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Effect of PVP loading on pervaporation performance of poly(vinyl alcohol) membranes for THF/water mixtures

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Abstract This work reports an experimental study on the pervaporative dehydration of an industrial solvent tetrahydrofuran (THF) using a blend membrane of PVA/PVP crosslinked with maleic acid. The influence of feed composition and permeate pressure on the pervaporation flux and selectivity has been investigated. The membrane was found to exhibit a water flux of 0.007 kg/m^2 h with a water selectivity of infinity for dehydration of 97% THF at 30 °C. FTIR of the blend was carried out to interpret its behavior on the basis of interactions between carbonyl groups of the cationic PVP and hydroxyl groups of the neutral PVA polymer. X-ray diffraction and sorption studies were carried out to study the degree of crystallinity and polymer–liquid interactions. The variation in film morphology was examined by scanning electron microscopy (SEM). Pervaporation experiments showed that high selectivity and promising permeability were obtained with a 9:1 blending ratio of PVA/PVP membrane crosslinked with 5 wt% maleic acid.

Introduction

Pervaporation is a membrane process, which uses a polymeric membrane as a separative barrier between the vapor and the liquid phases of a membrane. In this process, the membrane is brought into contact with the liquid mixture at atmospheric pressure. The liquid permeates through the membrane and vaporizes thereafter by maintaining a low vapor pressure at permeate side through a vacuum pump. This process is potentially useful when distillation is difficult to apply for breaking of azeotropic mixtures, close-boiling components, isomeric mixtures, or alcohol solutions [2].

Poly(vinyl alcohol) (PVA) membranes are widely used in pervaporation dehydration processes as it has excellent characteristics such as high selectivity towards water, chemical stability, film-forming ability in spite of poor physical stability in aqueous media [4]. PVP is commonly used in medicine and electrochemical applications [1, 5, 7]. PVP was chosen for blending since the hydrogen bonds between the two polymers could hinder the PVA crystallization and make the membranes more permeable to molecular species.

Tetrahydrofuran (THF) is a strong aprotic solvent, commonly used in the pharmaceutical industry due to its broad solvency for both polar and non-polar compounds. THF and water form a homogeneous azeotrope at 5.3 wt% water and thus simple distillation is not feasible to dehydrate THF below this concentration.

The present investigation is an attempt to enhance the performance of PVA membranes for dehydrating THF–water mixtures by blending the polymer with poly(vinyl pyrrolidone) (PVP). This work also explores the effect of varying the blend ratios on the separation performance parameters such as flux and selectivity. In order to gain a more detailed picture of the molecular transport phenomenon, sorption measurements are conducted to explain the mechanism of interaction between the polymers constituting the blend as well as pervaporation results.

Experiment

Feed stock

PVA with a molecular weight (MW) of 50,000 g/mol was purchased from Loba Chemie, Mumbai. PVP from Aldrich

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Chemical Co., USA of molecular weight 125,000 was used. Hydrochloric acid (HCl) and maleic acid (MA) were purchased from s.d. Fine Chemicals, Mumbai. Isopropanol was purchased from Loba Chemie, Mumbai. Deionized water with a conductivity of 20 μS/cm was generated in the laboratory.

Membrane preparation

PVA/PVP membranes were prepared by solution casting and solvent evaporation technique. A 10 wt% PVA solution at 90 °C and 1 wt% PVP solution at room temperature were prepared individually. Blends were then prepared by mixing the individual solutions in different ratios as listed in Table 1. The mixture was stirred for a long period for homogeneity. The bubble-free solution was cast on to a petri dish and evaporated. The dried membranes were then post-treated with maleic acid (5 wt%) for about 2 h so as to crosslink PVA.

Experimental method

Experiments were carried out on a 100 mL batch level for 4–5 h as described in detail elsewhere [6]. 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 to determine the flux and then analyzed by GC to evaluate selectivity.

Flux and selectivity equations

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

$$J_i = \frac{w_i}{A\,t} \tag{1}$$

where W_i represents the mass of permeate (kg), A is the membrane area (m^2) and t represents the evaluation time (h).

Table 1 Effect of blending ratio on pervaporation performance for THF–water (96.89/3.11 w/w) mixture

PVA/PVP blend ratio	Permeate composition		Flux (J_i) (kg/m^2 h)	Selectivity (α)
	THF	Water		
PVA	1.49	98.51	0.30	2067.42
9:1	0	100.0	0.007	∞
8:2	0.19	99.81	0.05	16043.75
7:3	1.12	98.87	0.28	2740.84
6:4	1.21	98.79	0.36	2550.39
5:5	4.22	95.78	0.14	707.98

The membrane selectivity is the ratio of permeability coefficients of water and solvent and can be calculated from their respective feed (X) and permeate (Y) concentrations as given below:

$$\alpha = \frac{Y_{H_2O}/Y_{THF}}{X_{H_2O}/X_{THF}} \tag{2}$$

Quite often, pervaporation separation index (PSI) is used to describe the overall performance of a membrane for a selected feed mixture as the product of flux and selectivity:

$$PSI = J_i * \alpha \tag{3}$$

Degree of swelling

Dynamic and equilibrium swelling of the known weighed pieces of crosslinked polymer films were carried out at 30 °C until equilibrium was attained in THF/water azeotropic mixtures and as well as individual components. Sorption was one of the controlling steps in PV separation in the solution-diffusion models. After the swelling equilibrium state was reached, the swollen membranes were weighed and the sorption is calculated as:

$$\text{Sorption} = \frac{M_{wet} - M_{dry}}{M_{dry}} \tag{4}$$

Membrane characterization

FTIR studies

FTIR spectra were scanned using a Nicolet-740, Perkin-Elmer-283B FTIR Spectrometer. Figure 1a, b shows the FTIR spectra of the plain and crosslinked PVA/PVP blends. The membranes were examined for the molecular structure after chemical modifications. Polymers are perfectly compatible and miscible via the hydrogen bond interactions between the C=O groups of PVP and OH groups in PVA. The strong absorption peak at 1099 cm^{-1} in Fig. 1a has been assigned to the –OH stretching in PVA. As it is seen from the spectra of the blended membranes the change in the intensity of the peak around 1099 and 1333 cm^{-1} is attributed to the CO–HO hydrogen bond in PVA/PVP blends. The spectrum (Fig. 1b) shows peaks as a sharp absorption band at 1725 cm^{-1}, which is the characteristic band that represents crosslinking of PVA with maleic acid.

XRD studies

A Siemens D 5000 powder X-ray diffractometer (Siemens, Wultzberg, Germany) was used to study the solid state morphology of crosslinked and uncrosslinked blends of

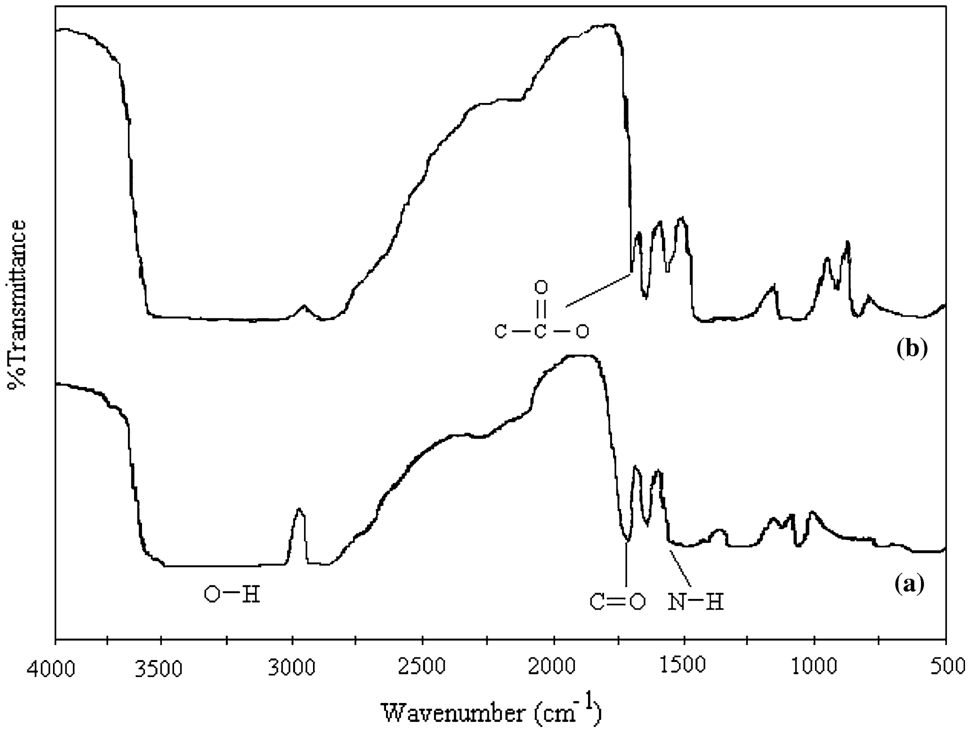


Fig. 1 FTIR spectra of uncrosslinked (*a*) and crosslinked (*b*) PVA/PVP blend membrane

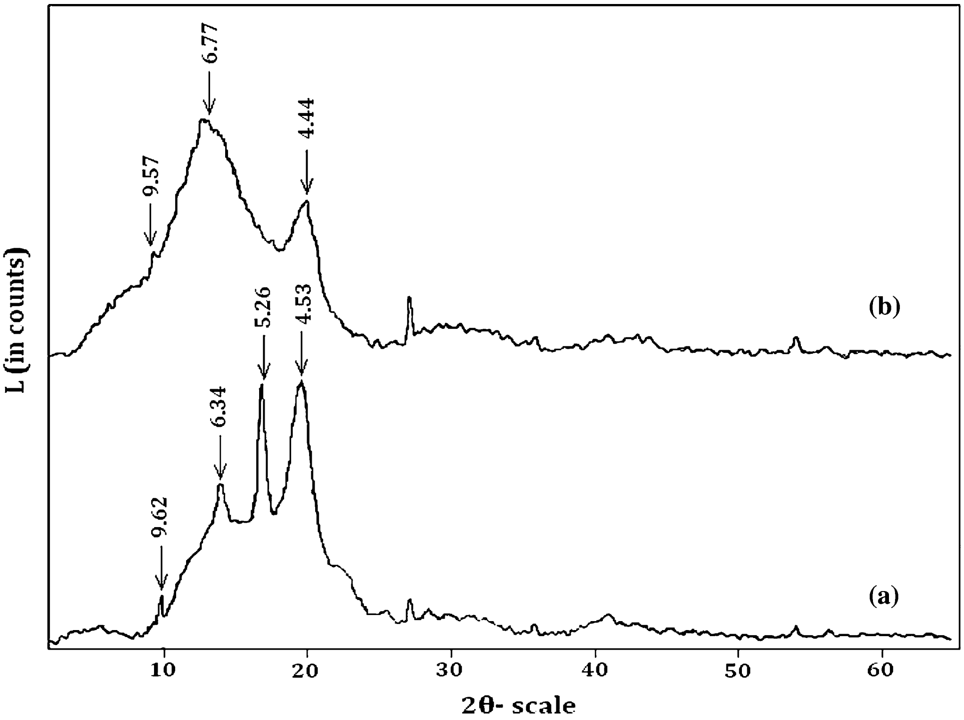


Fig. 2 XRD spectra of uncrosslinked (*a*) and crosslinked (*b*) PVA/PVP blend membrane

PVA/PVP in Fig. 2a, b. The XRD spectra of the blend show amorphous nature with broad peaks at $2\theta = 10°$ and $20°$. This indicates the presence of higher free volumes in the blend, which might result in reduction in selectivity and increased fluxes. The reduction in effective *d*-spacing from 4.53 Å ($2\theta = 20°$) for uncrosslinked blend to 4.44 Å for the crosslinked one, suggests the occurrence of reaction between the polar groups of PVA and PVP. On the other hand, the reduction in effective *d*-spacing from 9.62 Å ($2\theta = 10°$) for the uncrosslinked blend (Fig. 2a) to 9.57 Å in the crosslinked blend membrane (Fig. 2b) indicates shrinkage in the inter-segmental spacing occurring due to

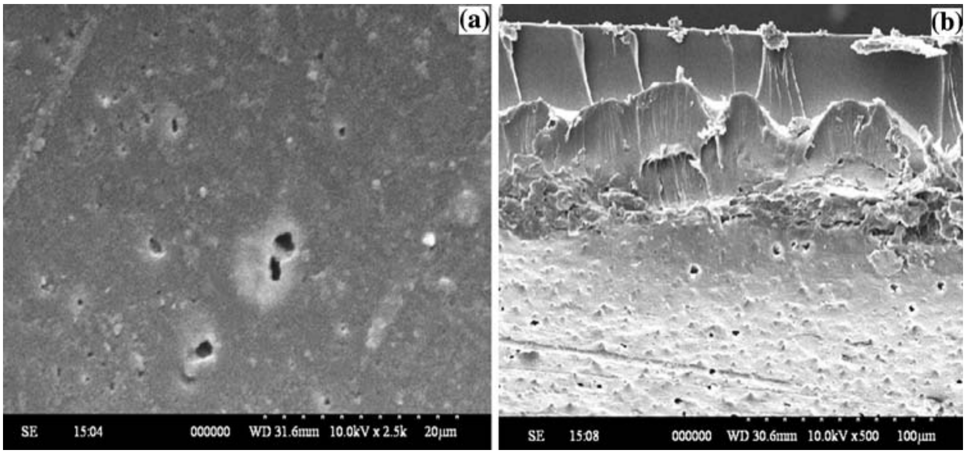


Fig. 3 Surface (**a**) and cross-sectional (**b**) view of PVA/PVP blend membrane

crosslinking, which would improve the selective permeation of the membrane.

SEM studies

SEM photographs of the PVA/PVP blended membrane are shown in Fig. 3a, b. It is obvious that the surface of the blended membrane is flat, and has neither pores nor cracks. The inner structure of the membrane is homogeneous with no defects or any obvious phenomena of micro-phase separation. This illustrates the good compatibility between PVA and PVP.

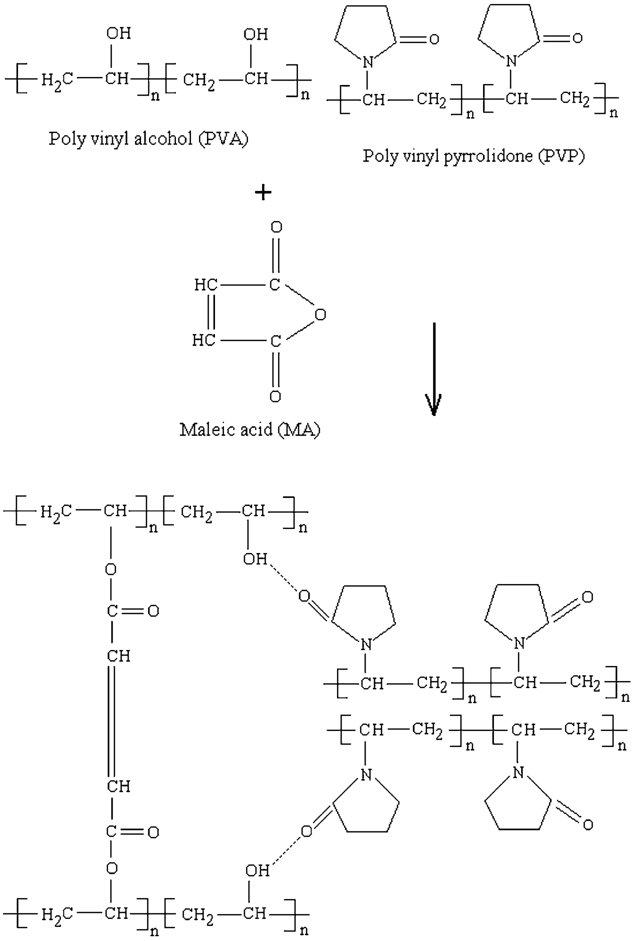
Pervaporation experimental results

Effect of PVP content

Table 1 illustrates the effect of PVP content in PVA/PVP membranes on pervaporation of water/THF mixtures. As PVP is more hydrophilic when compared to PVA (PVP alone could not be used to form films), the blend exhibited greater affinity towards water than plain PVA. As the PVP content was enhanced, the blend membrane became more hydrophilic and showed variation in flux and selectivity. Scheme 1 represents the interaction between the blended polymers and the crosslinking mechanism of PVA with maleic acid.

Effect of feed water concentration on membrane performance

The pervaporation performances of the PVA/PVP crosslinked blend membrane was investigated for varying feed compositions comprising 3.11% (w/w) to 14.96% (w/w) water keeping the other operating parameters constant. As the water concentration in feed increased an increase in flux was observed (Fig. 4). This is because mass transport through the hydrophilic membrane occurs by solution diffusion mechanism [8]. Increased swelling has a negative impact on membrane selectivity since the swollen and plasticized upstream membrane layer allows some THF molecules also to pass into the permeate side along with water, resulting in a drop in selectivity from infinity to



Scheme 1 Interaction between PVA–PVP and crosslinking of PVA with maleic acid

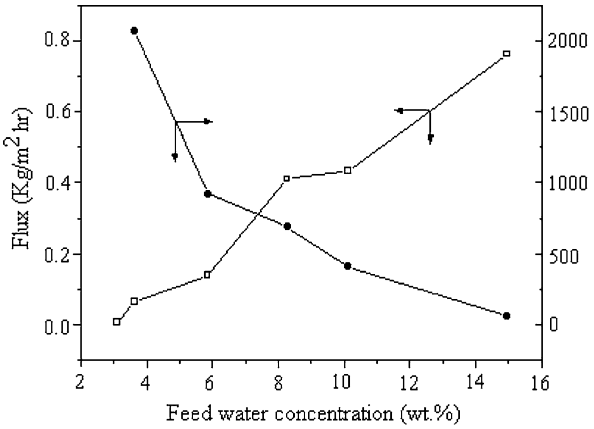


Fig. 4 Effect of feed water concentration on flux and selectivity

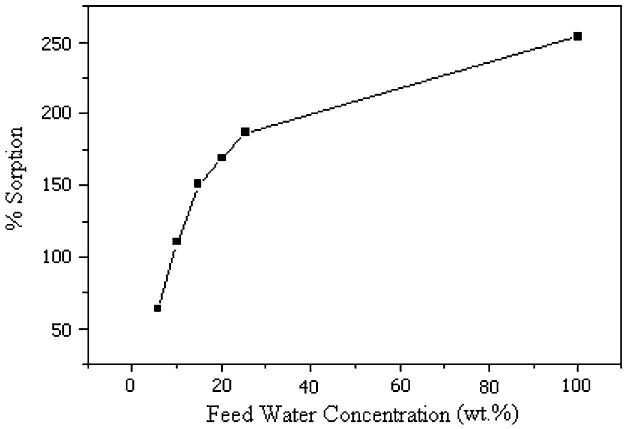


Fig. 6 Effect of sorption on the membrane

56.7. The separation performance of the membranes is evaluated in terms of pervaporation separation index (PSI), which gives the combined result of flux and selectivity. Moreover, the azeotropic composition (of 5.3% (w/w) water) was easily broken with a selectivity of 920 and flux of 0.14 kg/m^2 h.

Effect of permeate pressure on membrane performance

The permeate pressure was varied from 0.5 to 11 mmHg to study the permeation characteristics as shown in Fig. 5. This figure shows a considerable lowering of flux from 0.485 to 0.071 kg/m^2 h and the permeate water concentration reduced from 98.31 to 72.15% (w/w), resulting in a decrease in selectivity from 733.9 to 32.6. Under high-vacuum conditions (lower pressure), diffusion through the membrane is the rate-determining step of the pervaporation process and the diffusing water molecules experience a greater driving force, which enhances the desorption rate at the downstream side [3].

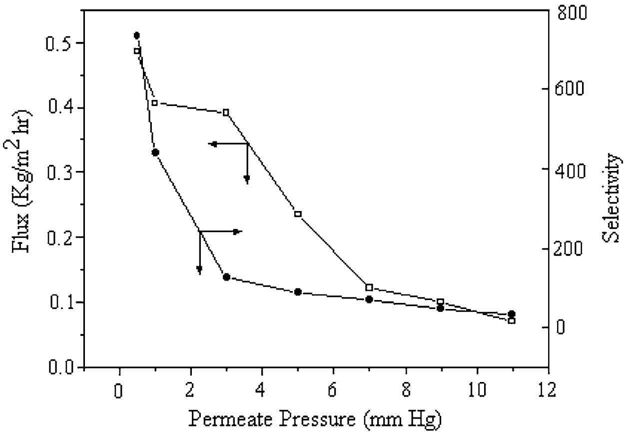


Fig. 5 Effect of permeate pressure on flux and selectivity

Sorption effects

Sorption is the other significant step apart from diffusion which determines pervaporation performance. The hydrophilic groups in this membrane are responsible for the preferential water sorption. The degree of swelling in the feed increased steadily with increasing water concentration (wt%) as shown in Fig. 6. This shows that the membrane interacts extensively with water and is capable of being highly selective towards the same during separation. Absorption of large amounts of water at high feed concentrations could cause enhanced swelling and subsequently a fall in membrane selectivity due to plasticization of the polymer chains.

Conclusions

In this paper PVA/PVP membranes crosslinked with maleic acid appear to have promising potential for dehydration of aqueous solution of THF especially at the azeotropic composition of 6 wt% concentration of water. PVP, as a modifier, was found to play a crucial role in improving pervaporation performance. With increasing PVP concentration in PVA/PVP blend membranes, permeate rate increased and selectivity decreased due to enhanced hydrophilicity and membrane free volume. The hydration of the membranes during pervaporation appeared as a dynamic process which involves a sorption–desorption balance. The blend membrane exhibits good flux, high selectivity, efficient solvent enrichment, and is highly stable such that it can be used for separation at any composition of the feed solution. In actual practice, pervaporation could be effectively combined with distillation in a hybrid process as THF could be distilled up to azeotropic composition from where on PV could be applied to achieve a final purity of >99% of THF.

References

1. Cassu SN, Felisberti MI (1997) Polymer 38:3907
2. Habib I (1998) Eur Polym J 34:955
3. Haung RYM (1991) Pervaporation membrane separation process. Elsevier Science Publishers, Amsterdam, The Netherlands
4. Lei Z, Ping Y, Yunbai L (2006) Sep Purif Technol 52:77
5. Seabra AB, Oliveira MG (2004) Biomaterials 25:3773
6. Sridhar S, Ravindra R, Khan AA (2000) Ind Eng Chem Res 39:2485
7. Tsutsumi H, Dio H, Oishi T (1997) J Power Source 68:364
8. Wijmans JG, Baker RW (1995) J Membr Sci 107:1