumar B.K. [b] and M. Y. Kariduraganavar[b*]

[a] Department of Chemistry, SDM College of Engg. & Technol, Dharwad 580003, INDIA
[b] Department of Chemistry, Karnatak University, Dharwad 580003, INDIA

Abstract

Hybrid membranes were prepared using poly(vinyl alcohol) (PVA) and tetraethylorthosilicate (TEOS) via hydrolysis followed by condensation. The membranes were subjected to swelling study and observed a remarkable decrease in degree of swelling with increasing the TEOS content in membranes and is attributed to the formation of hydrogen and covalent bonds in the membrane matrix. The pervaporation performance of these membranes for the separation of water-dioxane mixtures was investigated in terms of feed concentration and the content of TEOS used as crosslinking agent. The membrane containing 1:1.5 mass ratio of PVA and TEOS gave the highest separation selectivity of 14,992 with a flux of 0.70 x 10^{-1} *kg/*m^2 *h at 30*^oC *for 10 mass % of water in the feed. For all the membranes the observed values of water flux are very close to the values of total flux in the investigated composition range, signifying that the developed membranes are highly water selective. From the temperature dependence of diffusion and permeation values, the Arrhenius apparent activation parameters have been estimated. The resulting activation energy values, obtained for water permeation being lower than those of dioxane permeation values, suggest that the membranes have higher separation efficiency. The activation energy values calculated for total permeation and water permeation are close to each other for all the membranes, signifying that coupled-transport is minimal as due to higher selective nature of membranes. The negative heat of sorption values (*ΔH_S*) for water in all the membranes suggests the Langmuir's mode of sorption.*

***Keywords**: poly(vinyl alcohol), TEOS, hybrid membranes, pervaporation, selectivity, activation energy.*

1. Introduction

Increased awareness of both environmental and energy needs has resulted in significant efforts in industrial sector to develop energy efficient separation processes. Compared to the traditional phase separation processes such as distillation, membrane separation techniques are energy efficient with an easy operation and low cost. These techniques are greatly appreciated in a variety of applications in the medical, food, industrial, energy and environment fields. Pervaporation (PV), a membrane based separation technique is a hybrid between a liquid and a gas separation process, and is very effective and economical for the separation of water from organic solvents and solvent mixtures . The principles of PV can be best understood through explanation of two step processes: an evaporation process and a membrane transfer process. It is especially promising for separation of organic liquid mixtures such as azeotropes or close boiling liquids.

Most research efforts on the PV process have been focused on the separation of water-alcohol systems, and the separation of water-dioxane mixtures has received relatively less attention. Dioxane is a clear liquid that dissolves in water at all concentrations. It forms an azeotropes at 18.1 mass % of dioxane concentration. It is primarily used as a solvent in the manufacture of chemicals, as a laboratory reagent and as a media with water in electrochemical research . It is also used in the preparation of cosmetics, detergents and shampoos. When this chemical release to environment, sunlight does not react with dioxane directly but can change dioxane to different compounds. In water it is stable and does not degrade and affect the aquatic life. It is reported that acute accidental exposure to high amount of vapours of this have caused death in people. The US Department of health and human services reasonably anticipated 1.4-dioxane as human carcinogen on the basis of sufficient evidences. Hence it is very much essential to separate 1.4-dioxane from industrial waste. Because of the small differences in the volatilities of water and dioxane in dilute aqueous solution, azeotropic distillation is preferable instead of binary distillation. Lee et al. prepared poly(dimethyl siloxane-co-siloxane) membranes and studied for pervaporation separation of dioxane-water system. They got the flux 0.108 kg/m^2h and the selectivity is 16.3. Wang et al. reported 0.417kg/m^2h flux with selectivity 663

---

*Corresponding author: **Kariduraganavar** at 70°C for sodium alginate composite membranes . In PV, membrane plays a vital role as it functions as a selective barrier for the mixtures to be separated. Hence, to meet the desire needs various membranes have been prepared and used for the dehydration of organics. Among these the crosslinked poly(vinyl alcohol) (PVA) membranes have been investigated frequently since hydroxyl groups of PVA form strong interactions with water through hydrogen bonding. Though these membranes yields better PV performances, but still fail to achieve satisfactory results. This may be due to greater degree of crosslinking density or higher degree of swelling. To overcome such problems, hydrophilic membranes with optimized degree of crosslinking density using suitable crosslinker are required for the effective mass separation. A better way is to establish the inorganic crosslinking segments between the linear chains through chemical reaction to improve the membrane toughness. In doing so, with a minimum degree of crosslinking density one can retain more number of hydrophilic groups in the polymer matrix so as to improve the overall PV performances.

In the recent years the organic-inorganic hybrid materials via sol-gel process have attracted great attention. This is because of their potential advantages over the conventional materials due to their extra ordinary properties arising from the synergism between the organic inorganic characteristic properties. From the practical point of view as a membrane material in separation, these hybrid materials have a promising future due to unique advantages such as flexibility, high mechanical strength, thermal stability and excellent processibility. Moreover, among the recent researches, these hybrid membranes are viewed as next generation materials in many applications. They were prepared by directly incorporating the silane groups as the precursors to get Si-O-Si backbone which provides thermal stability, mechanical strength and less swelling capacity.

PVA is a possible candidate for the dehydration process of aqueous organic mixtures owing to its good chemical stability, film-forming ability and high hydrophilicity, except for its poor stability in aqueous solution. Therefore, PVA needs to be insolubilized by crosslinking or other modifications so as to get a stable membrane with good mechanical properties and selective permeability towards water. Insolubilization of PVA by crosslinking with maleic acid, glutaraldehyde and phenylene diamine has been well documented by many investigators. Recently, hybrid materials in which the organic and inorganic compounds are ideally homogenous are being studied in various fields.

This has prompted us to extend the study of these membranes for the separation of water-dioxane mixtures. An effort to control the membrane swelling by introducing an inorganic group as a crosslinker into PVA matrix *via* hydrolysis and followed by condensation reaction using the sol-gel method was made. The TEOS content with respect to that of PVA was varied to improve the membranes' performances. The physical and spectroscopic properties of the deriatized membranes in relation to their structure variations were investigated. The resulting membranes were employed for PV separation of water-acetic acid mixtures at 30, 40 and 50°C. We report here the experimental results of permeation flux, separation selectivity and diffusion coefficients at different temperatures. The diffusion coefficients have been calculated from the Fick's equation. From the temperature dependency of permeation flux and diffusion coefficients data, the Arrhenius activation parameters have been estimated. These results are discussed in terms of PV separation efficiency of the membranes.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (M.W. ~1,25,000), Dioxane and hydrochloric acid were purchased from s. d. fine Chemicals Ltd., Mumbai, India. Tetraethylorthosilicate (TEOS) was procured from E. Merck (India) Ltd., Mumbai. All the chemicals are of reagent grade and were used without further purification. Double distilled water was used throughout the study.

2.2. Membrane preparation

Poly(vinyl alcohol) (4 g) was dissolved in 100 ml deareated-distilled water at 60°C. The hot solution was filtered and to the filtrate, a known amount of TEOS and 1 ml of concentrated HCl as an acid catalyst were added to carry out the sol-gel reaction. The solution was stirred overnight at room temperature and the resulting homogeneous solution was cast onto a glass plate with the aid of a casting knife. The membranes were allowed to dry at room temperature for 2-3 days and the completely dried membranes were subsequently peeled off. The mass ratio of TEOS with respect to PVA was varied as 0.25, 0.5, 1.0, 1.5 and the resulting hybrid membranes were designated as M-1, M-2, M-3 and M-4, respectively.

2.3. Fourier transform infrared (FTIR) spectroscopy

The reaction between PVA and TEOS was confirmed using FTIR spectrometer (Nicolet, Impact-410, USA). Membrane samples were ground well to make KBr pellets under a hydraulic pressure of 400 kg/cm^2 and spectra were recorded in the range of 400–4000 cm^{-1}.

2.4. Wide-angle X-ray diffraction (WAXD)

Morphology of the hybrid membranes was studied at room temperature using a Brucker's D-8 advanced wide-angle X-ray diffractometer. The X-ray source was nickel-filtered Cu Kα-radiation (40 kV, 30 mA). The dried membranes of uniform thickness (±40μm) were mounted on a sample holder and scanned in the reflection mode at an angle 2θ over a range from 5 to 40◦ at a speed of 8◦/min.

2.5. Swelling measurements

The equilibrium sorption experiments were performed in different compositions of water-dioxane mixtures using an electronically controlled oven (WTB Binder, Germany). The mass of the dry membranes were first determined and these were equilibrated by soaking in different compositions of the mixtures in a sealed vessel at 30°C for 24 h. The swollen membranes were weighed as quickly as possible after careful blotting using digital microbalance. All experiments were performed at least three times, and the results were averaged. The percent degree of swelling (*DS*) was calculated as:

$$DS\,(\%) = \left(\frac{W_s - W_d}{W_d}\right) x100 \qquad (1)$$

where W_s and W_d are the masses of the swollen and dry membranes, respectively.

2.6 Pervaporation experiments

PV experiments were performed using an indigenously designed apparatus as shown in our previous articles Fig.1(A&B) . The effective surface area of the membrane in contact with the feed mixture is 34.23 cm^2 and the capacity of the feed compartment is about 250 cm^3. The vacuum in the downstream side of the apparatus was maintained (10 Torr) using a two-stage vacuum pump (Toshniwal, Chennai, India). The water composition in the feed mixture was varied from 10 to 50 mass %. The test membrane was allowed to equilibrate for about 2 hours in the feed compartment before performing the PV experiment with a known volume of feed mixture. After an equilibrium was attained, the permeate was collected in traps immersed in the liquid nitrogen on the downstream side at timed intervals and experiments were carried out at 30, 40 and 50°C. The flux was calculated by weighing the permeate on a digital microbalance (Mettler B204-S, Toledo, Switzerland) with an accuracy of ± 0.01mg. The compositions of water and dioxane were estimated by measuring the refractive index of the permeate within an accuracy of ± 0.0001 units using Abbe's Refractometer (Atago-3T, Japan) and using standard graph of refractive index *vs* known compositions of water-dioxane mixture. The results from the permeation of water-dioxane mixtures during the pervaporation were reproducible, and the errors inherent in the pervaporation measurements were in the order of a few percent.

From the PV data, separation performances of the membranes can be assessed in terms of total flux (*J*), separation selectivity (α_{sep}) and pervaporation separation index (*PSI*) and these were calculated, respectively, using the following equations:

$$J = \frac{W}{A.t} \qquad (2)$$

$$\alpha_{sep} = \frac{P_w / P_{IPA}}{F_w / F_{IPA}} \qquad (3)$$

$$PSI = J\ (\alpha_{sep} - 1) \qquad (4)$$

Here, *W* is the mass of permeate (kg); *A*, the area of the membrane in contact with the feed mixture (m^2): *t*, the permeation time (h); P_w and $P_{dioxane}$ are the mass fractions of water and dioxane in the permeate, respectively. F_w and $F_{dioxane}$ are the respective mass fractions of water and dioxane in the feed.

3. Results and discussion

3.1. Formation of PVA/TEOS hybrid membrane

Figure 2 shows the process of polycondensation reaction of TEOS . In the process of preparing PVA/TEOS hybrid membrane, TEOS was hydrolyzed in presence of an acid catalyst, giving silanol groups. The resulting silanol groups yielded siloxane bonds due to the dehydration or dealcoholysis reaction with other silanol groups or ethoxy groups during the membrane drying. These reactions led to cohesive bodies between siloxane in the membrane. Since these bodies of siloxane were dispersed in the membrane, the silanol groups of siloxane and the hydroxy groups of PVA formed hydrogen and covalent bonds, which are the crosslinking points.

3.2. Membrane characterization

3.2.1. FTIR studies

The incorporation of inorganic groups into a PVA matrix was confirmed by FTIR studies. Fig. 3 shows the FTIR spectra of pure PVA membrane and those of membranes with different loading of TEOS content. A characteristic strong and broad band appeared at around 3400 cm^{-1} in pure PVA spectra (M) corresponds to O-H stretching vibrations of the hydroxyl groups. The intensity of this broad band gradually decreased from membrane M-1 to M-4 with increasing TEOS content, indicating that some of the –OH groups of PVA involved in condensation reaction with silanol groups of TEOS, forming covalently bonded crosslinks between polymer segments. Further, multiple bands appeared in the spectra (M) at around 1000–1100 cm^{-1} are assigned to C- O stretching. The increase in the intensity of these bands from membrane M-1 to M-4 with increasing TEOS content, suggest the formation of Si-O-C bonds between the linear polyethylene segments, since Si O stretching also appears at the same wavelength of C O stretching.

3.2.2. X-ray diffraction studies

To study the effect of TEOS on the membrane morphology, X-ray diffraction was employed and the patterns for PVA and its hybrid membranes are presented in Fig. 4. The pure PVA membrane (M) exhibits a typical peak that appeared at $2\theta = 20^{o}$ thus, it can be assigned to be a mixture of (101) and (200). On the other hand, diffraction patterns of the hybrid membranes show that as the degree of crosslinking density increased from membrane M-1 to M-4, the intensity of the peak decreased continuously at around $2\theta = 20^o$, owing to the formation of Si-O-C bonds between the linear polyethylene segments. This reveals that the uncrosslinked PVA membrane exhibits more crystalline domains than those of crosslinked hybrid membranes. From the patterns, it can also be observed that there is a shift in the position of the peaks of hybrid membranes from the pure PVA membrane. This implies that the silanol groups of TEOS crosslinks with reactive –OH groups of PVA in crystalline domain, results in the compression of the amorphous region, thereby making the structure more compact. This compact structure favours the selective transport of water.

3.3. Effect of feed composition and TEOS content on membrane swelling

The characteristics of the sorption (swelling) mechanism depend on the membrane structure, the difference between the affinities of the components towards membrane, the mutual interaction of components and the way of interaction of each component with the membrane affects the interaction of other penetrant with the membrane [19-21]. Therefore, the properties of membrane sorption play an important role in PV process. Figure 5 shows the swelling behavior of the hybrid membranes in different mass % of water-dioxane mixture at 30^{o}C. It is noticed that the degree of swelling increased almost linearly for all the membranes with increasing water concentration up to 50 mass % in the feed. The increase of preferential sorption of water with increasing water content may be due to small water molecule and strong interactions occurring between the water molecules and reactive -OH groups present in the membrane matrix. On the other hand, the degree of swelling decreased drastically from membrane M-1 to M-4 throughout the investigated range. This is mainly due to a reduction of free-volume and hydrophilic groups upon increasing the TEOS, since silanol groups of TEOS underwent the formation of covalently bonded crosslinks with the reactive -OH groups.

3.4. Effect of feed composition and TEOS content on pervaporation properties

Figure 6 shows the effect of feed composition on the total permeation flux for all the membranes at 30^{o}C. It is observed that the total permeation flux increased almost linearly for all the hybrid membranes with increasing the amount of water in the feed. This is due to an increase of selective interaction between water molecules and hydroxyl groups of hybrid membranes. This interaction becomes more predominant at higher concentration of water, since water causes a greater degree of interaction than that of dioxane with these membranes. On the contrary, the permeation flux decreased monotonically from membrane M-1 to M-4 with increasing the crosslinking density as can be seen in Fig. 7. This is because of significant reduction of free-volume in the membrane matrix and its decreased hydrophilic character, owing to the formation crosslinks between the linear polyethylene units. The results of X-ray also support this explanation. To see the extent of permeation of individual components, we have plotted the individual fluxes as a function of mass % of TEOS in membranes at 10 mass % of water in the feed as shown in Fig. 8. From the plot, it is clearly noticed that the water flux values are very close to the values of total flux and hence they are overlapping each other for all the membranes. This is clearly manifested that the membranes developed in the present study having higher crosslinking density are found to be highly selective towards water.

The overall selectivity of a membrane in PV process is generally determined on the basis of interaction between the membrane and permeating molecules, molecular size of the permeating species and pore diameter of the membrane. Figure 9 displays the effect of water composition on the selectivity for all the membranes. It is observed that the selectivity decreased significantly for all the membranes with increasing water concentration in the feed. Here the increased swelling of the membrane has a negative impact on the membrane selectivity. The swollen and plasticized upstream membrane layer allows some of the dioxane molecules to escape into the permeate side along with water molecules indicating a drop in selectivity. On the other hand, the selectivity increased linearly from membrane M-1 to M-4 upon increasing the crosslinking density as seen from Fig. 9. This is due to a reduction of free-volume in membrane matrix and decreased hydrophilic character of the membranes, which together responsible for the increased selective interaction between membrane and the water molecules.

The calculated results of total flux and selectivity, fluxes of water and dioxane measured at 30^{o}C for all the membranes in different compositions of feed mixture are presented in the Table 1 and 2, respectively. It is observed that there is a systematic increase in total flux, water flux and flux of dioxane with respect to water composition in the feed, while these values decreased with increasing the crosslinking density in the membranes. However, the systematic effect of water composition and crosslinking density was noticed on the selectivity.

3.5. Pervaporation separation index (PSI)

Pervaporation separation index (*PSI*), which is a relative measure of the separation ability of a membrane, has been defined as the product of total permeation and separation factor. This index can be used as a relative guideline index for the design of pervaporation membrane separation pro++++cesses and also to select a membrane with an optimal combination of flux and selectivity. Figure 10 shows the variation of *PSI* as a function of TEOS content in the membranes for 10 mass % of water in the feed at 30^{o}C. It is found that *PSI* values increased with increasing crosslinking density (M-1 to M-3). However, for membrane M-4, the PSI value totally decreased. This may be due to a considerable loss of hydrophilic character at higher crosslinking density and as a result, selectivity remarkably decreased towards the water. This signifying

Table 1 Pervaporation flux and separation selectivity for different membranes at 30oC for different mass % of water in the feed

Mass % of water	J_p x 10^1 (kg/m^2 h)				α_{sep}			
	M-1	M-2	M-3	M-4	M-1	M-2	M-3	M-4
10	2.41	2.12	1.40	0.70	2804	5285	9991	14992
20	2.68	2.35	1.85	1.19	223	847	1022	1246
30	3.19	2.75	2.28	1.52	114	130	214	124
40	3.38	3.20	2.69	1.73	57	72	103	129
50	4.29	3.66	3.06	2.82	10	17	34	37

Table 2 Pervaporation Fluxes of Water and Dioxan for Different Membranes at 30oC for Different Mass % of Water in the feed

Mass % of water	J_W x 10^1 (kg/m^2 h)				$J_{Dioxane}$ x 10^3 (kg/m^2 h)			
	M-1	M-2	M-3	M-4	M-1	M-2	M-3	M-4
10	2.40	2.12	1.40	0.69	0.77	0.36	0.13	0.04
20	2.63	2.33	1.84	1.18	4.72	1.10	0.72	0.38
30	3.06	2.70	2.26	1.49	6.24	4.83	2.46	2.81
40	3.28	3.12	2.64	1.69	9.92	8.26	5.53	3.99
50	3.91	3.46	2.97	2.74	38.6	19.9	8.81	8.71

Table 3 Diffusion Coefficients of Water and Dioxan for Different Membranes Calculated at 30oC from eq. 6 for Different Mass % of Water in the Feed

Mass % of water	D_w x 10^7 (m^2/s)				$D_{Dioxane}$ x 10^9 (m^2/s)			
	M-1	M-2	M-3	M-4	M-1	M-2	M-3	M-4
10	5.24	4.56	2.94	1.43	0.84	0.39	0.14	0.05
20	2.76	2.43	1.90	1.21	5.77	1.35	0.88	0.46
30	2.11	1.85	1.54	1.02	8.71	6.75	3.44	2.93
40	1.70	1.60	1.35	0.87	11.30	13.5	9.02	3.25
50	1.61	1.42	1.21	0.69	75.80	39.0	17.20	16.0

Table 4 Pervaporation Flux and Separation Selectivity for Different Membranes at Different Temperatures for 10 Mass % of Water in the Feed

Temp. (^{o}C)	J_p x 10^1 (kg/m^2 h)				α_{sep}			
	M-1	M-2	M-3	M-4	M-1	M-2	M-3	M-4
30	2.41	2.12	1.40	0.70	2804	5285	9991	14992
40	4.78	3.86	3.50	0.86	1075	1050	2299	2804
50	9.69	7.43	4.68	1.60	304	502	701	806

Table 5 Arrhenius Activation Parameters for Permeation and Diffusion and Heat of Sorption

Membranes	M-1	M-2	M-3	M-4
E_p (kJ/mol)	56.62	51.07	49.42	33.42
E_D (kJ/mol)	67.86	59.10	53.81	34.23
E_{pw} (kJ/mol)	55.57	50.41	48.26	32.28
E_{Dw} (kJ/mol)	67.85	59.02	53.27	33.51
$E_{pDioxane}$ (kJ/mol)	145.92	146.69	190.63	190.70
ΔH_s (kJ/mol)	-11.24	-8.03	-4.39	-0.81

that the membranes of the present study showed better performances at higher crosslinking density up to a maximum extent of 1:1.5 mass % of TEOS to PVA.

3.6. Diffusion coefficient

In pervaporation process, the mass transport of a binary liquid mixture through a non-porous polymer membrane is generally described by the solution-diffusion mechanism, which occurs in three steps: sorption, diffusion and evaporation . Thus, the selectivity and permeation rates are governed by the solubility and diffusivity of each component of the feed mixture to be separated. In the process, because of establishing the fast equilibrium distribution between the bulk feed and the upstream surface of a membrane, diffusion step controls the migration of penetrants. Therefore, it is important to estimate the diffusion coefficient, D_i of penetrating molecules to understand transport mechanism.

From the Fick's law of diffusion, the diffusion flux can be expressed as :

$$J_i = -D_i \frac{dC_i}{dx} \qquad (5)$$

where J is the permeation flux per unit area (kg $m^{-2}s^{-1}$), D is the diffusion coefficient (m^{-2} s^{-1}), C is the concentration of the permeant (kg m^{-3}), subscript i stands for water or dioxane and x is the diffusion length (m). For simplicity, it is assumed that the concentration profile along the diffusion length is linear. Therefore, the diffusion coefficient can be calculated using the equation :

$$D_i = \frac{J_i \delta}{C_i} \qquad (6)$$

where C is the weight concentration of component i at the membrane surface of the feed side and δ is the membrane thickness. The calculated values of D_i at 30°C are presented in the Table 3. As similar to pervaporation study, the diffusion coefficients of water as well as dioxane decreased from membrane M-1 to M-4, due to a reduction of pore size with increasing the crosslinking density. As the water in the feed concentration increases the diffusion coefficient values of dioxane increased continuously for all the membranes. This is expected due to a detoriation of membrane selectivity towards water with increasing water composition in the feed.

3.7. Effect of temperature on membrane performances

The effect of operating temperature on pervaporation performances for 10 mass % of water in the feed was studied and results are presented in Table 4. It is observed that the permeation rate was found to increase from 30 to 50°C, whereas the separation factor decreased. This is because of decreased interaction between water molecules and, permeants and membrane at higher temperature, which predominate the plasticizing effect on the membrane. This intern facilitates the transport of water molecules along with dioxane molecules, while reducing the selectivity.

The temperature dependence of the permeation and diffusion rates can be expressed by an Arrhenius type relationship ,

$$X = X_o \exp\left(\frac{-E_x}{RT}\right) \qquad (7)$$

where X represents diffusion (D) or permeation (J), X_o is a constant representing pre-exponential factor of J_o or D_o, E_x represents activation energy for pervaporation or diffusion depending upon the transport process under consideration and RT is the usual energy term. As the feed temperature increases, vapour pressure in the feed compartment also increases, but the vapour pressure at the permeate side is not affected. These results in an increase of driving force with increasing the temperature.

Arrhenius plots are shown in Figs.11and 12 for the temperature dependence of permeation flux, fluxes of water and dioxane, and diffusion of water, respectively. From the least square fit of these linear plots, the activation energies values for total permeability (E_p), individual permeabilities of water (E_{pw}) and dioxane ($E_{pdioxane}$) and total diffusivity (E_D) were estimated and results so obtained are presented in Table 5.

From Table 5, it is observed that the apparent activation energy values of water permeation (E_{pw}) are significantly lower than those of dioxane permeation ($E_{pdioxane}$), suggesting a higher separation efficiency of the membranes. In all the membranes, the activation energy values of water and total permeation (E_p) are almost close to each other, signifying that coupled-transport (water and dioxane) is minimal as due to higher selective nature of membranes. The E_p and E_D values ranged between 33.42 and 56.62 kJ/mol, and 34.23 and 67.86 kJ/mol, respectively. Using these values, we have further calculated the heat of sorption as:

$$\Delta H_s = E_{pw} - E_{Dw} \qquad (8)$$

The resulting ΔH_s values are included in Table 6. The ΔH_s values give the additional information about the transport of molecules through the polymer matrix. It is a composite parameter involving contributions from Henry's and Langmuir's type of sorption. Henry's law states that the heat of sorption will be positive for liquid transport leading to the dissolution of chemical species into that site within the membrane, giving an endothermic contribution to the sorption process. However, Langmuir's sorption requires the pre-existence of a site in which sorption occurs by a hole filling mechanism, giving an exothermic contribution. The ΔH_s values obtained in the present study are negative for all the membranes, suggesting that Langmuir's sorption is still predominant, giving an exothermic contribution.

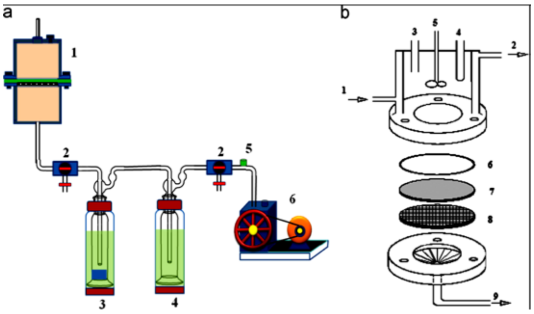

Fig. 1a Schematic representation of pervaporation apparatus: (1) pervaporation cell; (2) vacuum control valves; (3) permeate cold trap; (4) moisture cold trap; (5) pressure sensor; (6) vacuum pump.

Fig. 1b Schematic diagram of pervaporation cell: (1) water inlet; (2) water outlet; (3) feed inlet; (4) thermometer jacket; (5) stirrer; (6) o-ring; (7) membrane; (8) sintered disk; (9) permeate outlet.

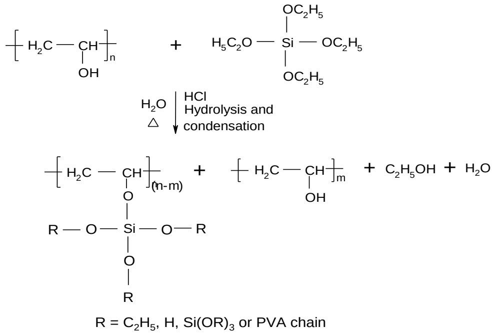

Fig. 2 Scheme for the synthesis of PVA based hybrid membrane.

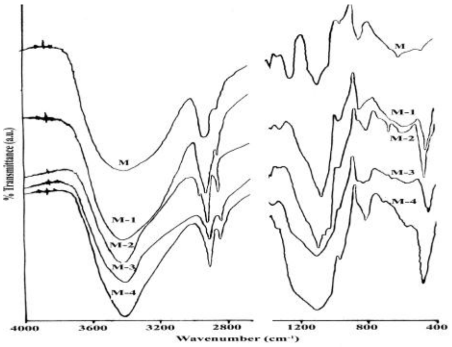

Fig. 3 FTIR spectra of pure PVA and its hybrid membranes: (M) 0 mass %; (M-1) 0.25 mass %; (M-2) 0.5 mass %; (M-3) 1.0mass %; (M-4) 1.5 mass % of TEOS.

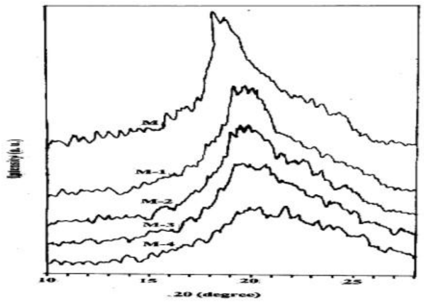

Fig. 4 Wide-angle X-ray diffraction patterns of pure PVA and its hybrid membranes: (M) 0 mass %; (M-1) 0.25 mass %; (M-2) 0.5 mass %; (M-3) 1.0mass %; (M-4) 1.5 mass % of TEOS.

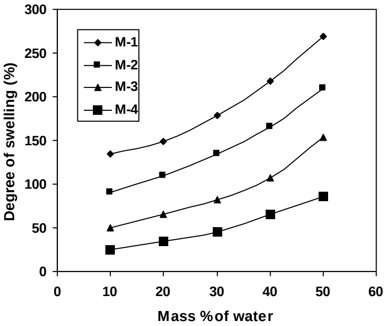

Fig. 5 Variation of degree of swelling with different mass % of water in the feed for different hybrid membranes.

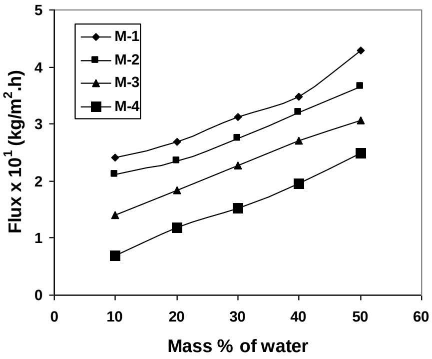

Fig. 6 Variation of total pervaporation flux with different mass % of water in the feed for different hybrid membranes.

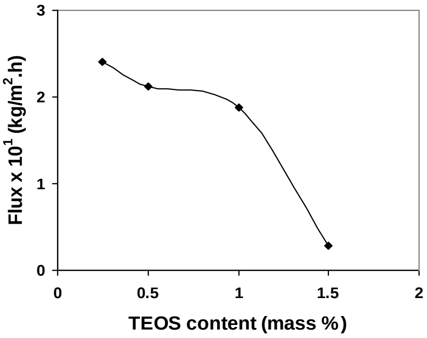

Fig. 7 Variation of total pervaporation flux with different mass % of TEOS at 10 mass % of water in the feed.

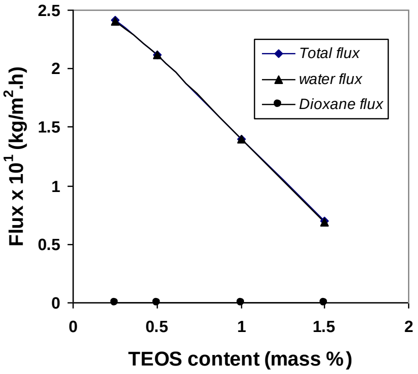

Fig. 8 Variation of total flux, and fluxes of water and dioxane with different mass % of TEOS at 10 mass % of water in the feed.

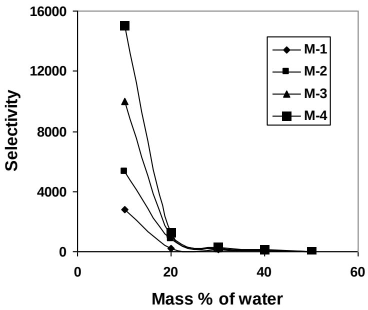

Fig. 9 Variation of pervaporation separation in selectivitydex with different mass % of TEOS at 10 mass % of water in the feed.

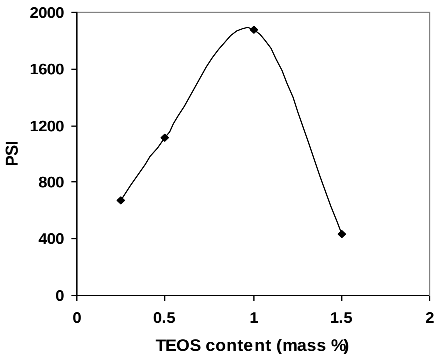

Fig. 10 Variation of pervaporation separation index with different mass % of TEOS at 10 mass % of water in the feed.

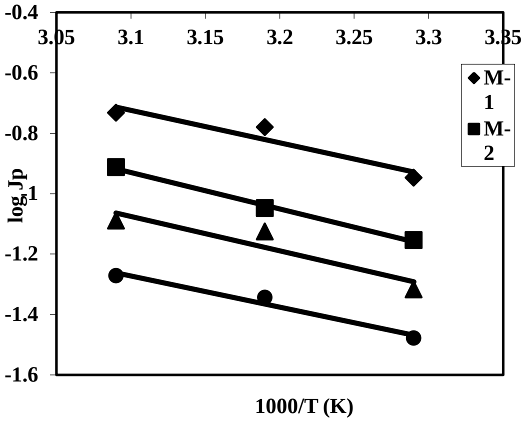

Fig. 11 Variation of log J_p with temperature for different hybrid membranes at 10 mass % of water in the feed.

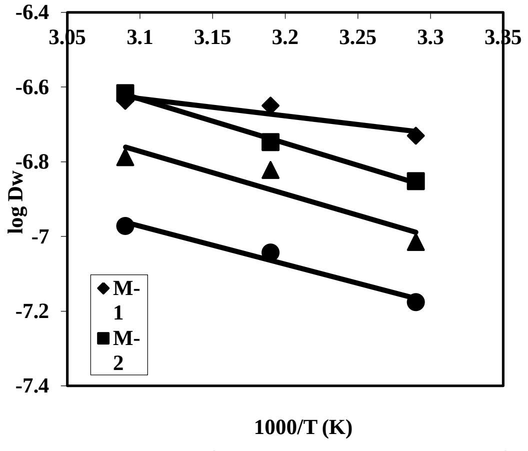

Fig. 12 Variation of log D_w with temperature for different hybrid membranes at 10 mass % of water in the feed.

4. Conclusions

Hybrid membranes incorporated with higher amount of TEOS showed a significant performance while separating water-dioxane mixtures. The performance of these membranes was explained on the basis of a reduction of free-volume and decreased hydrophilic character owing to the formation of covalently bonded crosslinks. The membrane containing 1:1.5 mass ratio of PVA and TEOS showed the highest separation selectivity of 14992 with a flux of 0.70×10^{-1} kg/m^2 h at 30^{o}C for 10 mass % of water in the feed. The PV separation index data also support that membrane with a higher degree of crosslinking density showed an excellent PV performance. Experimental data also reveal that the total flux and water flux are almost equivalent in the investigated range, manifesting that the developed membranes are highly water selective.

The significant lower apparent activation energy values obtained for water permeation as compared to dioxane permeation are attributed to higher separation efficiency of the membranes. Further, the activation energy values of total permeation and water permeation are close to each other, signifying that coupled transport is minimal due to the selective nature of membranes.

The estimated E_p and E_D values ranged between 33.42 and 56.62 kJ/mol, and 34.23 and 67.86 kJ/mol, respectively. In all the membranes, the Langmuir's mode of sorption dominates over the process, giving an exothermic contribution.

Acknowledgement

The authors gratefully acknowledge the financial support given by Department of Science and Technology, New Delhi (No.: SR/WOS-A/CS-48/2007).

References

T. Kostov Uragami, T. Katayama, T. Miyata, H. Tamura, T. Shiraiwa and A. Higuchi (2004), Dehydration of an Ethanol/water Azotrope by novel organic-Inorganic Hybrid Membranes based on Quaterniz*ed Chitosan and Tetraethoxysilane,* Biomacromolecules, Vol. 5, pp 126

A. A. Kittur, S. M. Tambe, S. S. Kulkarni and M. Y. Kariduraganavar (2004) Pervaporation Separation of Water–Acetic Acid Mixtures Through NaY Zeolite-Incorporated Sodium Alginate Membranes, *J. Appl. Polym. Sci*., Vol. 94, pp 2101-2109

M. Ghazali, M. Nawawi and R.Y.M. Huang (1997), Pervaporation dehydration of isopropanol with chitosan membranes, *J. Membrane Sci*., Vol. 124, pp 53-62.

S. S. Kulkarni, S. M. Tambe, A. A. Kittur and M. Y. Kariduraganavar (2006), Modification of Tetraethylorthosilicate Crosslinked Poly(vinyl alcohol) Membrane Using Chitosan and Its Application to the Pervaporation Separation of Water–Isopropanol Mixtures, Vol.99, pp 1380-1389.

Q. G. Zhang, Q. L. Liu and J. H. Chen (2007) Dehydration of isopropanol by Novel Poly(vinyl alcohol)-Silicone Hybrid Membranes, Vol. 46, pp 913-920.

www.astdr. Edu. Gov/coxfiles/phy 187.html

Y. T. Lee, K. Iwamoto, H. Sekimoto and M. Seno (1989), Pervaporation of water-dioxane mixtures with poly(dimethyl Siloxane-co-siloxane membranes prepared by sol-gel process, J. Membrane Sci., Vol. 42, pp169-182.

X. P. Wang, N. Li, W. Z. Wang (2001), Pervaporation properties of novel alginate composite membranes for dehydration of organic solvents, *J. Membrane Sci.,* Vol. 193, pp 85-95.

A. M. Sajjan, B.K. Jeevan Kumar, A. A. Kittur and M. Y. Kariduraganavar (2013), Development of novel grafted hybrid

PVA membranes using glycidyltrimethyl ammonium chloride for pervaporation separation of water–isopropanol mixtures, *Journal of Industrial and Engineering Chemistry,* Vol.19 pp 427–437

A.M. Sajjan, B.K. Jeevan Kumar, A.A. Kittur and M.Y. Kariduraganavar (2013), Novel approach for the development of pervaporation membranes using sodium alginate and chitosan-wrapped multiwalled carbon nanotubes for the dehydration of isopropanol, *Journal of Membrane Science* Vol. 425, pp 77–88.

P.S. Rachipudi, A.A. Kittur, A.M. Sajjan, R.R. Kamble and M.Y. Kariduraganavar (2013), Solving the trade-off phenomenon in separation of water–dioxin mixtures by pervaporation through crosslinked sodium–alginate membranes with polystyrene sulfonic acid-co-maleic acid, *Chemical Engineering Science*, Vol. 94 pp 84–92

A. A. Kittur, S. S. Kulkarni, S.M. Tambe and M.Y. Kariduraganavar (2006), Preparation of novel composite membranes for the pervaporation separation of water-acetic acid mixtures, *J. Membrane Science,* Vol. 285, pp 420-431.

S. S. Kulkarni, A. A. Kittur, M. I. Aralaguppi and M. Y. Kariduraganavar (2004), Synthesis and characterization of hybrid membranes using poly(vinyl alcohol) and tetraethylorthosilicate for the pervaporation separation of water-isopropanol mixtures, *J. Appl. Polym. Sci*., Vol. 94, pp 1304-1315.

S. J. Huang, H. K. Lee and W. H. Kang (2005), Preparation and Characterization of proton conductive phosphosilicate Membranes based on Inorganic-organic hybrid materials, *Bull. Korean Chem. Soc*., Vol 26, pp 241-247.

C. Guizard, A. Bac, M. Barboiu (2001), Hybrid organic-inorganic membranes with specific transport properties: Applications in separation and sensors technologies, *Sep. Purif. Technol*., Vol. 25, pp 167-180

L. Cot, A. Ayral, J. Durand (2000), Inorganic membranes and solid state sciences, *Solid state Sci.,* Vol. 2, pp 313-334.

F. Peng, L. Lu, H. Sun (2005), Hybrid Organic-Inorganic Membranes: Solving the Trade-off between Permeability and Selectivity, *Chem. Mater.,* Vol. 17, pp. 6790-6796.

M.Y. Kariduraganavar, A.A. Kittur, S.S. Kulkarni, K. Ramesh (2004), Development of novel pervaporation membranes for the separation of water–isopropanol mixtures using sodium alginate and NaY zeolite, *Journal of Membrane Science,* Vol., 238, pp. 165–175.

P.J. Flory (1953), Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, pp. 509

P.J. Flory, J. Rehner Jr. (1943), Statistical mechanics of cross-linked polymer networks. II. Swelling, *J. Chem. Phys.* Vol..11, pp. 521.

C. Bartels-Caspers, E. Tusel-Langer, R.N. Lichtenthaler (1092), Sorption isotherms of alcohols in zeolite-filled silicone rubber and in PVA composite membranes, *J. Membr. Sci.* Vol. 70, pp 75.

Y.M. Lee, D. Bourgeois, G. Belfort (1989), Sorption, diffusion and pervaporation of organics in polymer membranes, *J. Membr. Sci.* Vol. 44, pp. 161.

I. Cabasso, J. Jagu-Grodzinski, D. Vofsi (1974), A study of permeation of organic solvents through polymeric membranes based on polymeric alloys of polyphosphonates and acetyl cellulose. II. Separation of benzene, cyclohexane and cyclohexene, *J. Appl. Polym. Sci.* Vol.18, pp. 2137.

S.T. Hwang, K. Kammermeyer (1975), Membrane in Separations, *Wiley-Interscience,* New York, 1975

A. Yamasaki, T. Iwatsubo, T. Masuoka, K. Misoguchi (1994), Pervaporation of ethanol/water through a poly(vinyl alcohol)/cyclodextrin (PVA/CD) membranes, *J. Membr. Sci.* Vol. 89, pp 111

S.P. Kusumocahyo, M. Sudoh (1999), Dehydration of acetic acid by pervaporation with charged membranes, *J. Membr. Sci.* Vol. 161 pp 77.

R.Y.M. Huang, C.K. Yeom (1991), Pervaporation separation of aqueous mixtures using crosslinked poly(vinyl alcohol) membrane. III. Permeation of acetic acid–water mixtures, *J. Membr. Sci.* Vol. 58, pp 33.