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Dehydration of 1,4-dioxane by pervaporation using crosslinked calcium alginate-chitosan blend membranes

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Summary

Sodium alginate (SA) and chitosan (CS) blended membranes were crosslinked with maleic anhydride (MA) for the separation of 1,4-dioxane/water mixtures at 30°C by pervaporation (PV). The membranes were characterized by Fourier transform infrared (FTIR) analysis and Ion Exchange Capacity (IEC) to verify the crosslinking. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) pattern were used to observe the thermal degradation and crystalline nature of the membrane respectively. The membrane performance was studied by calculating flux, selectivity, and pervaporation separation index. Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of the membranes in pure liquids as well as in binary mixtures. The effects of experimental parameters such as feed composition, membrane thickness, and permeate pressure on separation performance of the crosslinked membranes were determined. The experimental result suggested that the membrane has a good potential for breaking the aqueous azeotrope 1,4-dioxane.

Introduction

In the recent years pervaporation (PV) is rapidly emerging as an economical and a simple alternative to conventional energy-intensive technologies for separating azeotropes [1], close boiling liquids [2], isomers or temperature-sensitive liquid mixtures [3]. Unlike distillation process, the separation mechanism in PV is not based on relative volatility of the components, but on the difference in sorption and diffusion properties of the feed components as well as permselectivity of the membrane. Since the existence of PV technique for more than three decades, a number of different types of hydrophilic and hydrophobic membranes have been developed for the PV separation of binary mixtures [4]. One of the useful industrial applications of PV separation has been the dehydration of organic mixtures [5-7]. Such separations usually employ water-selective membranes.

1,4-Dioxane is miscible with water in all proportions. It forms an azeotrope at 18 wt.% concentration of water and hence, dehydration of 1,4-dioxane greater than 99%

purity is a formidable task if one chooses to apply distillation. Hydrophilic groups absorb water molecules preferentially, which leads to both high flux and high separation factors. Natural anionic and cationic polysaccharides SA and CS respectively, have been used extensively to synthesize membranes for PV separation studies due to their abundant availability, biocompatibility, biodegradability and commercial viability. SA is highly soluble in water and available in marine algae and seaweeds. It has good membrane forming properties with other polymers in addition to good chemical resistance and high permselectivity to water. However, very high hydrophilicity of carboxylic and hydroxyl groups present in SA renders the membrane unstable in aqueous solution during PV. It is pointed out that alginic acid membrane is not strong to operate in the 50% 1,4-dioxane. Water solubility and mechanical weakness of alginic acid membrane has been a drawback in its possible use as a PV material inspite of its excellent permselectivity for water. To improve the mechanical stability of membrane, SA needs to be blended with other polymer. CS, is the deacetylated product of chitin, which is the second most abundant biopolymer in the nature next to cellulose. CS has amino and hydroxyl groups that can participate in interaction resulting in high permselectivity for water. Chitosan has been proven to have good film forming properties with mechanical and chemical resistance.

A search of the literature indicated that several studies are reported on dehydration of 1,4-dioxane by PV and use of crosslinked alginate-CS membranes. Rao et al. [8] studied dehydration of 1,4-dioxane using poly(vinyl alcohol)/polyethyleneimine blend membranes. Glutaraldehyde crosslinked based membranes were widely used for dehydration of 1,4-dioxane [9-13]. Aminabhavi et al. [14] studied the PV dehydration of 1,4-dioxane using alginate and poly(vinyl alcohol) blended alginate membranes. In the present investigation, the authors developed novel membranes by blending alginate with chitosan followed by crosslinking with maleic anhydride.

Experimental

Materials

SA, CS having an average molecular weight of 500,000 and 300,000, respectively, were purchased from Aldrich Chemical Co., USA. 1,4-dioxane of purity 99.9% was purchased from S.D. Fine Chemicals, Mumbai. Isopropanol, maleic anhydride and calcium chloride were purchased from Loba Chemicals, Mumbai. Double distilled water of conductivity <0.02 S/cm was used through out the experiment work.

Membrane preparation and crosslinking

Membranes were prepared by solution casting and solvent evaporation technique. SA and CS solutions of 2 wt.% were prepared by dissolving SA and CS in 2% oxalic acid. The suspensions were stirred for 2 hrs at 40-50°C. The solutions were allowed to stay over night before use to enable the gas bubbles to escape. The casting solution was prepared by mixing together the SA and CS solutions with 1:3 ratio respectively. The blend solution was then stirred for a period of 1/2 hr for homogeneity and kept aside for 1 hr to obtain a bubble free solution. The homogeneous solution was cast on to a clean glass plate and allowed to evaporate water to dryness in atmosphere at room temperature resulting in the formation of dense non-porous blend membrane. The

SA/CS blended membranes were pretreated with 2 % CaCl$_2$ solution for 24 hrs at room temperature in order to improve its properties by replacing sodium ions by calcium ions [15]. The resulting calcium alginate-chitosan membranes (CA/CS) were washed with distilled water to remove excess calcium. CA/CS was further crosslinked with 3.5 wt.% MA in a isopropanol-water (90/10 vol.%) bath containing 1 vol.% of concentrated H$_2$SO$_4$ as catalyst for 3hrs. After removing the membranes from the crosslinking bath, the membranes were washed with water repeatedly and dried in an oven at 80°C and labeled as M-CA/CS. The membranes were prepared by varying volumes of the blend solution of same composition. The average thickness of the each membrane was measured by a micrometer screw gauge.

Pervaporation and analytical procedure

PV Experiments were carried out following the procedure described in the earlier literature [13, 16]. The indigenously constructed pervaporation manifold was operated at a vacuum as low as 0.5 mmHg in the permeate line. The effective area of the membrane in contact with the feed stream was 19.6 cm^2. The feed consisting of 1,4-dioxane and water was stirred vigorously with a speed of 150 rpm during experiments to minimize concentration polarization. Permeate was condensed and collected in a liquid nitrogen cold trap for 6 hrs. Tests were carried out at room temperature (30±2°C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed in a Sartorius electronic balance with an accuracy of 10^{-4} g to determine the flux. Analysis of permeate composition was carried out by measuring the refractive index of the mixture with an accuracy of ±0.001 units, using a Abbe Refractometer (Advance Research Instruments Company, New Delhi, India). A calibration plot of refractive index versus percent composition of water-1,4-dioxane was obtained with the known quantities of mixture components.

Flux and selectivity equations

The flux J of a given species, say faster permeating component i of a binary liquid mixture comprising of i (water) and j (1,4-dioxane) is given by:

$$J_i = W_i / A_t \tag{1}$$

where *Wi* represents the mass of water in permeate (kg), A is the membrane area (m^2) and t represents the evaluation time (hr). In the present study, even though membranes of different thickness were fabricated, the flux was normalized and reported for the constant thickness of 10 µm. The membrane selectivity (α) is the ratio of permeable coefficients of water and 1,4-dioxane and can be calculated from their respective concentrations in feed (x) and permeate (y) as given below:

$$\alpha = y(1-x)/x(1-y) \tag{2}$$

Pervaporation separation index (*PSI*), which is a measure of the separation capability of a membrane, is expressed as a product of selectivity (α) and flux (J),

$$PSI = J\alpha \tag{3}$$

Membrane characterization

Both SA/CS and M-CA/CS membranes were characterized by FTIR, XRD and TGA. The FTIR spectrum was scanned using Thermonicolet FTIR-200 series spectrometer. A Seifert X-ray diffractometer was used to study the solid state morphology of SA/CS and M-CA/CS in powdered form. X-rays of 1.546^{o}A wavelength were generated by a Cu K_{α} source. The angle of diffraction was varied from 5° to 60° to identify the change in the crystal structure and intermolecular distances between the intersegmental chains after crosslinking. The *d*-spacing value can be calculated from the Braggs equation:

$$2d \sin \theta = \lambda \qquad (4)$$

where *d* is effective *d*-spacing; θ is angle of contact/diffraction; λ is wavelength. Thermal stability of the polymer films was examined, using Seiko 220TG/DTA analyzer, from 30 to 600°C at a heating rate of 10°C/min with continuous flushing with pure nitrogen gas at 200 ml/min. The samples were subjected to TGA to determine the thermal stability and decomposition characteristics.

Sorption studies

In order to evaluate membrane-liquid affinities, a weighed samples of circular pieces of the polymer films (3 cm diameter) were soaked in 1,4-dioxane/water mixtures of various concentrations. The swollen samples were taken out after different soaking periods and quickly weighed after carefully wiping out excess liquid to estimate the amount absorbed at the particular time *t*. The film was then quickly placed back in the solvent. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. Degree of swelling (DS) was calculated from the equation:

$$DS = M_s / M_d \qquad (5)$$

where M_s was the mass of the swollen polymer and M_d was the mass of the dry polymer in grams. The percentage sorption is obtained from the equation:

$$\% \, Sorption = (M_s - M_d)100 / M_d \qquad (6)$$

Determination of the ion exchange capacity

Ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1 gram of the dry polymer. The degree of substitution indicates the average number of acid groups present in the polymer. To determine the degree of substitution by acid groups, M-CA/CS and SA/CS specimens of similar weight were soaked in 50ml of 0.01N Sodium hydroxide solution for 12 hr at ambient temperature. Then, 10ml of the solution was titrated with 0.01N sulfuric acid. The membrane was regenerated with 1M hydrochloric acid, washed with water till is free from acid and dried to a constant weight. The IEC was calculated according to the equation,

$$IEC = (B - P)(0.01 * 5) / m \qquad (7)$$

where *B* was the amount of sulfuric acid used to neutralize blank sample soaked in NaOH (ml), *P* was the amount of sulfuric acid used to neutralize the sulfonated membrane soaked in NaOH (ml), 0.01 was the normality of the sulfuric acid, '5' was

the factor corresponding to the ratio of the volume of NaOH used to soak the polymer to the volume taken for titration, and m was the sample mass (grams).

Results and discussion

Alginate polymer contains D-mannuronic acid and L-guluronic acid. D-mannuronic acid exists in 1C conformation and is connected in the β-configuration through the 1- and 4- positions and L-guluronic acid has the 1C conformation and is α-1, 4- linked in the polymer [17]. Because of the particular shapes of the monomers and their modes of linkage in the polymer, the geometries of the G-block regions, M-block regions, and alternating regions are substantially different. Specifically, the G-blocks are buckled while the M-blocks have a shape referred to as an extended ribbon. If two G-block regions are aligned side by side, a diamond shaped hole results. This hole has dimensions that are ideal for the cooperative binding of calcium ions. When calcium ions are added to a sodium alginate solution, such an alignment of the G-blocks occurs; the calcium ions are bound between the two chains like eggs in an egg box [18]. Roger et al. [19] reported the complete conversion of sodium alginate in to calcium alginate in about 10 min after addition of sodium alginate to calcium chloride solution. The sodium alginate-chitosan (SA/CS) membrane was converted into calcium alginate-chitosan (CA/SA) membrane on treatment with calcium chloride. The CA/CS membrane was further crosslinked with maleic anhydride (MA).

A model of the possible interaction is shown in Scheme 1, which represents the formation of ionic complex between cationic group (–NH$_3^+$C) of chitosan polymer and anionic group (–COO−) of alginate polymer. Further the addition of MA induces covalent crosslinking and results in formation of H-bonding in addition to electrostatic interactions. It was noticed that the M-CA/CS blends were optically clear to the naked eye. No separation into two layers or any precipitation was noticed when allowed to stand for one month at room temperature. An estimation of the number of groups present before and after crosslinking gives an idea of the extent of crosslinking.
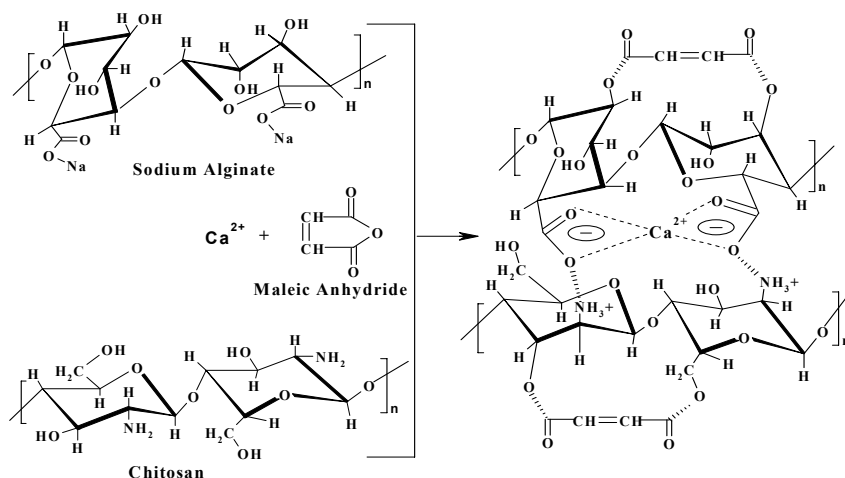
Scheme 1. Structural representation of sodium alginate/chitosan blended membrane pre-treated with calcium chloride and crosslinked with maleic anhydride

Membrane characterization

Ion exchange capacity (IEC)
The amount of residual hydroxyl and acetyl groups in blend membranes after crosslinking was estimated from IEC studies. It was found that SA/CS blend had an IEC of 3.82 mequiv./g, whereas MA crosslinked polymer exhibited an IEC of 1.84 mequiv./g. The IEC results showed that almost 50% of hydroxyl groups present in the unmodified SA/CS have now formed cross links with MA. The IEC, which is equivalent to the total number of acetyl and hydroxyl groups present in the membrane, decreased upon crosslinking because some hydroxyl groups and acetyl groups were consumed during the reaction [16]. A model of the possible interaction shown in Scheme 1 represents the crosslinking reaction occurring between SA/CS blend, Ca^{2+} and MA. To the best of our knowledge, it is the first kind of study wherein the combination of Ca^{2+} and MA was employed as a crosslinking agent. The membrane could withstand the solvent environment and pervaporation conditions employed in this study.

FTIR studies
The FTIR spectrum of SA/CS (Figure 1(a)) shows the characteristic absorption band at 3610 cm^{-1} (broad signal of –OH and –NH-) and the broad band appearing at 1827 cm^{-1} confirms the presence of $-NH_3^+C$ group in the SA/CS membrane. The other bands at 1671 cm^{-1} (amide), 1485 cm^{-1} (carboxylate), 1365 cm^{-1} (-CH$_2$ bending), 1202 cm^{-1} (-COO$^-$ group), 1183 cm^{-1} (C-C stretching) and 907 cm^{-1} (skeletal vibrations involving the C-O stretching) are the characteristics of SA/CS blend membrane structure [20]. The spectrum confirms the complexation between the dissociated carboxylate groups of SA (COO$^-$) and protonated amino groups from CS through electrostatic interaction. Moreover, as the polyion complex formation proceeds, the O–H bonding would also be expected because of an increase in intermolecular interaction such as hydrogen bonding between SA and CS. In addition to the peaks observed in the spectrum of SA/CS membrane, the FTIR spectrum of M-CA/CS (Figure 1(b)) exhibits an

absorbance band at 2215 cm^{-1}. This is the characteristic band of $-C-\overset{\overset{\text{O}}{\|}}{C}-O-$, indicating the presence of maleic anhydride in the membrane. The presence of calcium was confirmed by calcium elemental test. The model structure proposed in Scheme 1 was well in accordance with the FTIR spectra.
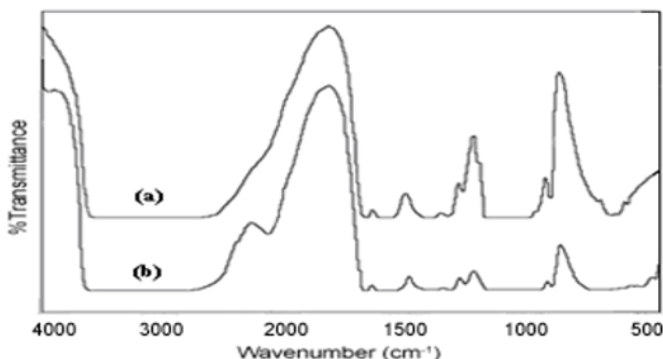

Figure 1. FTIR spectra of (a) SA/CS and (b) M-CA/CS blend membranes

XRD studies

X-ray diffraction studies provide information on the nature of the compound as well as on the spacing between the clusters of the polymer chains. On crosslinking, the polymer chains are in close compaction with one another and thus a reduction in the cluster space may be encountered. The effective *d*-spacing (*d*) gives an indication of cluster space existing in the polymer before and after crosslinking. The X-ray diffractograms of SA/CS and M-CA/CS blend membranes, shown in Figure 4, have no sharp peaks indicating the amorphous nature of the membranes. The XRD spectra of the SA/CS (Figure 2(a)) exhibits a broad peak at $2\theta = 20^{\circ}$, which may be due to the intermolecular interaction such as the formation of hydrogen bonding between SA and CS [21]. M-CA/CS membrane appears to be more amorphous than SA/CS as its diffraction pattern has no peak. On crosslinking the peak that appears at $2\theta = 20^{\circ}$ in the diffraction pattern of SA/CS disappears due to disturbance of the bonds in M-CA/CS blended membrane. The *d*-spacing values are 4.3 A$^{\circ}$ for SA/CS and 3.6 A$^{\circ}$ for M-CA/CS membranes. The reduction in effective *d*-spacing from 4.3 A$^{\circ}$ to 3.6 A$^{\circ}$ indicates the shrinkage in cell size or inter-segmental spacing occurring due to crosslinking, which would improve the selective permeation of the membrane.
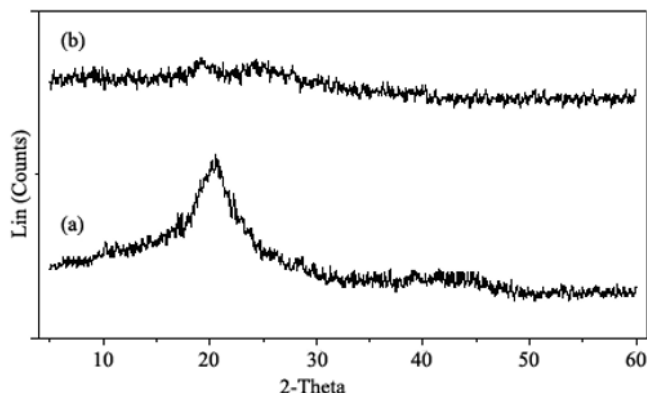

Figure 2. X-ray diffractograms of (a) SA/CS and (b) M-CA/CS blend membranes

TGA studies

The thermal degradation behavior of membranes was examined following the weight loss as function of temperature. The TGA curves for SA/CS and M-CA/CS are shown in Figure 3. The TGA curve of SA/CS blend exhibits a single weight loss stage ranging between 220-280°C followed by a final decomposition at 280°C. The weight loss stage can be attributed to the decomposition of main chain in the blend. The TGA curve of M-CA/CS blend exhibits two weight loss stages between 170-240°C and 260-350°C followed by a final decomposition around 450°C. The weight loss in the first stage can be attributed to decomposition of calcium chelate and covalent crosslinking of MA with SA and CS, and weight loss in the second stage can be attributed to splitting of the main chain before final decomposition of the polymer. TGA analysis indicates that the crosslinked (M-CA/CS) membrane possesses higher thermal stability than uncrosslinked membrane (SA/CS).
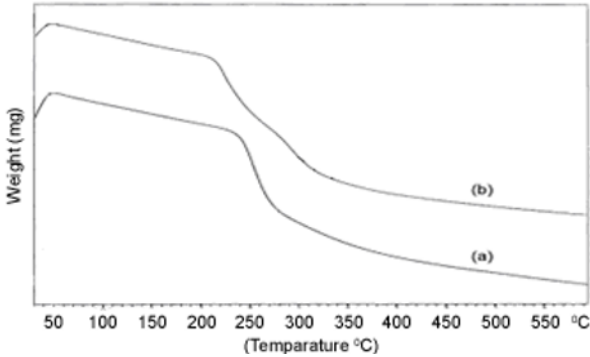
Figure 3. TGA curves of (a) SA/CS and (b) M-CA/CS blend membranes

Pervaporation results

Effect of feed composition
The variation of pervaporation performance with composition of feed mixtures over a wide range at 30°C was investigated using crosslinked blend membranes (M-CA/CS). The pervaporation performance of M-CA/CS membrane was investigated for varying feed composition between 5 - 30 wt.% water keeping other operating parameters such as permeate pressure and membrane thickness constant. For this study, the membrane thickness and permeate pressure were maintained at 45 μm and 0.5 mmHg, respectively. As expected, a rise in the feed concentration of water produced an increase in the water- normalized flux from 0.53 to 0.81 kg m^{-2} h^{-1} 10 μm (Figure 4). Mass transport through the hydrophilic blend membrane occurs by solution diffusion mechanism [22]. In addition, the sorption data for binary feed mixtures presented in Table 1 also show a high degree of sorption for the crosslinked membrane. At 100% water composition, the sorption was very high (133.84%) for M-CA/CS membrane. This shows the hydrophilic nature of the membrane, which has affinity for water and is capable being selective towards the same during separation.
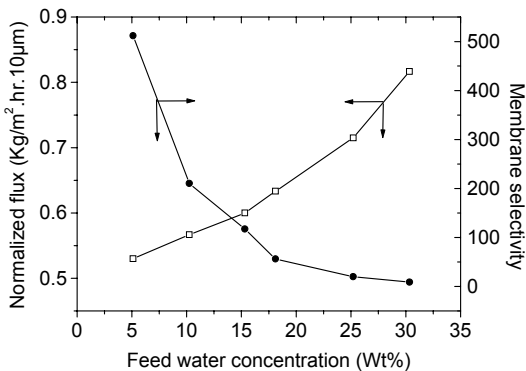

Figure 4. Effect of feed water composition on PV performance of M-CA/CS membrane (membrane thickness 45 μm and permeate pressure at 0.5 mmHg)

Table 1. Effect of feed concentration on degree of swelling, percentage sorption and PSI values

Feed water concentration (wt.%)	Degree of swelling	% of sorption	PSI
0.00	1.03	2.8	--
6.1	1.07	6.9	271.4
10.4	1.17	12.7	119.2
16.0	1.21	20.9	70.4
18.6	1.25	24.8	35.6
26.0	1.35	34.7	14.3
30.4	1.41	40.7	7.19
100.0	2.34	133.8	--

The degree of swelling correspondingly rises with an increase in the feed water concentration resulting in enhanced flux. However, increased swelling has a negative impact on membrane selectivity since the swollen and plasticized upstream membrane layer allows some 1,4-dioxane molecules also to escape into the permeate side along with water. Therefore, the permeate water concentration was found to reduce from 96.5 to 79.3% indicating a drop in selectivity from 512 to as low as 8.8 over the same feed concentration range of 5–30% water as reported in Figure 4. However, it was worth mentioning that the membrane showed promising results for dehydrating feeds having 5–20% water. Moreover, the azeotropic composition of 82 wt.% 1,4-dioxane was easily broken by pervaporation.

Effect of membrane thickness
The effect of varying membrane thickness on separation performance was studied at azeotropic feed composition (82 wt.% 1,4-dioxane) and permeate pressure at 0.5 mmHg by synthesizing membranes of thickness ranging from 45 to 150 μm. The variation in selectivity with membrane thickness was high. Generally, selectivity was constant or increased marginally with rising thickness. With an increase in the membrane thickness, a gradual reduction in the flux from 0.063 to 0.051 kg m^{-2} h^{-1} is clearly evidenced from Figure 5. Though the availability of polar groups enhances with an increase in the thickness, flux decreases since diffusion becomes increasingly retarded as the feed molecules have to travel a greater distance to reach the permeate side. The permeate concentration of water varied from 92.5 to 98.5 wt.% indicating the increase
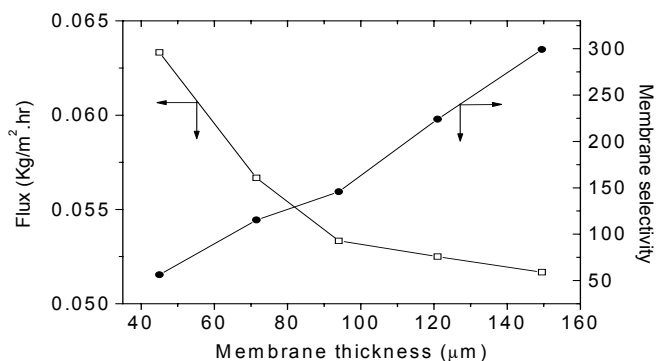
Figure 5. Effect of membrane thickness on PV performance (azeotropic feed composition 18 wt.% of water and permeate pressure at 0.5 mmHg)

in selectivity from 56.2 to 299. In pervaporation process, the upstream layer of the membrane was swollen and plasticized due to absorption of feed liquid and allowed unrestricted transport of feed components. In contrast, the downstream layer was virtually dry due to continuous evacuation in the permeate side, and therefore, this layer formed the restrictive barrier which allowed only interacting and small size molecules such as water to pass through. It was expected that the thickness of the dry layer would increase with an increase in the overall membrane thickness resulting in improved selectivity as observed in the present case.

Effect of permeate pressure

The permeate pressure was varied from 0.5 to 9.5 mmHg to study the separation characteristics at a constant membrane thickness of 45 μm and azeotropic feed composition. At lower pressures (high vacuum), the influence of the driving force on the diffusing molecules in the membrane was high, and resulted in the components being swept out immediately from the permeate side causing high mass transfer rates. Figure 6 shows that the membrane exhibits considerable lowering of normalized flux from 0.63 to 0.25 kg m^{-2} h^{-1} 10 μm as well as a reduction in selectivity from 56.2 to 7.5 with an increase in permeate pressure from 0.5 to 9.5 mmHg. Under high vacuum conditions, diffusion through the membrane was the rate determining step of the pervaporation process and the diffusing water molecules experience larger driving force, which enhances the desorption rate at the downstream side. Lower vacuums reduce the driving force, thus slowing desorption of molecules. In such cases, the relative volatilities of the two components of the mixture govern the separation factor of the membrane.
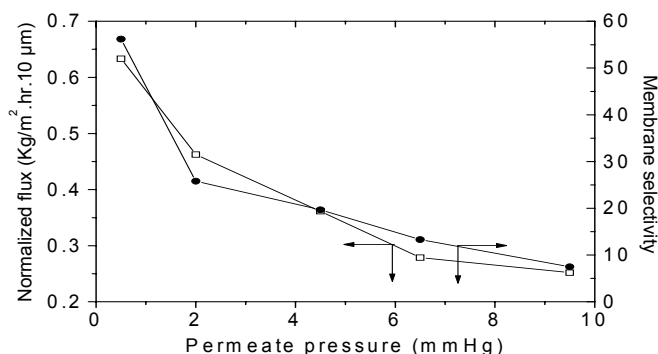

Figure 6. Effect of permeate pressure on PV performance (azeotropic feed composition 18 wt.% of water and membrane thickness 45 μm)

Comparison of present work with literature

Pervaporation performance of the M-CA/CS membrane is compared with the literature data and is reported in Table 2. From the Table, it can be noted that the M-CA/CS membranes synthesized in the study yielded comparable flux and showed relatively better selectivity. However, it can be mentioned that a marginally good selectivity combined with fluxes render the crosslinked blend suitable for dehydration of 1,4-dioxane/water mixtures. Furthermore, the ease in fabrication of these membranes associated with low cost render them more attractive for pervaporation separation of aqueous 1,4-dioxane.

Table 2. Comparison of flux and selectivity of M-CA/CS membrane with literature

Membrane	Normalized flux (kg.m^{-2}.h^{-1}.10 μm)	Selectivity	Reference
M-CA/CS	0.63	56.20	Present work
PVA/PEI	0.73	44.01	8
GA-PVA/PEI	2.20	33.34	13
PVA/NaAlg	2.00	60.00	15
Poly(dimethylsiloxane-co-siloxane)	1.08	16.30	23
Sodium alginate-g-polyacrylamide	5.23	57.50	24
PVA/Zeolite T	3.09	59.00	25

PVA: poly(vinyl alcohol); PEI: polyethyleneimine; GA: glutaraldehyde; NaAlg: sodium alginate.

Conclusions

In this study, the blend membrane of SA/CS was prepared, pre-treated with calcium chloride and further crosslinked with MA for pervaporation-based dehydration of 1,4-dioxane/water mixture. The number of groups crosslinked in SA/CS blend polymer was identified from the IEC studies. Characterization of the crosslinked membranes by FTIR and XRD confirmed the crosslinking reaction. The membranes showed adequate thermal stability to withstand the PV experimental conditions. FTIR spectroscopy confirmed the predicted interaction between the SA/CS blend and the cross linker. With increasing feed water compositions, the membrane performance exhibited a reduction in selectivity and an improvement in flux due to increased swelling. As expected, with increasing membrane thickness, selectivity improved, but flux decreased. Higher permeate pressure caused a reduction in both flux and selectivity. Pervaporation could be combined with distillation in an integrated process wherein the former overcomes the azeotropic barrier of 1,4-dioxane (82%) after which the latter was applied to achieve final purity.

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