

Modification of Tetraethylorthosilicate Crosslinked Poly(vinyl alcohol) Membrane Using Chitosan and Its Application to the Pervaporation Separation of Water–Isopropanol Mixtures

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ABSTRACT: Tetraethylorthosilicate crosslinked poly(vinyl alcohol) membrane was modified by varying the amounts of chitosan. The resulting membranes were characterized by Fourier transform infrared spectroscopy and differential scanning calorimetry. The effects of chitosan content and feed composition on the pervaporation performance of the membranes were analyzed. The modified membranes exhibit simultaneous increase of both flux and selectivity. The membrane containing 15 mass % of chitosan shows the highest separation selectivity of 2991, with a flux of 2.39×10^{-2} kg/(m² h) at 30°C for 10 mass % of water in the feed. The total flux and flux of water are almost overlapping each other, manifesting that the membranes could be used effectively to break the azeotropic point of water–isopropanol mixture, so as to remove water from the isopropanol. From the temperature dependent diffusion and permeation values, the Arrhenius activation parameters were

estimated. The activation energy values obtained for water permeation ($E_{p,w}$) are significantly lower than those of isopropanol permeation ($E_{p,IPA}$), suggesting that the membranes developed here have higher separation ability for water–isopropanol system. In addition, difference was negligibly small between the activation energy values of total permeation (E_p) and water permeation ($E_{p,w}$), indicating that coupled transport is minimal because of a higher selective nature of membranes. The E_p and E_D values ranged between 40.92 and 52.60, and 39.58 and 52.47 kJ/mol, respectively. The positive heat of sorption (ΔH_s) values observed in all the membranes suggests that Henry's mode of sorption is predominant. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1380–1389, 2006

Key words: tetraethylorthosilicate; chitosan; pervaporation; selectivity; activation energy; isopropanol

INTRODUCTION

Pervaporation (PV) is a unique among the membrane separation techniques, in which a phase change takes place across the membrane.^{1,2} The removal of a certain liquid is accomplished by the partial pressure difference created on feed and permeate sides of the membrane. The principles of PV can be best understood through explanation of a two-step process³: an evaporation process and a membrane transfer process. In the evaporation process, the temperature of the feed liquid is elevated to the point where a saturated vapor is formed. When the feed enters the apparatus, the saturated vapor comes in contact with the membrane. In the second step process, the vapor diffuses from the feed side to the permeate side across the membrane.

In the process, membrane plays a decisive role, as it functions as a selective barrier for the mixture to be separated. Hence, to meet the needs of the process, various membranes have been prepared and used for the dehydration of alcohols.^{4–13} Among these, the crosslinked poly(vinyl alcohol) (PVA) membranes have been investigated frequently, since hydroxy groups of PVA form strong interaction with water through hydrogen bonding.¹⁴ The crosslinked PVA membranes, supported on poly(acrylonitrile), have been commercialized in 1982 by Gesellschaft Fur Trenntechnik (GFT) mbH, Germany.¹⁵ Since then, numerous attempts have been made to improve the separation capability of the membranes. Among these, insolubilization of PVA by crosslinking with maleic acid, glutaraldehyde, and phenylene diamine has been well documented by many investigators.^{16–20} These membranes yield better PV performances, but still fail to achieve satisfactory results. This may account either for greater degree of crosslinking density or for higher degree of swelling due to less crosslinking density. To circumvent these problems, it is best to establish the inorganic crosslinks between the linear polymer

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chains, since inorganic bonds are known to improve the toughness of the membranes.^{21–23} In doing so, with a minimum degree of crosslinking density, one can retain more number of hydrophilic groups in the polymer chains, so as to improve the overall PV performance. In addition, composites made of organic and inorganic materials have been recognized in various fields^{24,25} as functional materials that have the merits of lightness, pliability, and molding of organic materials, plus the heat-resistance and strength of inorganic materials. As represented by fiber-reinforced plastics, these composites consist of a dispersed phase from the organic and inorganic compounds on the order of micrometer size. Consequently, physical properties of these composites are due to the additivity rule of each component. Recently, the size of the dispersed phase in the order of a nanometer or molecular size has been controlled, and hybrid materials, in which the organic and inorganic components are ideally homogeneous, are being studied in various fields. The hybridization of organic and inorganic components is dependent on the sol-gel method, in which starting materials are in solution from and their syntheses at a low temperature are possible.^{26–29} Thus, it is possible to homogeneously hybridize the organic and inorganic components.

Keeping this in mind, we had prepared different PVA membranes in our previous study by varying the amount of tetraethylorthosilicate (TEOS) using sol-gel method.³⁰ Among these, the membrane containing 1.5 mass % of TEOS exhibited the highest selectivity of 900, with a least flux of 9.2×10^{-3} kg/(m² h). Therefore, in the present study, an effort has been made primarily to enhance the flux of this membrane by suitably interposing chitosan in the membrane matrix in different proportions using the same sol-gel method. The chitosan was selected in view of its significant affinity towards water, good film forming ability, and functional groups that can be easily modified apart from its good mechanical strength and chemical stability.^{31–33} The physical and spectroscopic properties of the derivatized membranes in relation to their structure variations were investigated. The relationship between the structure of the hybrid membranes and their permeation and separation characteristics for the aqueous isopropanol solution during the PV is discussed in detail. From the temperature dependence of the permeation flux and diffusion coefficients, the Arrhenius activation parameters were estimated. These results were discussed in terms of the PV separation ability of the membranes.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) ($\bar{M}_w \sim 125,000$; degree of hydrolysis 86–89%), isopropanol, acetic acid, and hy-

drochloric acid were purchased from S. D. Fine Chemicals Ltd., Mumbai, India. Tetraethylorthosilicate (TEOS) was procured from E. Merck (India) Ltd., Mumbai. Chitosan ($\bar{M}_w \sim 200,000$; N-deacetylation degree 75–85%) was purchased from Sigma-Aldrich Chemicals, USA. All the chemicals were of reagent grade and used without further purification. Double distilled water was used throughout the research work.

Membrane preparation

PVA (4 g) was dissolved in 100 mL of deaerated distilled water at 60°C. To the hot solution, 6 g of TEOS and 1 mL of concentrated HCl as catalyst were added for the sol-gel reaction and the reaction mixture was stirred overnight at the same temperature. The solution was then filtered using a fritted glass disk-filter to remove undissolved residue particles and the solution was left overnight to release the effervescence. The resulting homogenous solution was spread onto a glass plate with the aid of a casting knife in a dust-free atmosphere at room temperature. After being dried for 2–3 days, the membrane was subsequently peeled off and designated as M.

To prepare modified hybrid membranes, a known amount of chitosan, which was dissolved in a minimum amount of 1% acetic acid solution, was added into a solution of above sol-gel reaction. The mixed solution was stirred overnight at room temperature. The rest of the procedure was followed as mentioned earlier. The amount of chitosan with respect to PVA was varied from 5, 10, and 15 mass %, and the membranes thus obtained were designated as M-1, M-2, and M-3, respectively. The dried chitosan-incorporated membranes were in the form of chitosan salt and these were treated with base solution containing 0.1M ammonia in 75% aqueous ethanol. The duration of treatment was 24 h, during which the cationic amine groups ($-\text{NH}_3^+$) were converted into free amine groups ($-\text{NH}_2$). The scheme for protonation and regeneration of chitosan is given in Figure 1. This prevents the solubilization of incorporated chitosan in water. After the treatment, the membranes were rinsed thoroughly in double distilled water with frequent changing to remove residual ammonia. The membranes were then dried in air. The thickness of resulting dry membranes was measured at different points using Peacock dial thickness gauge (Model G, Ozaki MFG. Co. Ltd., Japan) with an accuracy of ± 5 μm and the average thickness was considered for calculation. The thickness of the membranes was found to be 45 ± 5 μm .

Fourier transform infrared spectroscopy

The modification of crosslinked PVA with chitosan was confirmed using a Fourier transform infrared

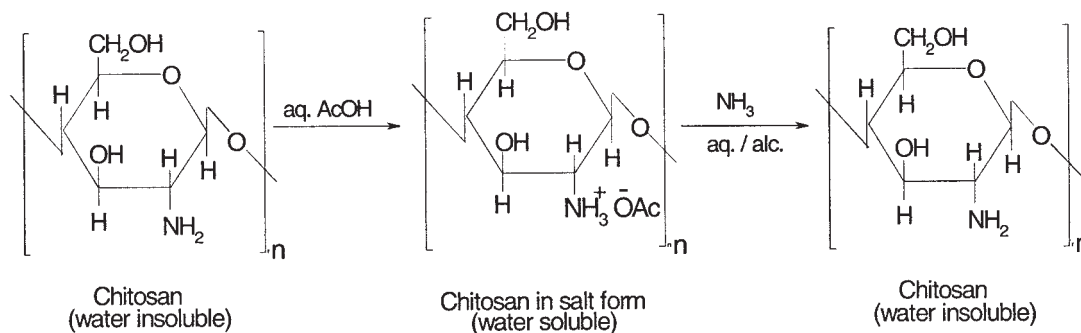


Figure 1 Scheme for protonation and regeneration of chitosan.

(FTIR) spectrometer (Nicolet, Impact-410, USA). Membrane samples were ground well to make KBr pellets under a hydraulic pressure of 400 kg/cm² and the spectra were recorded in the range of 400–4000 cm⁻¹. In each scan, the amount of membrane sample and KBr were kept constant to measure the intensities of characteristic peaks with respect to the amount of chitosan added.

Differential scanning calorimetry

Thermal properties of the membranes were measured using a differential scanning calorimeter (Rheometric Scientific DSC-SP, UK). Sample weights ranged from 5 to 8 mg were heated from ambient temperature to 350°C at a heating rate of 10°C/min. The intercept point of the slopes was taken as the glass transition temperature (T_g). A repeat run, following cooling at 10°C/min, exhibited reproducibility within ± 1.5 for T_g values.

Swelling measurements

The degree of membranes swelling was carried out with different compositions of water–isopropanol mixtures using an electronically controlled oven (WTB Binder, Germany). The masses of the dry membranes were first determined and these were equilibrated by soaking in different compositions of the feed mixture in a sealed vessel at 30°C for 24 h. The swollen membranes were weighed as quickly as possible after careful blotting on a digital microbalance (Mettler B204-S, Toledo, Switzerland) within an accuracy of ± 0.01 mg. All the experiments were performed at least three times and the results were averaged. The percent degree of swelling (DS) was calculated as:

$$DS(\%) = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (1)$$

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

Pervaporation experiments

PV experiments were performed using an indigenously designed apparatus reported in our previous articles.^{30,34} The effective surface area of the membrane in contact with the feed mixture was 34.23 cm² and the capacity of the feed compartment was about 250 cm³. The vacuum in the downstream side of the apparatus was maintained (1.33224×10^3 Pa (10 Torr)) using a two-stage vacuum pump (Toshniwal, Chennai, India). The test membrane was allowed to equilibrate for about 2 h in the feed compartment at the corresponding temperature before performing the PV experiment with fixed compositions of the feed mixture. After attaining a steady state, the experiments were carried out at 30, 40, and 50°C and the permeate was collected in a trap immersed in the liquid nitrogen jar on the downstream side at a fixed time of intervals. The water composition in the feed mixture was varied from 10 to 50 mass %. The flux was calculated by weighing the permeate on a digital microbalance. The compositions of water and isopropanol were estimated by measuring the refractive index of the permeate within an accuracy of ± 0.0001 units using an Abbe's refractometer (Atago-3T, Japan) and by comparing it with a standard graph that was established with the known compositions of water–isopropanol mixtures. All the experiments were performed at least three times, and the results were averaged. The results of permeation for water–isopropanol mixtures during the PV were reproducible within admissible range.

From the PV data, separation performance of the membranes was assessed in terms of total flux (J), separation selectivity (α_{sep}), and pervaporation separation index (PSI). These were calculated respectively using the following equations:

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

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

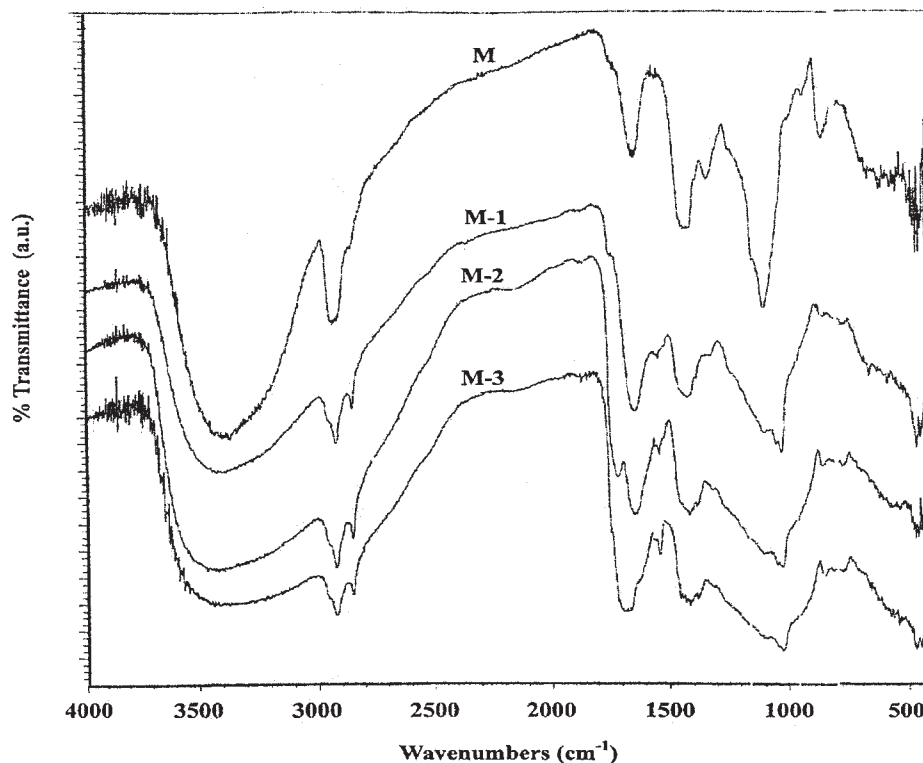


Figure 2 FTIR spectra of TEOS crosslinked PVA and its modified membranes: (M) 0 mass %; (M-1) 5 mass %; (M-2) 10 mass %; and (M-3) 15 mass % of chitosan.

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

where W is the mass of permeate (kg); A , the effective area of the membrane (m^2); t , the permeation time (h); P_w and P_{IPA} are the mass percent of water and isopropanol in the permeate, respectively. F_w and F_{IPA} are the respective mass percent of water and isopropanol in the feed.

RESULTS AND DISCUSSION

Membrane characterization

FTIR studies

Figure 2 illustrates the FTIR spectra of TEOS crosslinked PVA membrane and its modified membranes. A characteristic strong and broad band appeared at around 3400 cm^{-1} and multiple bands appeared between 1000 and 1100 cm^{-1} in TEOS crosslinked PVA membrane (M) are respectively assigned to —OH stretching vibrations of hydroxyl groups and Si—O—C bonds formed between PVA and TEOS. All these peaks match with those reported by Kariduraganavar et al.³⁴ and Robertson and Mauritz.³⁵ The intensity of —OH band decreased marginally while broadening from membrane M to M-3 by the incorporation of chitosan and increasing its mass in the membrane matrix. Although it is unusual when

a large number of —OH groups introduced into membrane matrix, but this expected due to reduction of free —OH groups in the matrix owing to the formation of intermolecular hydrogen bonding.³⁶ Similarly, the intensity of multiple bands corresponds to Si—O—C bands, decreased systematically from membrane M to M-3 by the incorporation of chitosan and increasing its mass. This is simply because of a reduction of Si—O—C bands character by increasing the amount of chitosan in the membrane matrix. Further, a prominent peak was noticed at around 1550 cm^{-1} in the chitosan-incorporated membranes, and is assigned to NH_2 deformation absorption band of chitosan. Generally, NH_2 deformation absorption band appears at around 1650 cm^{-1} , but in the present study, a shift towards lower frequency is attributed to hydrogen bonding effect.³⁷ All these are clearly evident to the incorporation of chitosan in the network of crosslinked PVA membrane.

Glass transition temperature

Figure 3 shows the effect of chitosan contents on the T_g of TEOS crosslinked PVA membrane. Generally, mixing of two or more polymers gives different T_g values due to noncompatibility. This occurs when the polymers have low combinatorial entropy of mixing. However, in the present study, it is observed that there is

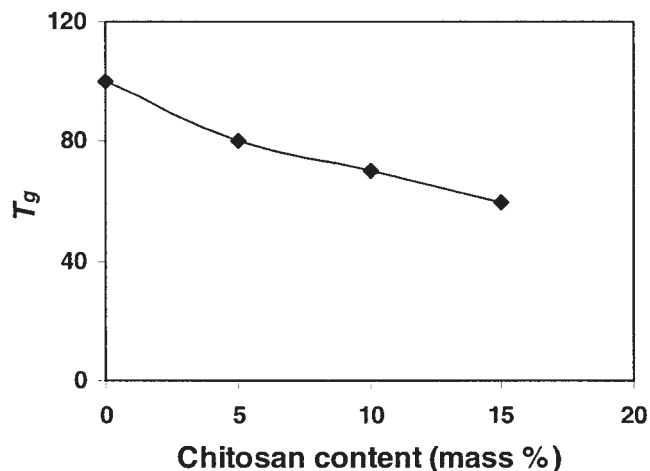


Figure 3 Effect of chitosan on glass transition temperatures.

only one T_g for each membrane even though membrane is made by mixing of chitosan and crosslinked PVA. This may be due to the formation of intermolecular hydrogen bonding interaction. This is in good agreement with the FTIR results. On other hand, the T_g of the membranes did not increase with increasing chitosan content, but decreased marginally from membrane M to M-3. This is expected, since chitosan is known to be soft segmental molecule.

Effects of feed composition and chitosan content on membrane swelling

Sorption mechanism is an important factor for membrane swelling in PV process, as it controls the transport of permeating molecules under the chemical potential gradient. Therefore, to study the effects of feed composition and chitosan content on membrane swelling, the percent degree of swelling was plotted with respect to different mass percent of water in the feed at 30°C as shown in Figure 4. It is noticed that the degree of swelling increased almost linearly for all the membranes with increasing mass percent of water in the feed. This is due to an increase of strong interaction between water molecules and the membrane containing $-\text{NH}_2$ and $-\text{OH}$ groups. However, the degree of swelling becomes more predominant for the membrane containing the highest amount of chitosan (M-3), signifying that higher the amount of chitosan greater will be the degree of interaction with the water molecules than those of alcohols. On the other hand, chitosan-incorporated membranes showed greater degree of swelling at all water compositions when compared with TEOS crosslinked membrane. This is mainly attributed to the introduction of $-\text{NH}_2$ groups and increase of $-\text{OH}$ groups on the membrane matrix by the incorporation of chitosan. These are responsible

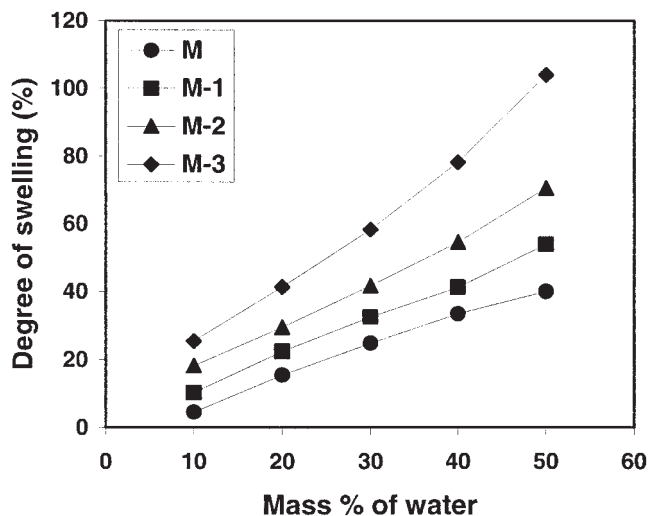


Figure 4 Variation of degree of swelling with different mass percent of water in the feed at 30°C for crosslinked and its modified membranes.

for further increase of interaction with the selective permeants, resulting to preferential sorption of water.

Effects of feed composition and chitosan content on PV properties

Figure 5 shows the effect of feed composition on the total permeation flux for all the membranes at 30°C. It is observed that the total permeation flux increased for all the membranes with respect to mass percent of water in the feed and this is in accordance with the results observed in the swelling study. However, the increase was significant at higher concentration of wa-

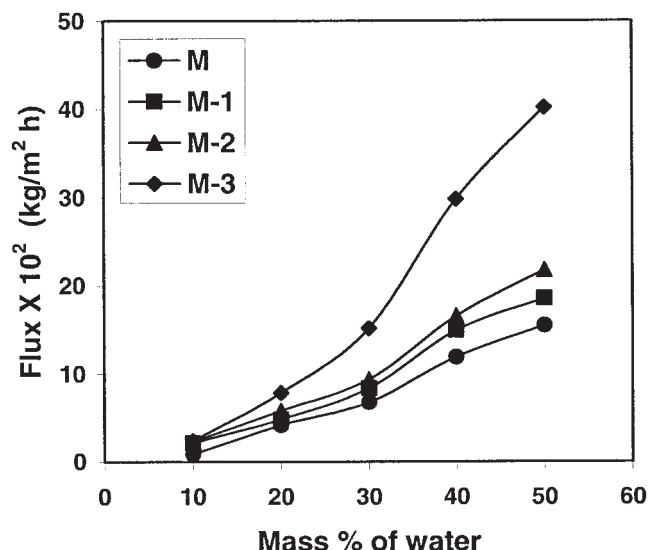


Figure 5 Variation of total PV flux with different mass percent of water in the feed at 30°C for crosslinked PVA and its modified membranes.

ter particularly for membrane M-3, which possesses the highest amount of chitosan. This is mainly because of the introduction of —NH_2 groups and further increase of —OH groups by the incorporation of chitosan. These are highly influenced for greater interaction between the membrane and water molecules at higher concentration of water in the feed. On the other hand, the permeation flux increased from membrane M to M-3 at all investigated water compositions by the incorporation of chitosan and increasing its mass in the membrane matrix. This is because of increased interaction between the membrane and selective permeants.

The efficiency of the membranes in PV process is generally assessed based on the permeation of individual components. Therefore, the extent of permeation of individual components was determined by plotting the total flux, and fluxes of water and isopropanol as a function of chitosan content in the membrane for 10 mass % of water in the feed as shown in Figure 6. From the plot, it is clearly noticed that the total flux and flux of water are almost overlapping each other and thereby, the flux of isopropanol is negligibly small for all the membranes, suggesting that the membranes developed in the present study by the incorporation of chitosan are highly selective towards water with a tremendous improvement in the flux when compared with TEOS crosslinked PVA membrane.

In PV process, the overall selectivity of a membrane is generally explained on the basis of interaction between the membrane and permeating molecules, molecular size of the permeating species, and the pore diameter of the membrane.^{2,34} Figure 7 displays the effect of water composition on the selectivity for all the

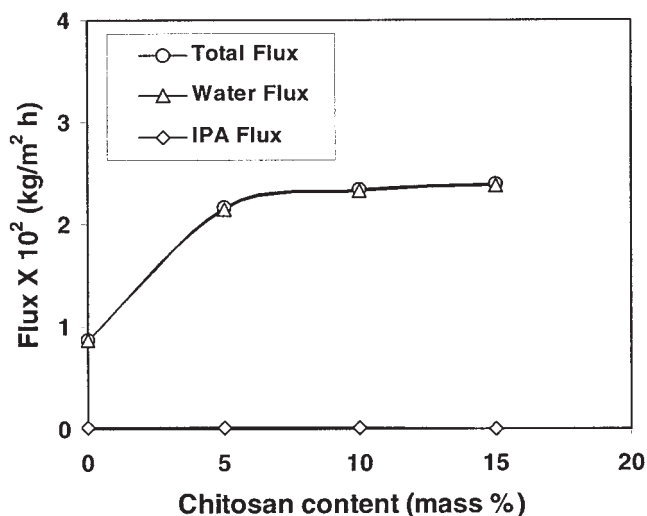


Figure 6 Variation of total flux, and fluxes of water and isopropanol with different mass percent of chitosan at 30°C for 10 mass % of water in the feed.

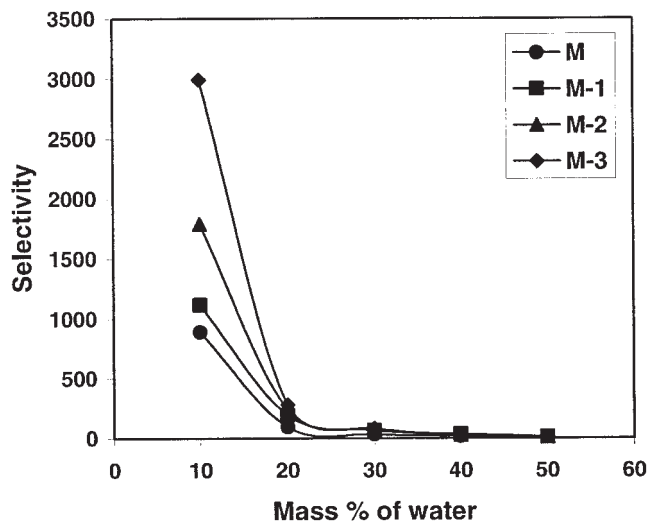


Figure 7 Variation of separation selectivity with different mass percent of water in the feed at 30°C for crosslinked PVA and its modified membranes.

membranes. It is observed that the selectivity of all the membranes decreased drastically from 10 to 20 mass % of water in the feed and then, it was decreased gradually with further increasing the water concentration. At higher concentration of water in the feed, the membranes swell greatly because of the formation of a strong interaction between the membrane and water molecules, while suppressing the interaction within the membrane material (i.e., between chitosan and TEOS crosslinked PVA). As a result, selectivity decreases drastically at higher concentration of water in the feed, irrespective of the amount of the chitosan in the membrane matrix.

On the contrary, the selectivity increased significantly from membrane M to M-3 upon increasing the chitosan content in the membrane matrix. This is due to a greater molecular interaction occurring between the interactive groups of crosslinked PVA and incorporated chitosan, and increased hydrophilic character of the membrane. These are together responsible for the increased selective interaction between the membrane and water molecules. This can be clearly observed from Figure 8, showing the variation of flux and selectivity as a function of chitosan content in the membrane at 10 mass % of water in the feed. Generally, with increasing density of the membrane either by increasing the crosslinking density or by incorporating the another polymer in the membrane matrix, the permeation flux decreases and selectivity increases.^{38,39} However, in the present study, both the permeation flux and selectivity increased simultaneously with increasing chitosan content in the membrane. Although this is in contrast to the trade-off phenomenon existing between flux and selectivity in PV experiment, a significant enhancement of hydro-

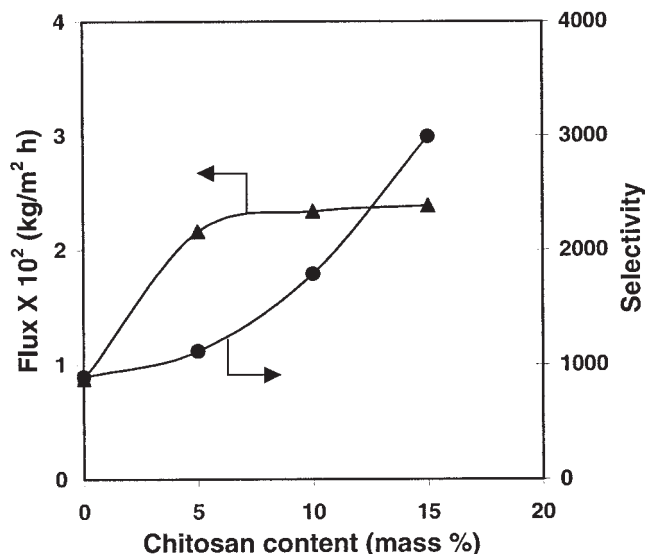


Figure 8 Variation of flux and selectivity with different mass percent of chitosan at 30°C for 10 mass % of water in the feed.

philicity and selective adsorption overcome the situation by the incorporation of chitosan in the membrane matrix.^{2,40}

Calculated results of water and isopropanol fluxes measured at 30°C for all the membranes at different composition of the feed mixture are presented in Table I. It is observed that there is a systematic increase of water flux with increasing chitosan content and water composition in the feed. The flux values of isopropanol increased with increasing water composition in the feed, but these values did not show systematic effect on the chitosan content. This is possibly because of error encountered while measuring meager amount of permeated isopropanol, otherwise, these values would have been decreased with increasing chitosan content. Therefore, it is manifested that water influences greater interaction with the membrane than that of chitosan. Secondly, increase of chitosan content in the membrane matrix leads to increase the intermolecular interactions between chitosan and crosslinked PVA membrane.

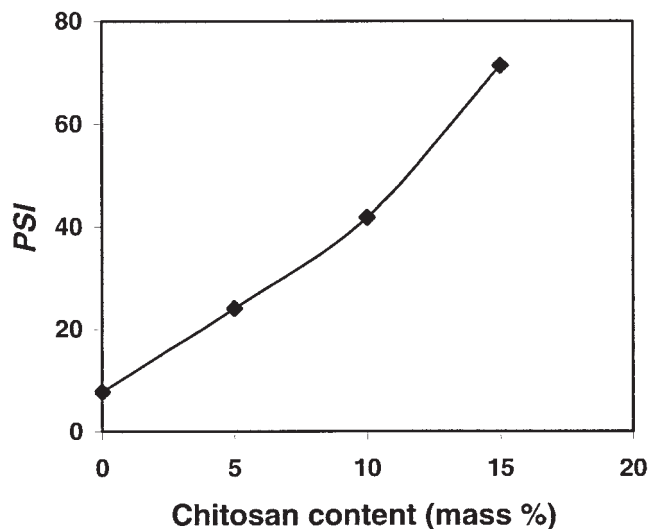


Figure 9 Variation of PSI with different mass percent of chitosan at 30°C for 10 mass % of water in the feed.

Effect of chitosan content on PSI

Figure 9 shows the effect of chitosan content on the PSI for 10 mass % of water in the feed at 30°C. It is observed that the PSI values increased almost linearly with increasing chitosan content in the membrane, signifying that the membranes incorporated with higher amount of chitosan showed an excellent performance for the separation of isopropanol mixtures. This is because the incorporation of chitosan into a membrane matrix not only enhanced membranes' hydrophilicity, but also enhanced the intermolecular hydrogen bonding interaction within the membrane. These are together responsible for the significant performance in the present study.

Diffusion coefficient

Mass transport of a binary liquid mixture through a nonporous polymer membrane in PV process is generally described by the solution-diffusion mechanism, which occurs in three steps: sorption, diffusion, and evaporation.⁴¹ Thus, the selectivity and permeation

TABLE I
Pervaporation Flux Data for Water and Isopropanol for Different Membranes at 30°C for Different Mass Percent of Water in the Feed Mixture

Mass percent of water	$J_w \times 10^2$ (kg/(m ² h))				$J_{IPA} \times 10^3$ (kg/(m ² h))			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
10	0.87	2.14	2.33	2.38	0.09	0.17	0.12	0.07
20	4.01	4.74	5.72	7.75	1.67	0.97	0.93	1.10
30	6.34	8.07	9.10	14.78	4.41	2.84	2.82	4.10
40	11.03	14.35	15.74	28.41	8.94	5.98	8.29	14.30
50	14.19	17.19	20.24	37.41	13.2	14.10	15.90	28.20

TABLE II
Diffusion Coefficient of Water and Isopropanol for Different Membranes Calculated at 30°C from eq. (6) for Different Mass Percent of Water in the Feed

Mass percent of water	$D_w \times 10^8$ (m ² /s)				$D_{IPA} \times 10^9$ (m ² /s)			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
10	1.73	4.31	4.69	4.80	0.07	0.13	0.09	0.05
20	4.04	4.78	5.78	7.85	1.40	0.81	0.78	0.92
30	4.26	5.43	6.13	10.00	4.21	2.71	2.69	3.91
40	5.54	7.22	7.92	14.40	9.96	6.66	9.22	16.00
50	5.70	6.93	8.15	15.20	17.60	18.90	21.30	37.60

rates are governed by the solubility and diffusivity of each component of the feed mixture to be separated. In PV process, because of establishing the fast equilibrium distribution between the bulk feed and the upstream surface of a membrane,^{42,43} diffusion step controls the migration of penetrants. Therefore, it is important to estimate the diffusion coefficient, D_i , of penetrating molecules to understand the mechanism of molecular transport.

From the Fick's law of diffusion, the diffusion flux can be expressed as⁴⁴:

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

where J is the permeation flux per unit area (kg/(m² s)), D is the diffusion coefficient (m²/s), C is the concentration of the permeant (kg/m³), subscript i stands for water or isopropanol, 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 equation⁴⁵:

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

where δ is the membrane thickness. The calculated values of D_i at 30°C are presented in the Table II. It is noticed that diffusion coefficients of water as well as isopropanol behaved as similar to PV results given in Table I. However, there is a considerable increase in diffusion coefficients for all the membranes in both the

cases with increasing the amount of water in the feed. This is expected because of a considerable deterioration of membrane selectivity as discussed in PV study for establishing a strong interaction between the water molecules and membrane.

Effect of temperature on membrane performances

Effect of operating temperature on the PV performance for water–isopropanol mixtures has been studied for all the membranes at 10 mass % of water in the feed, and the resulting values are presented in Table III. It is observed that the permeation rate was found to increase from 30 to 50°C for all the membranes, while decreasing the separation factor remarkably. This is because high temperature not only decreases the intermolecular interaction between permeants, but also decreases within the membrane material, resulting to increase free —OH and —NH₂ groups on the membrane. These are responsible for predominating the plasticizing effect on the membrane due to greater swelling. Therefore, the permeation of diffusing molecules and the associated molecules through the membrane becomes easier, leading to an increase of total permeation flux, while suppressing the selectivity.

The temperature dependence of the permeation and diffusion rates can be expressed by the Arrhenius-type equation⁴⁶:

$$X = X_0 \exp\left(\frac{-E_x}{RT}\right) \quad (7)$$

where X represents permeation (J) or diffusion (D), X_0 is a constant representing pre-exponential factor of J_0

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

Temperature (°C)	$J_p \times 10^2$ (kg/(m ² h))				α_{sep}			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
30	0.87	2.16	2.34	2.39	891	1116	1791	2991
40	2.14	4.23	4.95	6.19	141	171	216	441
50	2.37	6.59	7.55	8.63	120	130	141	248

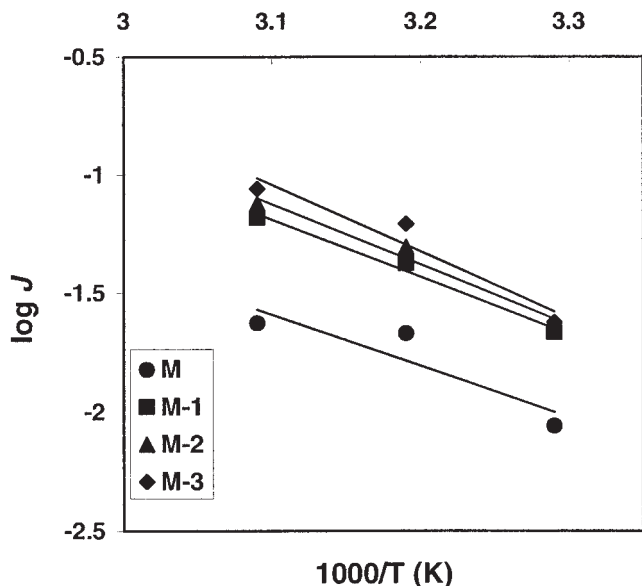


Figure 10 Variation of $\log J$ with temperature for 10 mass % of water in the feed.

or D , E_x represents activation energy for permeation or diffusion depending on the transport process under consideration, and RT is the usual energy term. With increasing feed temperature, the vapor pressure in the feed compartment increases, but the vapor pressure at the permeate side is not affected. These result in an increase of driving force with increasing temperature.

Arrhenius plots are shown in Figures 10 and 11 for the temperature dependence of total permeation flux and diffusion, respectively. From least-squares fits of these linear plots, the activation energies for total permeation (E_p) and diffusion (E_D) were estimated. Sim-

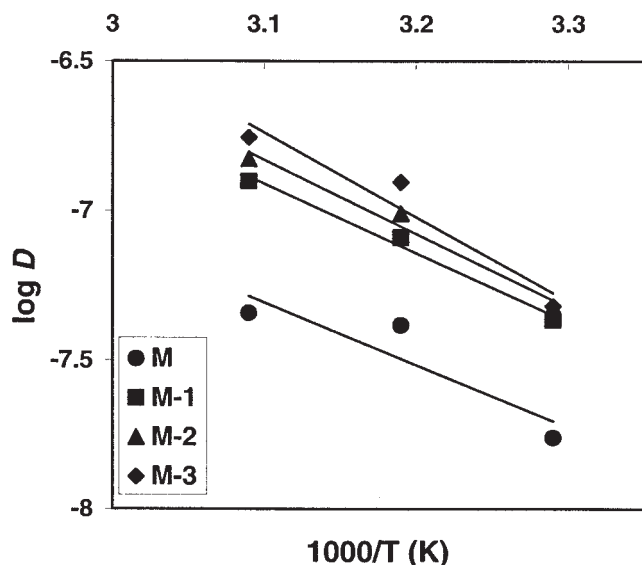


Figure 11 Variation of $\log D$ with temperature for 10 mass % of water in the feed.

TABLE IV
Arrhenius Activation Parameters for Permeation, Diffusion, and Heat of Sorption for Water

Parameters (kJ/mol)	M	M-1	M-2	M-3
E_p	40.92	45.50	47.89	52.60
E_D	39.58	44.66	47.23	52.47
E_{pw}	38.36	43.08	45.57	51.27
E_{pIPA}	120.91	131.40	149.73	153.49
ΔH_s	1.34	0.84	0.66	0.13

ilarly, we have estimated the activation energies for permeation of water (E_{pw}) and isopropanol (E_{pIPA}), but the plots are not given to avoid the crowding. The values thus obtained are presented in Table IV.

From the Table IV it is observed that the activation energy values for water permeation (E_{pw}) are 2–3 times lower than those of isopropanol permeation (E_{pIPA}), suggesting that membranes are highly selective towards water. Further, it is observed that the activation energy values for total permeation (E_p) and water permeation (E_{pw}) are almost close to each other for all the membranes, signifying that coupled transport (water and IPA) is minimal as due to higher separation efficiency. The E_p and E_D values ranged between 40.92 and 52.60 kJ/mol, and 39.58 and 52.47 kJ/mol, respectively. Using these values, we have calculated the heat of sorption as:

$$\Delta H_s = E_p - E_D \quad (8)$$

The resulting ΔH_s values are included in Table IV. The ΔH_s values give the additional information about the transport of molecules through the polymer matrix. It is a composite parameter involving contributions of both Henry's and Langmuir's type of sorption.⁴⁷ The 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, the 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 positive for all the membranes, suggesting that Henry's sorption is predominant, giving an endothermic contribution.

CONCLUSIONS

In this study, we have modified TEOS crosslinked PVA membrane by varying the amount of chitosan. The membranes were subjected to separate the water-isopropanol mixtures. The modified membranes have shown the best and most stable PV separation characteristics. An increase of chitosan content in the mem-

brane matrix results the simultaneous increase of both permeation flux and selectivity. This was explained on the basis of a selective adsorption and significant enhancement of hydrophilicity of the membrane matrix. The PV separation index data also indicate that membranes incorporated with higher amount of chitosan showed an excellent performance while separating water-isopropanol mixture. This is because of increased hydrophilicity and intermolecular hydrogen bonding interaction within the membrane. The membrane containing 15 mass % of chitosan shows the highest separation selectivity of 2991 and a flux of 2.39×10^{-2} kg/(m² h) at 30°C for 10 mass % of water in the feed. Experimental data also reveal that the total flux and flux of water are almost overlapping each other for all the modified membranes in the investigated range of water composition, suggesting that the developed membranes are highly water selective, and this is in accordance with diffusion data. Temperature effect study shows the increase in permeation flux and decrease in selectivity with increase in temperature. This is because of predominating the plasticizing effect, when the interactions become weaker at higher temperature between the permeants, and permeants and membrane. The membranes show significant lower activation energy values for water permeation (E_{pw}) than that of isopropanol permeation (E_{pIPA}), suggesting that modified membranes have significantly higher separation efficiency. The estimated E_p and E_D values ranged between 40.92 and 52.60 kJ/mol, and 39.58 and 52.47 kJ/mol, respectively. All these membranes exhibit positive ΔH_s values, indicating that sorption is mainly dominated by the Henry's mode of sorption, giving an endothermic contribution.

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