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Phosphorylated chitosan membranes for the separation of ethanol–water mixtures by pervaporation

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ABSTRACT

Dense membranes of chitosan were prepared and ionically crosslinked with phosphoric acid for varying intervals of time. The membranes were characterized by FTIR and XRD to confirm cross-linking. TGA and IEC studies were conducted to assess the thermal stability and estimate the number of interactive groups left in the membrane after crosslinking. Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of the membranes in pure liquids as well as binary mixtures. The phosphorylated chitosan membrane crosslinked for 2 h showed good mechanical strength and strong potential for breaking the azeotrope of 95.58 wt% ethanol by exhibiting a high pervaporation selectivity of 213 with substantial water flux of 0.58 kg/(m^2 h). Pervaporation experimental parameters such as feed composition, membrane thickness and permeate pressure were varied to identify optimum operating conditions.

1. Introduction

Pervaporation, a potential industrial method for the separation of liquid mixtures, is considered to be a promising alternative to conventional energy intensive technologies, like extractive or azeotropic distillation in liquid mixture separation for being economical, safe and ecofriendly. Pervaporation separation is based on the differences in sorption and diffusion properties (Huang, 1990; Semenova, 1996) of the permeating compounds and is useful particularly for the separation of azeotropes and close boiling mixtures, isomers, besides heat sensitive and hazardous compounds (Feng & Huang, 1996; Yangishita, Maejima, Kitamoto, & Nakane, 1994). Most of the research efforts of the pervaporation have concentrated on the separation of alcohol–water system. One of its important applications in industry is the dehydration of aqueous ethanol.

The key to the success of pervaporation process is fabrication of suitable membranes yielding high permeability, good selectivity and sufficient mechanical strength (Huang & Feng, 1993). For the dehydration of alcohol mixtures, new membrane materials, containing hydrophilic clusters in the polymer matrix, are preferred. Ionic moieties, especially absorb water molecules preferentially, which lead to both high flux and high separation factors due to salting out effect on organic molecules (Sander & Soukup, 1998; Yangishita, Kitamoto, & Nakane, 1995). However, excessive hydrophilicity could cause swelling of the membrane resulting in low selectivity due to plasticization effect.

Chitosan, the deacetylated form of chitin, is the second most abundant biopolymer in nature. Chitosan has both reactive amino and hydroxyl groups which can participate in chemical reactions (Muzzarelli, 1977; Muzzarelli, 2011). These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the chitosan membrane (Busca, Berardinelli, Resini, & Arrighi, 2008). However, the separation factor for alcohol–water for chitosan itself is not high because its free amine form is water insoluble. Chitosan membranes have thus been modified and extensively studied for the dehydration of alcohols (Lee & Shin, 1991; Nam & Lee, 1997; Shieh & Huang, 1997; Uragami & Takigawa, 1990; Young, Sang, & Dong, 1997) and other industrial solvents like dimethylsulphoxide and ethylene glycol (Sang & Young, 1999; Won, Feng, & Lawless, 2002; Yao, Peng, Goosen, Min, & He, 1993). Amino functional group in chitosan is so reactive that this polymer can be easily modified to *N*-alkyl chitosan membrane for the dehydration of ethanol (Li, Xu, Qusay, & Li, 2006), by acetylation for separation of ethanol/toluene and methanol/toluene mixtures (Huang, Moon, & Pal, 2000), benzoyl-chitosan membrane for the separation of benzene–cyclohexane mixture (Charathi, Houde, Kulkarni, & Kulkarni, 1991), surface modification (Wei, Zhejun, Qiufang, Zhennan, & Xinping, 2010), by introducing carbopol (Jing et al., 2010), by grafting (Jolly, Arjumand, Padmeshwary, & Mahadevappa, 2010) or crosslinked with toluene diisocyanate (Osada & Nakagawa, 1992) to achieve enhanced properties. In the present study, chitosan membranes were modified by

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phosphorylation for the separation of ethanol–water mixtures. The membranes were characterized extensively by different techniques to study separation mechanisms and subjected to varying operating conditions to investigate their pervaporation performance.

2. Experimental

2.1. Materials

Chitosan, with the degree of deacetylation of 84% and average molecular weight of 500,000 was purchased from Chemopol, Nellore, India. Ethanol, acetone, glacial acetic acid and orthophosphoric acid of high purity were purchased from Loba Chemie, Mumbai, India. Deionized water (conductivity = 0.02 μS/cm) was generated in the laboratory itself.

2.2. Membrane preparation

A 2% (w/v) solution of chitosan in 2% (v/v) aqueous acetic acid was prepared. The solution was then stirred for a period of half an hour and filtered to remove undissolved matter. A bubble-free solution was cast onto a clean glass plate and evaporated to dryness in atmosphere at room temperature to obtain a dense nonporous membrane. The solvent was air-dried at room temperature for 24 h followed by vacuum drying in an oven at 40 °C, to remove the presence of residual solvent, if any.

2.3. Phosphorylation

Chitosan membranes were crosslinked with phosphoric acid by immersing the films in a bath containing a mixture of isopropyl alcohol (IPA) (440 mL), phosphoric acid (50 mL) and 10 mL of water. The degree of crosslinking was controlled by varying the duration of exposure of the membrane in the bath from 30 min to 4 h. The resulting films were washed in deionized water for 4–5 h followed by vacuum drying for a period of 5 h at elevated temperature (40 °C) in a closed oven to remove the remaining traces of solvent.

2.4. Pervaporation procedure

Experiments were carried out in a 100 mL batch level with a pervaporation manifold operated at a vacuum as low as 0.25 mmHg in the permeate line. The membrane area in the pervaporation cell assembly was approximately 20 cm^2. The experimental procedure is described in detail elsewhere (Sridhar, Ravindra, & Khan, 2000). Permeate was collected for duration of 8–10 h. Tests were carried out at room temperature until reproducibility was obtained. The collected permeate was weighed after allowing it to attain room temperature in Sartorius electronic balance (accuracy: 10^{-4} g) to determine the flux and then analyzed by gas chromatography to evaluate the membrane selectivity.

2.5. Flux and selectivity equations

In pervaporation, the flux '*J*' of a given species, say faster permeating component '*i*' of a binary liquid mixture comprising of *i* (water) and *J* (ethanol) is given by:

$$J_i = \frac{W_i}{At} \tag{1}$$

where W_i represents the mass of water in permeate (kg), *A* the membrane area (m^2) and *t* represents the evaluation time (h). In the present study, though different membrane thicknesses were utilized, the flux has been normalized and reported for a thickness of 10 μm. The membrane selectivity is the ratio of permeability coefficients of water and ethanol and can be calculated from their respective concentrations in feed and permeate as given below:

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

where *x* and *y* represent the feed and permeate concentrations of the faster permeating component '*i*', which is water in the present case.

Quite often, pervaporation separation index (PSI) is used to describe the overall performance of a membrane for a selected feed mixture. This can be calculated from the product of water flux, *J* and selectivity, α:

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

2.6. Analytical procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (Model 5765) installed with thermal conductivity detector (TCD) and packed column of 10% DEGS on 80/100 Supelcoport of 1/8 in. ID and 2 m length. The oven temperature was maintained at 70 °C (isothermal) while the injector and detector temperatures were maintained at 150 °C each. The sample injection size was 1 μL and pure hydrogen was used as the carrier gas at a pressure of 1 kg/cm^2. The GC response was calibrated for this particular column and conditions with known compositions of ethanol–water mixtures and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

2.7. Membrane characterization

Membrane characterization was done by various methods such as FTIR, XRD, TGA, sorption studies and ion exchange capacity to determine the effect of crosslinking and separation mechanisms.

2.7.1. FTIR studies

The FTIR spectra of unmodified and crosslinked membranes were scanned-using Nicolet-740, Perkin-Elmer-283B FTIR Spectrometer.

2.7.2. XRD analysis

A Siemens D 5000 powder X-ray diffractometer was used to study the solid-state morphology in powdered form. X-rays of 1.5406 Å wavelength were generated by a CuK source. The angle of diffraction was varied from 0 to 65° to identify the change in the crystal structure and intermolecular distances between the intersegmental chains after crosslinking.

2.7.3. Thermo gravimetric (TGA) analysis

Thermal stability of the polymer films was examined using Seiko 220TG/DTA analyzer from 25 to 600 °C heated at the rate of 10 °C/min and flushed with nitrogen gas at the rate of 20 mL/min. Samples were subjected to TGA before and after phosphorylation to determine the thermal stability and decomposition characteristics.

2.7.4. Swelling ratio

The degree of swelling of crosslinked membrane in various binary feed mixtures of concentrations ranging from 5 to 50 wt% water as well as pure water and ethanol was determined by soaking 3 cm diameter strips of the polymer film in the liquids. Films were soaked for time periods ranging from 30 min to 48 h followed by removing them from the liquids, wiping the surfaces quickly and weighing. Swelling ratio was determined by the following equation:

$$\text{Swelling ratio} = \frac{(W-D)}{D} \times \frac{1}{\rho_i} \tag{4}$$

W is the weight of the swollen membrane, D is the weight of the dry film and ρ_i is the density of the liquid in which the membrane was immersed.

2.7.5. Determination of ion exchange capacity [IEC]

In order to determine the effect of phosphorylation on CS and CA, ion exchange capacity (IEC) of the membrane was estimated. IEC indicates the number of groups present before and after crosslinking, which gives an idea about the extent of crosslinking. Thus, IEC gives the number of milli-equivalents of ions in 1 g of dry polymer. To determine IEC, the specimens of identical weights were soaked in 50 mL of 0.01 N NaOH solution for about 12 h at ambient temperature. Then, 10 mL of sample was titrated against 0.01 N H_2SO_4. The sample was regenerated with 1 M HCl, washed with water and dried to constant weight. IEC was then calculated as:

$$\text{IEC} = \frac{(B - P) \times 0.01 \times 5}{m} \quad (5)$$

where B is sulfuric acid used to neutralize the blank sample, P is sulfuric acid used to neutralize the PV membrane, 0.01 is the normality of sulfuric acid, the number 5 represents the factor corresponding to ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration and m represents the sample mass (g).

3. Results and discussion

The hydroxyl groups present in H_3PO_4 react with the amine groups of chitosan, resulting in strong ionic bonding between NH_3^+ functional group of the polymer and PO_4^{3-} of the acid. These interactions can also be confirmed by FTIR.

An estimation of the number of groups present before and after crosslinking gives an idea of the extent of crosslinking. The amount of residual interacting hydroxyl and amine groups in membranes after crosslinking was estimated from IEC studies. It was noted that unmodified chitosan showed IEC's of 0.52 mequiv./g where as their crosslinked films exhibited corresponding IEC's of 0.35 mequiv./g. The IEC, which is equivalent to the total number of interactive groups present in the membrane, decreased upon crosslinking because of the consumption of hydroxyl groups and amine groups during the crosslinking reaction (Yeom & Lee, 1998). The IEC results show that almost 67% of amine and hydroxyl groups present in the chitosan have now formed cross-links with phosphoric acid.

3.1. Membrane characterization

3.1.1. FTIR spectroscopy

The FTIR spectrum of chitosan shows the prominent peaks of hydroxyl and amide at 3461 and 1591 cm^{-1}, respectively. The peak at 1259 is due to N–CH_3 stretching. The peak at 1155 cm^{-1} is characteristic of the saccharide structure. Amino groups in chitosan and phosphoric acid have a Coulombic interaction, which cross-link the chitosan main chains ionically. The FTIR analysis of modified chitosan confirms that crosslinking has taken place by the reaction of amine group of chitosan with the hydroxyl group of phosphoric acid. Further the peak at 1672 cm^{-1} can be attributed to the NH_3^+ deformation, while a peak at 1250 cm^{-1} corresponds to P=O stretching.

3.1.2. X-ray diffraction (XRD)

The change in chitosan crystal structure and effective distance (d_{eff}) between intersegmental chains after crosslinking was determined by this technique. From the X-RD spectra (figure not shown), it was seen that both plain chitosan and its ionically crosslinked version (phosphorylated chitosan) exhibit semi-crystalline nature. Sharper peaks were seen in the diffractograms of phosphorylated chitosan membrane at 10° and 20° of 2θ which are related to two types of crystals: crystal 1 and crystal 2. Crystal 1 is responsible for separation as it corresponds to –OH and –NH_2 functional groups (Samuels, 1981). The d_{eff} decreased from 8.72 Å for chitosan to 8.35 Å in case of phosphorylated chitosan indicating smaller intermolecular distance in the amorphous part of the latter. Thus, the presence of ionic bonds in phosphorylated chitosan would not only cause salting out effect of organic molecules (Huang, 1990) but also make it more selective to water during the pervaporation process due to the shrinkage in crystal structure.

3.1.3. TGA analysis

Thermogravimetric analyses are depicted as curves to measure the thermal stability of the polymer against increasing temperature. It is observed that pure chitosan exhibited a major weight loss at 250 °C and final decomposition started at 410 °C. Comparatively, the corresponding thermal degradation of the phosphorylated chitosan membrane started at 300 °C and final decomposition at 500 °C. In both the cases the initial weight loss occurred due to the physical changes in the polymer such as dehydration and the final degradation occurs due to oxidation of the polymer with temperature and time. So the chitosan membrane exhibited enhanced thermal stability after crosslinking.

3.2. Pervaporation studies

3.2.1. Swelling characteristics

The effect of equilibrium sorption percentage of the phosphorylated membranes in water with varying time is shown in Fig. 1(a). From the graph, it is evident that the sorption percentage increased steadily up to 12 h and showed minimal change thereafter. Phosphorylated chitosan showed higher %sorption indicating the presence of polar groups in spite of crosslinking. The sorption behavior of phosphorylated chitosan in feed mixtures containing <4% water is shown in Fig. 1(b). The membrane was found to be stable for pervaporation under such low water concentrations ranging from 0.5 to 4 wt% and the corresponding %sorption was found to be varying from 1.49 to 4.2%, respectively. A huge difference in the %sorption with respect to water and ethanol can be evidenced which shows that the crosslinked membrane has high affinity for water and is capable of being selective towards the same during separation. However, absorption of large amounts of water at higher feed concentrations, could cause enhanced swelling and subsequently fall in membrane selectivity due to plasticization of the polymer chains.

3.2.2. Effect of crosslinking time

The effect of crosslinking time on pervaporation of ethanol–water mixture for phosphorylated chitosan is shown in Fig. 2. With increasing crosslinking time, it was evidenced that there was a substantial increase in separation factor with a corresponding drop in flux. This behavior is attributed to the decrease of free volume in the chains besides ionic interaction and hydrogen bonding between amino/hydroxyl groups in crosslinked chitosan and hydroxyl groups in water molecules with increasing crosslinking degree (Nam & Lee, 1999). As polymer membrane is crosslinked, the solubility of a feed liquid in the membrane is reduced, as can be deduced from the Flory–Rehner theory (Flory, 1953). As per the Flory–Huggins thermodynamics for mixing, a decrease in the overall solubility of the feed in the membrane results in an increase in the sorption selectivity. Crosslinking also reduces the mobility of the polymer segments and thus the diffusivity of permeating component. The reduced diffusivity as well as the solubility causes a decrease in pervaporation flux but an increase in separation factor (Nam & Lee, 1999) as evidenced in the figure. A gradual drop in the flux was noted with increasing crosslinking time whereas a substantial rise in

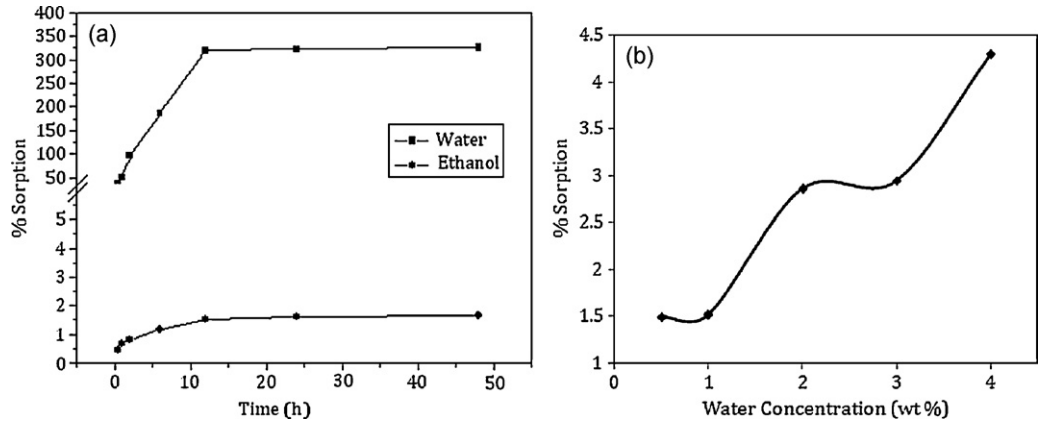

Fig. 1. (a) Sorption of phosphorylated chitosan membrane in water and ethanol at varying time intervals and (b) sorption of phosphorylated chitosan membrane in aqueous ethanol containing <4% water for a period of 48 h.

the selectivity was noticed with enhanced crosslinking time. The ideal crosslinking time was registered to be 2 h keeping the flux and selectivity in view. Furthermore, it was evidenced that the membranes crosslinked for long time were brittle and exhibited poor mechanical strength to suit pervaporation applications.

3.2.3. Effect of feed composition

Fig. 3 depicts the effect of feed water composition on flux and selectivity of phosphorylated chitosan membrane. The effects were investigated over a wide range of feed compositions at constant temperature of 30 °C, pressure of 0.5 mmHg and a membrane thickness of 30 μm, respectively. From the figure, it can be noticed that the permeate flux increased from 0.06 to 0.73 kg/(m^2 h 10 μm) whereas the selectivity correspondingly decreased from 7144.6 to 183 with an increase in feed water concentration from 0.63 to 10.23 wt%. This rise in the flux with increasing water concentration in the feed can be attributed to the swelling of the membrane due to the availability of more water molecules for sorption and diffusion (Wijmans & Baker, 1995). The preferential interaction of the crosslinked membrane with water molecules causes the membrane to swell, leading to plasticization and unrestricted transport of both the feed components through upstream layer. The polymer chains become more flexible and hence the transport through the membrane becomes easier for both the feed components resulting in higher flux, but reduced selectivity. A drop in the selectivity from 183 to 26 was observed for an increase in the feed water concentration from 10.23 to 52.3%, whereas the flux increased from 0.73 to 3.69 kg/(m^2 h 10 μm). The membrane was found to exhibit adequate stability and separation performance in feed water concentrations below 4%.

3.2.4. Effect of membrane thickness

The effect of membrane thickness on flux and selectivity was studied using synthesized membranes of different thicknesses varying from 30 to 150 μm at azeotropic composition and 0.5 mmHg permeate pressure. Fig. 4 shows a gradual decrease in the flux from 0.19 to 0.001 kg/(m^2 h). Though the availability of amine and hydroxyl groups enhances with an increase in membrane thickness, the flux decreased due to increasing resistance to the diffusion of the molecules through the entire thickness. Pervaporation selectivity is usually independent of membrane thickness. In pervaporation, the upstream layer of the membrane is swollen and plasticized due to absorption of feed liquid and allows unrestricted transport of feed components. In contrast, the downstream surface is virtually dry due to continuous evacuation in the permeate side and therefore this layer forms the restrictive barrier which allows only certain species to pass through. It is 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 where the selectivity increased from 213.1 to 244.6 as reported in the figure.

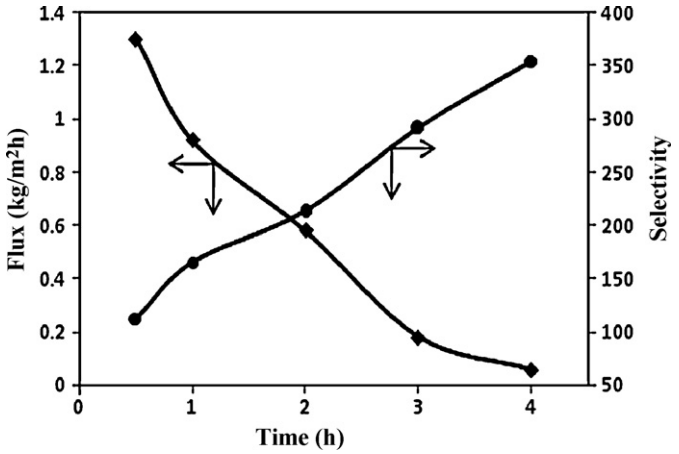

Fig. 2. Effect of crosslinking time of phosphorylated chitosan membrane on flux and selectivity.

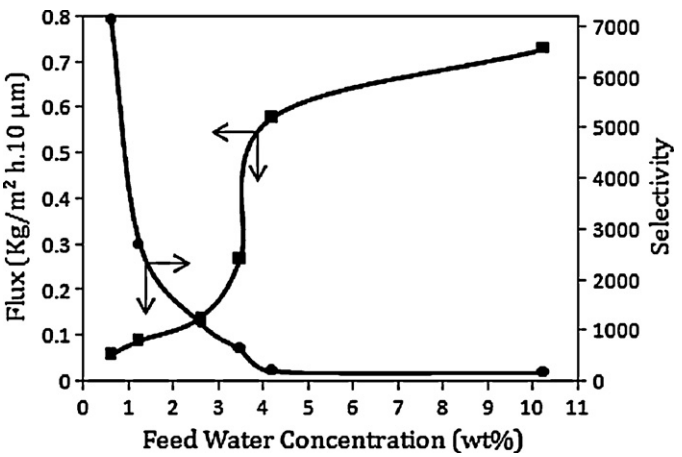

Fig. 3. Effect of feed water concentration on flux and selectivity of phosphorylated chitosan membrane.

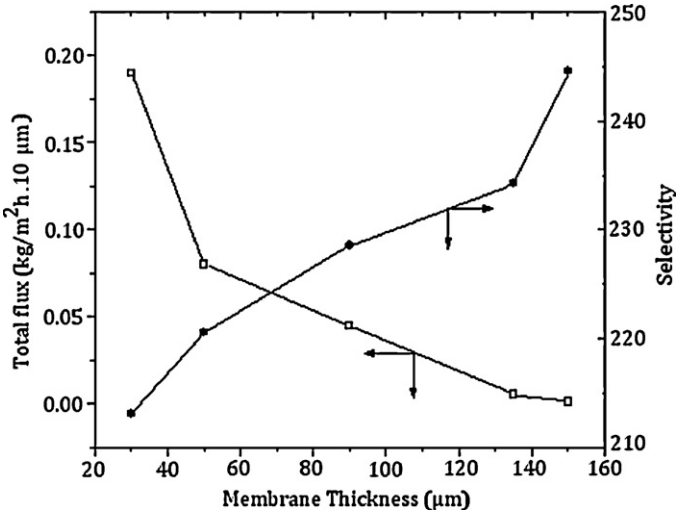

Fig. 4. Effect of membrane thickness on performance of phosphorylated chitosan membrane.

3.2.5. Effect on permeate pressure

The permeate pressure was varied from 0.5 to 10 mmHg, to study the permeation characteristics of cross-linked phosphorylated chitosan membrane at a constant thickness of 50 μm for azeotropic feed composition. Fig. 5, indicates the considerable lowering of flux from 0.58 to 0.018 kg/(m^2 h 10 μm) with increasing permeate pressure for the azeotropic composition. The corresponding selectivities decreased from 213.1 to 19.6. This variation in flux can be explained on the basis of Fick's law. An increase in the permeate pressure results in an increase of the activities of both permeants dissolved in the downstream layer of the membrane. Activity gradients across the thickness of the membrane consequently decline and permeation fluxes drop (Sheldon & Thompson, 1984). The change in permeate pressure also affects the selectivity. Diffusion through the membrane is the rate determining step of the pervaporation process and the diffusing water molecules experience larger driving force under high vacuum, which enhances the desorption rate at the downstream side. Lower vacuum (higher pressure) reduces the driving force, thus slowing desorption of the molecules. In such cases, the relative volatilities of the two components of the mixture govern separation factor of the membranes. Ethanol being more volatile than water, permeates competitively with water, thus lowering the concentration of water in permeate. At low pressure (high vacuum) the influence of driving force for diffusing molecules in the membrane is high and will result in the components being swept out immediately from the permeate side resulting in high mass transfer rates.

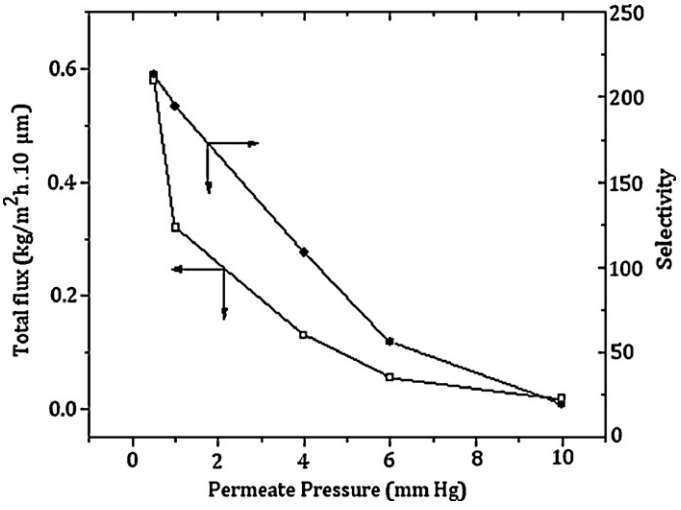

Fig. 5. Influence of permeate pressure on flux and selectivity of phosphorylated chitosan membrane.

4. Conclusions

Phosphorylated forms of chitosan were found to be promising for breaking the ethanol azeotropic barrier at 95.58 wt% of ethanol and very stable in feed water concentrations below 4%. Phosphorylation induces improved selectivity without causing a substantial loss in flux. Ionic crosslinking appears to be a promising technique for enhancing membrane selectivity with retention of flux. Characterization of the phosphorylated membrane by FTIR showed the occurrence of cross-linking whereas IEC studies indicated the existence of groups for the interaction, between the membrane and the liquids constituting the feed, despite crosslinking. WAXD studies revealed the membrane to be semi-crystalline and TGA found the membrane to be thermally stable. Sorption studies revealed that the modified chitosan membrane had higher affinity towards water than ethanol. With increasing feed water concentration, the membrane's performance was found to be affected substantially by an increase in the extent of swelling of the polymer which resulted in a rise in flux but reduction in selectivity. Increase in permeate pressure caused a reduction in both flux and selectivity for the membrane whereas increase in membrane thickness decreased flux and increased selectivity. In actual practice, pervaporation could be effectively combined with distillation in a hybrid process, where ethanol could be distilled up to azeotropic composition from where on pervaporation could be applied to achieve a final purity of ≥99.5% of the alcohol.

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