Water-Isopropanol 혼합물의 투과증발 분리를 위한 poly(vinyl alcohol)-phosphomolybdic heteropolyacid 혼합막

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Mixed matrix membranes of poly(vinyl alcohol) loaded with phosphomolybdic heteropolyacid for the pervaporation separation of water-isopropanol mixtures

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Abstract:

Mixed matrix membranes of poly(vinyl alcohol) (PVA), loaded with phosphomolybdic heteropolyacid (HPA) and crosslinked with glutaraldehyde have been prepared by the solution casting technique. Pervaporation (PV) experiments have been performed at 30℃ to separate water-isopropanol feed mixtures containing 10 to 40 wt.% of water. The membranes were characterized by DSC and DMTA to understand their thermal behavior and mechanical strength properties. At high content (i.e. 7 wt.% with respect to weight of PVA) of HPA, the mixed matrix membranes could extract water efficiently on the permeate side with a selectivity of 90,000 and a flux of 0.032 kg/m^{2}h for 10 wt.% of water containing feed mixture (the lowest feed composition of water studied). Flux of the mixed matrix membranes decreased with increasing concentrations of HPA.

1.Introduction

Liquid separation using polymer membranes has been an active area of research over many decades in view of its importance in process engineering as a clean technology. Innumerable types of polymers and their modifications have been attempted to develop membranes for such applications, but the recent trend has shifted towards the preparation of mixed matrix membranes involving filler and a polymer matrix. Inorganic compounds, when combined at the molecular level, with organic polymers could offer better advantages such as lightweight, flexibility, good moldability, high strength, thermal and chemical stability compared to the neat dense membranes[1]. Pervaporation (PV) is an efficient membrane-based technique used for the economical separation of liquid mixtures, especially aqueous - organic azeotropes, isomers, closely boiling mixtures, besides heat sensitive and hazardous compounds.[2].

In this Research, it has been demonstrated that by incorporating varying amounts of HPA, it is possible to develop the novel types of mixed matrix membranes of PVA for successfully testing them in PV dehydration of isopropanol. particularly; the PVA membrane containing 7 wt.% HPA exhibited a water selectivity to of 89,991 as compared to pristine crosslinked PVA membrane when tested for 10 wt.% water in the feed.

2. Experiments

2.1. Materials

Poly(vinyl alcohol)(MW: 125,000) with a degree of hydrolysis of 87%, isopropanol, glutaraldehyde(GA), HCl and Phosphomolybdic acid, $H3[P(Mo3O10)4]\cdot 2H2O$,were all purchased from s.d. fine chemicals, Mumbai, India. All other chemicals were of analytical reagent grade samples used without further purification.

2.2. Preparation of phosphomolybdic acid-incorporated PVA membranes

Phosphomolybdic acid-incorporated PVA mixed matrix membranes were prepared by the solution casting technique. PVA (4g) was dissolved deionized

water at 60℃ and the solution was filtered through a glass fiber filter to remove impurities. A known amount of phosphomolybdic acid (1, 2, 3, 4, 5, 6 and 7 wt.%) dissolved in 10 ㎖ of water was added to the prepared solution and was continuously stirred for 8 h at the ambient temperature. In situ crosslinking was done by adding 0.2 ㎖ of glutaraldehyde in acidic condition.. Membranes were dried at ambient temperature and peeled off from the glass plate. Membrane thickness was around 50±1.0m. Seven different mixed matrix membranes were prepared by incorporating 1, 2, 3, 4, 5, 6 and 7 wt.% phosphomolybdic acid with respect to weight of PVA.

2.3.Pervaporation experiments

Pervaporation experiments were performed in an apparatus designed indigenously [4], having effective surface area of the membrane in the cell is 28.27 cm^2: volume capacity of the cell is about 250 cm^3. Downstream side of the PV apparatus was continuously evacuated using a vacuum pump at a low pressure of 10 Torr. Experiments were performed with 10 to 40 wt.% water containing feed mixture. Feed and permeate were analyzed by using a refractometer (Atago, model 3T, Japan) as well as Nucon Gas Chromatograph (model 5765). The results of GC analysis agreed well with the refractive index measurements. Pervaporation selectivity (α), flux(J), permeation separation index (PSI) and enrichment factor (β)values have been calculated as follows:

$$\alpha = (P_w/P_{org})/(F_w/F_{org})$$
$$J = w/At$$
$$PSI = J(\alpha - 1)$$
$$\beta = C^P_w/C^F_w$$

where P and F are weight fractions of permeate and feed, respectively. Subscript w stands for water, org stands for isopropanol and C is concentration. Flux, J (kg/m^2 h) of water was calculated from the weight of liquid permeated, w(kg),effective membrane area, A (m^2) and measurement time, t (h).

3. Result and discussion

3.1. Scanning electron microscopy

Fig.1 shows a cross-sectional scanning electron micrograph of HPA/PVA-7 membrane. A molecular level distribution of HPA particles was observed into PVA matrix. During PV experiments, almost all the water molecules are adsorbed by HPA particles embedded in the PVA matrix. A uniform distribution of HPA particles into PVA matrix can be seen in the cross-sectional SEM photograph.
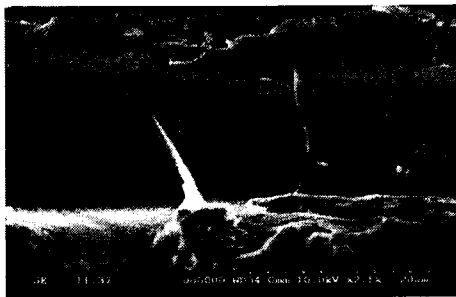

Fig 1. Cross-sectional scanning electron micrograph
of HPA/PVA-7 membrane

3.2. Differential scanning calorimetry (DSC)

DSC thermograms of the crosslinked PVA membranes containing different amounts of HPA are presented in Fig 2. PVA exhibited a relatively large and sharp endothermic curve dueto melting at 190℃ with an onset temperature at 170℃. The onset of melting temperature has shifted to lower temperature in case of mixed matrix membranes. With increasing HPA content, melting temperature has shifted to a lower region with the final melting temperature observed at 137℃ wt.% HPA containing PVA.

3.3. Degree of swelling(DS)

The % degree of swelling obtained from sorption experiments at 30 ○ .C for all mixed matrix membranes measured as a function of wt.% of water in the feed mixture. Fig. 3 shows DS of PVA membrane increased from with an
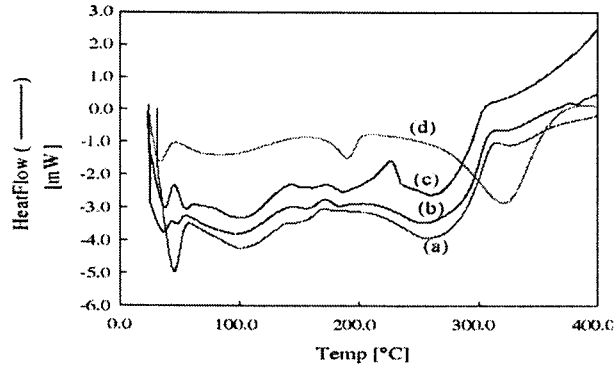
Fig 2. DSC thermograms of (a) PVA/HPA-1, (b) PVA/HPA-2, (c) PVA/HPA-3 and (d) pristine PVA membranes.

increasing water content of the feed mixture from 10 to 40 wt.%. A lower swelling was observed for PVA/HPA-1 membrane than for pristine PVA membrane; swelling decreased with increasing HPA content of thePVA membrane. Swelling results are in good agreement with the observed Tg values. Fig. 4 elucidates degree of swelling versus effect of HPA loading of the PVA matrix for 10 wt.% of water in the feed. The swelling results follow similar trends to those of flux of all the membranes.
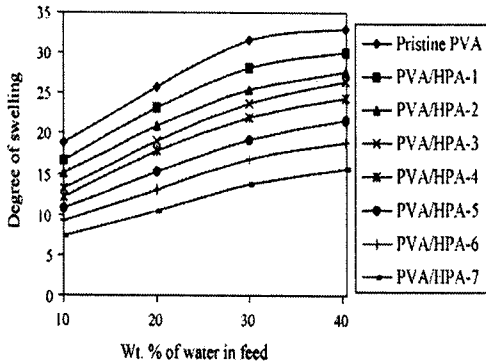

Fig 3. Degree of swelling vs. wt.% of HPA at 10 wt.% of water in the feed mixture at 30°C.
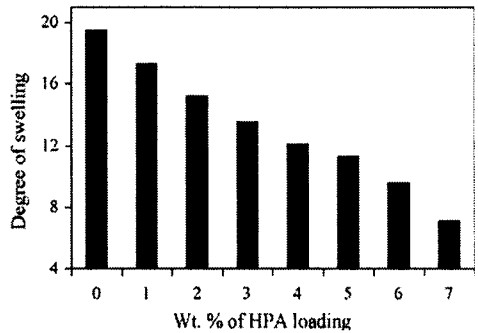

Fig 4. Degree of swelling vs. 10 wt.% of water in the feed mixture at 30°C.

3.4. Membrane performance

Membrane performance was studied by calculating flux and selectivity at different feed compositions of water-isopropanol feed mixtures (seefig 5). The mixed matrix membranes exhibited higher selectivity than the pristine PVA membrane, but flux values of all the mixed matrix membranes are lower than the pristine PVA membrane at all compositions of water in the feed. With an increasing amount of HPA in the PVA matrix, flux decreased, but selectivity increased considerably over that of pristine crosslinked PVA membrane. It may be noted that majority of studies have dealt with glutaraldehyde crosslinked PVA membranes in the presence of HCl and acetone mixture, wherein the latter is a non-solvent [5]. In the present study, PVA was crosslinked in situ with GA using HPA by maintaining the ratio between GA and PVA as the same and by varying the amount of HPA. Thus, HPA might act not only as reinforcing filler to PVA, but additionally, it would act as a reinforcing bridge between PVA segments and HPA due to electrostatic interactions.
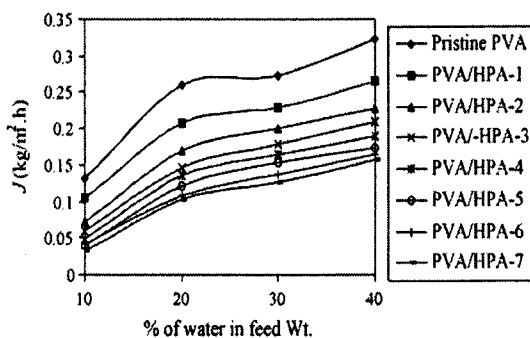

Fig 5 Flux vs. wt.% of water in the feed mixture at 30℃

3.5. Effect of HPA loadings

This prompted us to evaluate the effect of HPA on the PV performances of the mixed matrix membranes. It is observed that with increasing amount of HPA in the PVA matrix., membrane selectivity to water increased remarkably beyond 4 wt.% of HPA. This could be due to increased hydrophilic-hydrophilic interactions of the mixed matrix membranes with
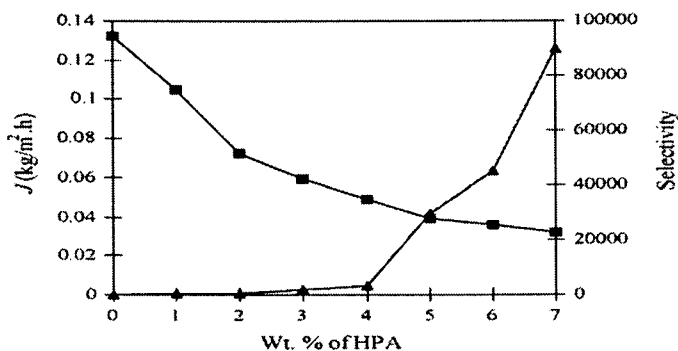
Fig 6. Flux and selectivity vs. wt.% of HPA in PVA matrix at 30°C. Symbols for selectivity (▲) and flux (■).

water molecules. from results notice that a selectivity of 77 observed for pristine PVA membrane was increased dramatically to 89,991 after the addition of 7 wt.% of HPA in PVA for the separation of 10 wt.% water containing feed. This effect clearly demonstrates the presence of HPA in PVA in enhancing membrane selectivity to water due to hydrophilic-hydrophilic interactions giving a lower flux.

4. References

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