



Preparation and Characterization of Poly (vinyl alcohol) Membrane for Pervaporation Separation of Water-Organic Mixtures

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(Received: December 20, 2011; Accepted: January 29, 2012)

ABSTRACT

Poly (vinyl alcohol) membranes were prepared by in-situ crosslinking of poly (vinyl alcohol) with glutaraldehyde as a crosslinking agent and hydrochloric acid as catalyst and the membranes were used to separate mixtures of IPA and water. Effects of feed composition, operating temperature, vacuum pressure and Reynolds number on permeation performance of the membranes were evaluated. The results showed that operating conditions have an effective influence on permeation properties of PVA membranes.

Key words: PVA membrane, Pervaporation, Crosslinking, Separation factor.

INTRODUCTION

Membrane-based pervaporation (PV) is an energy-intensive method for separating liquid mixtures compared to conventional distillation or cryogenic separation particularly involving azeotropic and closely boiling mixtures due to its high separation factor and flux rates¹⁻⁴. Separation efficiency depends on physicochemical properties of the membrane (hydrophobic or hydrophilic, chemical compatibility, mechanical strength, temperature resistance) and operation conditions (feed concentration, temperature, flow rate and pressure gradient across the membrane)⁵.

Hydrophilic polymeric materials have been widely investigated for PV dehydration. Poly

(vinyl alcohol) (PVA) is one of the most commonly polymer studied, because of its superior hydrophilic property, good film-forming ability and chemical stability⁶⁻⁸. However, PVA membranes have to be modified to restrict their swelling in aqueous solutions. So far, modification methods, such as crosslinking and blending, have been applied by many researchers, and water insolubility of PVA membranes has been improved dramatically, or swelling of the membranes reduced⁹.

In this work, PVA membranes were prepared by crosslinking of PVA with glutaraldehyde (GA) and heat treatment. Effects of operation conditions on performance of the membranes were also investigated.

EXPERIMENTAL

Membrane Preparation

PVA membranes were prepared by solution casting and solvent evaporation technique. PVA was dissolved in deionized water at 90°C then stirred for a period of 30 min to form a homogeneous solution. The solution was filtered through a glass fiber filter to remove insoluble impurities. *In situ* crosslinking was performed by adding GA and hydrochloric acid to the above solution and further stirred for about 3 h. The resulting solution was cast on a clean glass plate in a dust free environment to prepare the membrane. Membranes were dried at ambient temperature for 24 h and peeled off from the glass plate, then annealed at 125°C for 2-3 h.

PV Experiments

The prepared membranes were evaluated in PV separation using a setup as shown in figure 1. Mixtures of IPA-water with different concentrations were prepared and hold in a tank as feed volume of 5 L. The downstream pressure was maintained at about 1 mbar using a vacuum pump (Vac Torr), while the feed pressure was atmospheric. The feed temperature was controlled with a thermometer and a heater under the feed tank. The permeate vapor was collected in a cold trap in a liquid nitrogen trap to freeze the permeate. It was then heated to room temperature. The collected permeate sample was weighed to determine the flux. The analyses of feed

and permeate samples were performed by Gas Chromatography provided with a thermal conductivity detector (TCD) equipped with a DEGS or Tenax packed column of 1/8 in. i.d. having 2 m length. Permeation properties of the membranes were characterized by PV selectivity (α_{PV}) and total permeation flux (J_P) using the following equations, respectively:

$$\alpha_{PV} = \frac{y_A/y_B}{x_A/x_B} \quad \dots(1)$$

$$J_P = \frac{W_P}{At} \quad \dots(2)$$

Where y_A and y_B are mass fractions of water and IPA in the permeate, respectively and x_A and x_B are mass fraction of water and IPA in the feed, respectively. Flux of permeate, ($\text{kg}/\text{m}^2\cdot\text{h}$) was calculated using J_P , mass of permeate (kg); A , effective membrane area (m^2) and t , permeation time (h).

W_P

RESULTS AND DISCUSSION

Effect of feed composition on PV properties

Effects of feed composition on permeation flux and separation factor of PVA membranes are

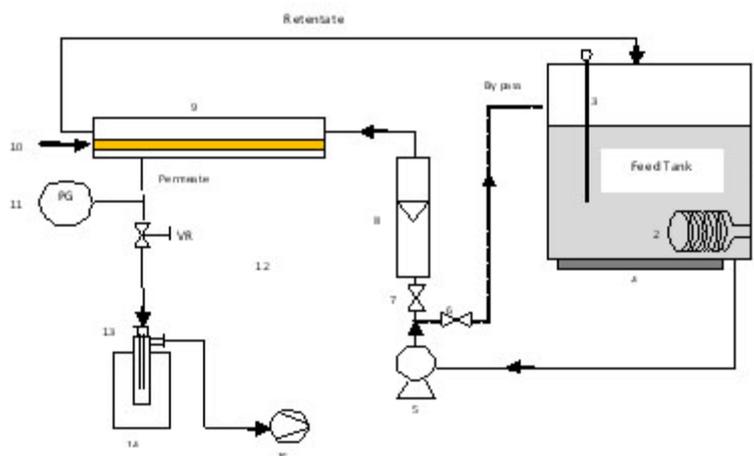


Fig. 1. Schematic diagram of the PV apparatus: (1) feed tank; (2) cooling coil; (3) thermal couple; (4) heater; (5) feed pump; (6,7) valve; (8) rotor flow meter; (9) membrane cell; (10) membrane; (11) pressure gage; (12) vacuum regulator; (13) permeate collection trap; (14) liquid nitrogen trap; (15) vacuum pump

presented in Fig. 2. As observed, permeation flux rapidly increases as the water content in the feed increases, and this is due to the membrane swelling. The swollen polymer has less resistance against IPA permeation because of the wider polymeric chains. As observed, with increasing the water content in the feed, permeation flux significantly increases from 0.107 to 0.429 (kg/m².h), but

separation factor sharply reduces from 179 to 45. The PVA membranes exhibit high hydrophilic properties due to the OH group of PVA, due to very strong interaction with water molecules and this consequently increases free volume of polymer chains and accordingly permeation flux. The increasing polymer free volume causes IPA and water molecules permeate transport more easily

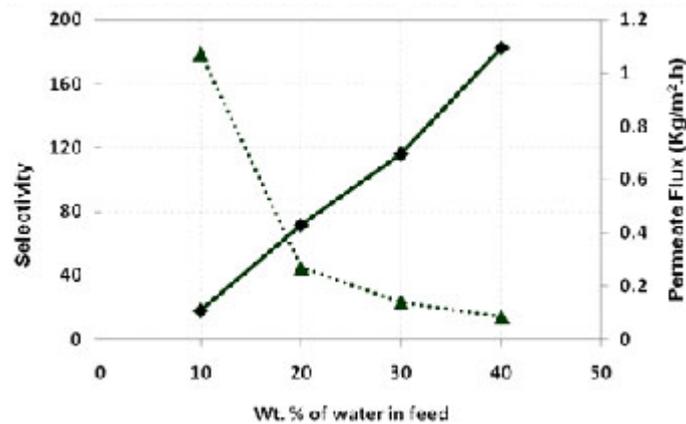


Fig. 2: Effect of feed composition on permeation flux and separation factor (with feed temperature of 30°C, permeate pressure of 1 mbar and Reynolds number of 1000)

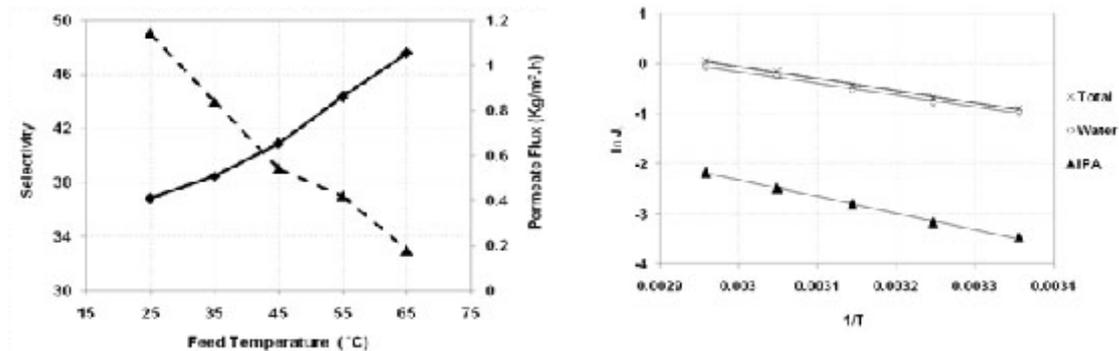


Fig. 3. (a) Effect of feed temperature on permeation and separation factor, (b) $\ln J_i$ versus $1/T$ (with feed composition of 20 wt. %, permeate pressure of 1 mbar and Reynolds number of 1000)

through the membrane and this decreases separation factor.

Effect of feed temperature on PV properties

Effects of feed temperature on permeation flux and separation factor were also studied. The

results are presented in Figure 3(a). It is well known that the operating temperature influences both the membrane intrinsic properties and driving force for transport of penetrates through the membrane. Increasing temperature increases thermal mobility of the polymer chains and consequently free

volume of the polymer matrix increase. Increasing free volume of the polymer matrix enhances transport of penetrates through the polymer media. As a result, permeation flux of water and IPA increase, however, the membrane selectivity reduces.

The driving force for permeation is the concentration gradient, resulting from the difference in partial vapor pressure of penetrates between feed and permeate mixtures. As the feed temperature increases, vapor pressure in the feed compartment increases, but vapor pressure at permeate side is not affected. This results in a higher driving force. Therefore, increasing the feed temperature affects the membrane performance in such a way that permeation flux increases, while water selectivity decreases.

Temperature dependency of permeation flux can be studied by the Arrhenius type relation as follows:

$$J_i = J_{i0} \exp\left(\frac{-E_{pi}}{RT}\right) \quad \dots(4)$$

Where J_{i0} is the Arrhenius constant, E_{pi} is the activation energy of permeating components, R is the universal gas constant and T is the feed temperature.

The Arrhenius plots of $\ln J_{tot}$, $\ln J_{water}$ and $\ln J_{IPA}$ versus $1/T$ are shown in Figure 3(b). The linear relationship observed suggests that temperature dependence on permeation flux follows the Arrhenius relationship.

Activation energies of the permeating components are listed in Table 1. As observed, the values of E_{pi} for both of water and IPA are positive. This indicates that permeation flux of the both permeating components increases with increasing feed temperature. If the value of E_{pi} is high, permeation flux would be more susceptible to change with temperature. As observed, $E_{p,IPA}$ is bigger than $E_{p,water}$, it means that the feed temperature has more influence on IPA flux than water flux. Therefore, increasing temperature results in less separation factor. At different temperatures, permeation flux of the both components and total flux are listed in Table 2. Accordingly, with increasing temperature, permeation flux of IPA increases more drastic rather than that of water and consequently separation factor of water decreases.

Effect of vacuum pressure on PV properties

PV operation is carried out by applying vacuum or sweep gas to the permeate side of the membrane, which creates a chemical potential difference between the permeate side and the feed side.

Table 1: Activation energies of the permeating components

Components	E_{pi} (kJ/mol)
Water	19.41
IPA	27.50
Water + IPA	20.15

Table 2: Effects of feed temperature on permeation performance.

Operating Temperature (°C)	α_{pv}	J_{tot}	J_{water}	J_{IPA}
25	49	0.411	0.380	0.031
35	44	0.507	0.465	0.042
45	39	0.652	0.591	0.061
55	37	0.859	0.775	0.084
65	33	1.053	0.939	0.114

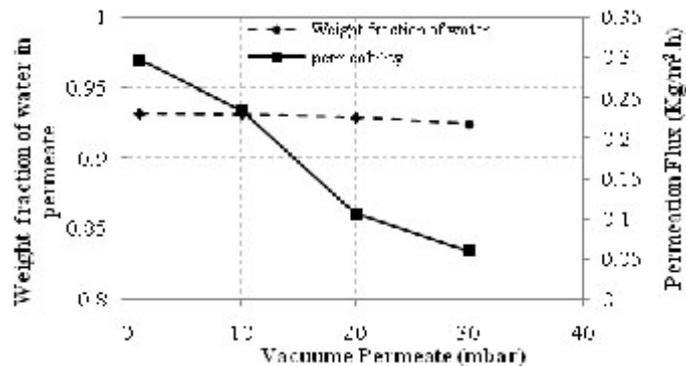


Fig 4. Effect of vacuum pressure on PV performance of the PVA membrane

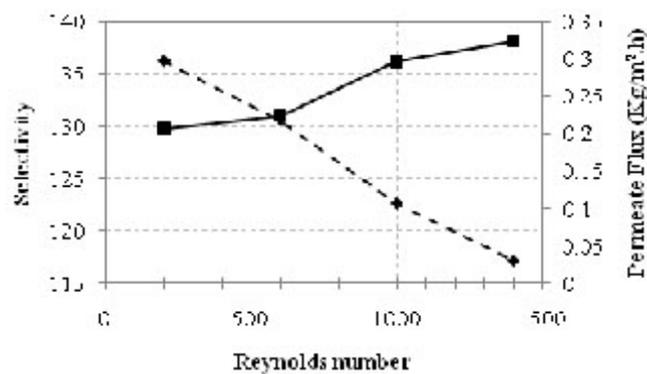


Fig. 5: Effect of Reynolds number on PV performance of PVA membranes.

The relationship between the permeate side pressure and the permeating component flux can be expressed by the following equation:

$$J_i^p = J_{i0}^p * (C_i \gamma_i P_i^0 - P_i^1) \quad \dots(5)$$

Where J_i^p is the permeation flux of species i , J_{i0}^p is the pressure-normalized permeation flux of species i through the membrane, C_i is the mole fraction of species i at the upstream surface of membrane, P_i^0 is the saturation vapor pressure of species i at the feed temperature, γ_i is the activity coefficient of species i in the feed and P_i^1 is the partial pressure of species i in the permeate side of membrane. Increasing vacuum pressure results in the higher partial pressure of species i increase, and thus, according to Equation 5, the less driving force through the membrane. Fig. 4 presents effect of vacuum pressure on PV properties. It can be observed that permeation flux decreases as the

permeate pressure increases. However, weight fraction of water in permeate did not change significantly.

Effect of Reynolds number on PV operation

Generally, increasing feed flow rate or Reynolds number results in the thinner boundary layer thickness and the bigger mass transfer coefficient. These are advantageous for permeation of water/IPA mixtures. The effect of Reynolds number on the membrane performance was studied using four Reynolds number levels so that laminar and turbulent patterns could be considered. PV experiments with Reynolds numbers of 200, 600, 1000 and 1400 were carried out. Vlasogiannis et al. were also studied on the pattern of flow in a membrane cell. According to their results, with Reynolds number of more than 600, turbulent pattern can be obtained⁴.

As observed in Figure 5, with increasing Reynolds number, the amount of turbulency in the feed solution increases and the boundary layer thickness decreases, i.e., the extent of concentration polarization on the upstream membrane surface of decreases. Therefore, mass transfer resistance of the boundary layer decreases leading to the higher permeation flux correspondingly. However, with increasing Reynolds number, permeation of both IPA and water increases and results the reduction of selectivity.

CONCLUSIONS

PVA membranes crosslinked by GA appear to have promising potential for dehydration

of aqueous solution of IPA. With increasing feed water concentration, the membrane's performance was found to be affected substantially by increase in the extent of swelling of the polymer which resulted in a rise in permeation flux but reduction in separation factor. The permeation flux increased as the feed temperature increased, but separation factor decreased. On other hand, the temperature dependence of permeation flux can be elucidated by an Arrhenius type relationship. Increasing permeation pressure (lower vacuum) caused a reduction in permeation flux and also water selectivity. With increasing Reynolds number the permeation flux decreased due to reduction of boundary layer thickness.

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