Comparison of Single and Double-Network PVA Pervaporation Performance: Effect of Operating Temperature

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Abstract

Thermal crosslinking sequential method applied for DN-PVAs generation efficiently. The swelling measurements investigated that the hydrophilicity of the membrane decreases because of the collaboration of the second thermal crosslinked PVA matrix. The dehydration performance of ethanol solution showed improved using the thermal crosslinked double network PVA membrane. The pervaporation dehydration of the water-ethanol mixture was investigated at different conditions. The separation selectivity showed a significant improvement, while the permeation flux declines due to the incorporation of the second PVA network under 95 % ethanol and at 40 °C. Increasing the feed temperature enhanced the permeability of the membrane, while decreasing the water content in the feed resulted in an increase in the selectivity. The overall results showed that, at high operating temperature and high ethanol concentration in the feed, the prepared membranes are highly selective towards the water with reasonable fluxes values. The influence of temperature permeation parameter and diffusion coefficient of the feed component is also discussed. The negative heat of sorption (ΔH_s) values calculated on the basis of the estimated Arrhenius activation energy values indicates that the sorption process is controlled by Langmuir's mode.

Keywords

thermal crosslinking, ethanol dehydration, hydrophilic pervaporation, double network, interpenetration, poly(vinyl alcohol)

1 Introduction

It is well known that bio-fuels including bio-ethanol have several environmental benefits. Among them, absolute ethanol containing 99.5 % (by mass) or more ethanol is in the greatest demand [1]. Ethanol was used to be dehydrated by the distillation separation process. However, high costs, low productivity are recognized as challenging problems leading to a crucial disadvantage and result in increasing the costs of the process essentially the industrial production of highly concentrated bioethanol [2, 3]. Pervaporation technology (PV) has received much attention due to its potential in energy efficiency, simplicity, economically friendly and high efficiency of separation [4–6].

The mechanism of the pervaporation is usually explained with the so-called solution-diffusion model. When the feed mixture is in direct contact with the membrane surface, one component of the liquid mixture is selectively adsorbed/ solved in the active layer of the membrane and then permeates through the membrane according to the mechanism of diffusion. The driving force is complex; typically the chemical potential difference is considered but applying sweep gas, or a vacuum pump also contribute to the permeation. The permeate is in the vapor phase, so the heat of evaporation is required in this separation process since phase change takes place [7]. The permeate is condensed and collected in a trap cooled by dry-ice or liquid nitrogen [1-4]. Poly(vinyl alcohol) (PVA) has been widely used for pervaporation process owing to its high hydrophilicity, film-forming ability, resistance to organic pollution, non-toxicity, biodegradable and chemical/thermal stability. PVA is a water-soluble synthesis polymer with -OH groups on its backbone, which crucially provides distinguishing sorption and diffusion of water in it and facilitates its modification [8, 9].

A second network (DN) of PVA can be efficiently produced with heat treatment which will overcome the drastically decrease of the permeation flux by introducing an extra hydrophilic group to the polymer network. Meanwhile, it enhances the selectivity of the membrane by withstanding the swelling behavior of PVA [5]. However, only a few studies reported the use of prepared DN membranes for alcohol dehydration where phase separation between the two networks frequently happens because of the elusive compatibility between the different polymers. Overcoming the miscibility between two networks and the inconsistency between the two polymers, DN would be prepared from the same polymer like the membrane [6–8].

The aim of this paper is to investigate the effect of feed temperature on dehydration performance of the prepared DN PVA composite membrane for 95 wt% ethanol (near the azeotrope) at 40, 50, and 60 °C. Effect of the second network on diffusion and several pervaporation properties was reported. Activation energies of permeation, diffusion, and heat of sorption ΔH_s are evaluated and the results are discussed.

2 Material and methods

Poly (vinyl alcohol) solution of 10 wt% is prepared by dissolving PVA powder (85000–124000 g/mol and 99 %+ hydrolyzed, Sigma-Aldrich, Germany) in distilled water on 90 °C and mixed until a homogeneous solution is formed. The first network of the membrane is obtained by casting the solution on a clean glass sheet using elecometer stainless steel casting machine with an initial casting thickness of 250 μ m. Next, the membrane is dried at room temperature for more than 24 h till totally dry and called pristine PVA, then the membrane is annealed in an oven at 40 °C for 3 h and named PVA. The second network of PVA is formed by casting the solution prepared previously. Consequently, the second network entirely dried at room temperature and the obtained film is designated as DN-PVA, and then thermally crosslinked at 120 °C over 1 h to obtain DN-PVAs.

2.1 Swelling measurements

Swelling measurements were done by immersing the dry weighted membranes in a different water-ethanol mixture at room temperature for 24 h to achieve equilibrium. Therefore, the membranes were taken out and dried carefully with tissue paper to remove the surface solution and weighted as fast as possible and immersed in the mixture solutions again. Each membrane was measured three times and the average was taken as the final result. The Degree of Swelling percentage is calculated by Eq. (1):

$$DS\% = (Ms - Md)/Md \times 100.$$
(1)

2.2 Pervaporation experiments

Pervaporation dehydration experiments are carried out using a P-28 membrane unit (CM-Celfa AG Company, Switzerland) with the effective membrane area 28.0 cm². The pressure in the permeate side is maintained 5.4 mbar using a vacuum pump. All the membranes are swelled in the feed for 2 h before the PV test, and the permeate is collected in cold traps immersed in liquid nitrogen. The concentration of the feed and permeate is measured by the RA-620 (accuracy ± 0.00002 , KEM Kyoto Electronics, Japan) refractometer. Separation performances of the membranes can be calculated on the basis of total flux (*J*) and separation factor (α PV):

$$J = W/(A \times t) \tag{2}$$

$$\alpha_{\rm PV} = \left(P_w / P_{eth} \right) / \left(F_w / F_{eth} \right) \tag{3}$$

where J is the flux; W is the collected permeate mass (kg); A is the effective area of the membrane (m²), and t is the permeation time (h), P_w , P_{eth} is the weight fraction of water and ethanol in the permeate mixture and F_w , F_{eth} are the mass fraction of water and ethanol in the feed mixture, respectively. The permeance (Q_i) and selectivity (β) can be calculated as follows:

$$Q_i = P_i / L = P_i / \left(x_i \gamma_i P_{i,\text{feed}}^\circ - y_i P_{\text{permeate}} \right)$$
(4)

$$\beta = Q_{\text{water}} / Q_{\text{ethanol}} \tag{5}$$

where P_i is the permeability of component *i* through the membrane, *L* is the membrane thickness (m), J_i is the mass flux of component *i* (g/(m² × h)), x_i is the mole fraction of component *i* in the feed liquid, γ_i is the liquid activity coefficient of component *i* in the feed, $P_{i,\text{feed}}^\circ$ is the pure component *i* feed vapor pressure under feed temperature (kPa) and y_i is the mole fraction of component *i* in the permeate, P_{permeate} is the pressure in the permeate side of the membrane (kPa).

3 Results and discussion

3.1 Effect of DN on pervaporation properties at different feed composition

Generally, the incorporation of the second network strongly affects membrane properties. Fig. 1 (a) and (b) summarizes



Fig. 1 Influence of the DN on the PV performance at 40 °C as function of feed concentration (a) Total flux, (b) Separation factor.

the flux and separation factor data for the pervaporation separation of the ethanol/water at different ethanol concentration in feed mixture at 40 °C. The water plasticization effect of water was reported by Park et al. [9].

Although, water has two plasticization behavior self and cross plasticizing effect. For the water - ethanol mixture, the permeation is depending on the self-plasticizing only as reported by Yeom and Huang [10]. However, both plasticization behavior are influenced by the feed concentration and operating temperature. The results show that increasing the water content results in increasing the fluxes while the separation factor is decreasing for both membranes. That is could be attributed to the fact that, increasing the water concentration in the feed will lead to increase the self-plasticizing and diminish the cross- plasticizing action. Therefore, increasing the membrane plasticization due to increasing the interaction between the water and the membrane. Moreover, the higher water content in the feed will results in higher swelling in the membrane. Consequently, increasing the free volume and the permeation flux while decreasing the separation factor [11].

One can see that the second network affect also on the swelling behavior of the membrane. Fig. 2 shows the swelling behavior of both membranes at the same conditions. It is clear that the double network membrane exhibits a lower swelling degree and it is increasing with higher



Fig. 2 Swelling behaviour of the DN-PVAs membrane compared to the pristine PVA membrane as function of water content in the feed.

water content in the feed solution. Although, the hydrophilicity of the membrane should be increasing with the incorporation of the DN of PVA due to the insertion of more hydrophilic groups to the network, the interaction between the two PVA networks result in diminishing the water during the condensation reaction [12, 13]. Additionally, heat treatment decreases the number of the hydroxyl group with further sweeping of water which leads to reducing the hydrophilicity of the polymer owing to the decrease of the solubility in water and resulting in a slight reduction in the swelling degree of the DN-PVAs [14, 15]. However, the swelling degree is increasing for both membranes with increasing the water content in the feed due to the increased affinity of the membrane towards water [16, 17].

3.2 Effect of operating temperature on DN pervaporation performance

From Fig. 3, it is observed that increasing the temperature of the feed mixture results in increasing the permeation flux for the both membranes. This is contributed to that increasing the temperature is increasing the polymer chain mobility and consequently the free volume [18]. Additionally, higher temperature results in higher driving force across the membrane hence the vapor pressure increasing at elevated temperature while the permeate side pressure is negligible. Therefore, increasing the fluxes of both membranes and decreasing the separation factor [19].

However due to the coalition of the second network of PVA results in a narrow network of the DN-PVAs. In addition, as result of the heat treatment, the alliance of membrane towards water has significantly decreased resulting in decreasing the water content in the swollen membrane [20]. Thus, the total permeation flux obtained from the DN-PVAs was lower comparing to the PVA membrane. On the contrast, the observed separation factor of the DN-PVAs is the highest and that due to the narrow network of the DN-PVAs membrane which allow only water (the smallest molecule size) to penetrate compares to the loose PVA structure.



Fig. 3 Effect of operating temperature on the dehydration performance of 95 wt% ethanol in the feed, (a) Flux, (b) Separation factor.

For better understandings the individual fluxes for water and ethanol through both membranes were evaluated and presents in Fig. 4.

Fig. 4, remarkably show that however the water flux for the pristine membrane is higher compared to the DN-PVAs. However, comparing the ethanol fluxes for both membranes, it is noticed that the ethanol flux of the DN-PVAs is significantly lower compared to the pristine membrane. This could be attributed to the narrow structure of the DN-PVAs which provide lower fluxes but higher selectivity for water.

Additionally, for better evaluation to the membrane the intrinsic properties (selectivity, water and ethanol permanence) were investigated from Eqs. (4) and (5) and represented in Fig. 5 (a), (b), and (c) respectively [19].

The graphs reveals that the selectivity of the DN-PVAs membrane is significantly higher than the pristine membrane. While ethanol permeance of the pristine membrane are much higher than the DN-PVAs membrane. That proves that the interpenetration of the second network increase the water selectivity of the membrane, however it decrease the water permeance. The temperature dependence of permeation and diffusion can be properly expressed by an Arrhenius type equation:



Fig. 4 Influence of operating temperature on the individual component fluxes at different temperature for dehydration of 95 wt% Ethanol in the feed.

$$X = X_0 \times \exp\left(\left(-E_x\right)/(RT)\right),\tag{6}$$

where E_x represents apparent activation energy for permeation or diffusion depending on the transport process under consideration and RT is the usual energy term.

Where the diffusion coefficient is estimate using the individual flux of component *i* through the membrane expressed by Fick's law as:

$$J_i = -D_i \left(\frac{dC}{dx} \right), \tag{7}$$

where J_i , D_i , and C_i are the permeation flux (kg/(m² × s)), the diffusion coefficient (m²/s) and the concentration (kg/m³) of component *i* in the membranes. For the sake of simplicity, it is assumed that the concentration profile along the diffusion length is linear and therefore, concentration-averaged diffusion coefficient D_i can be calculated with the following modified equation (Eq. (8)) where δ is membrane thickness. This assumption was reported in literature [20, 21].

$$D_i = (J_i \delta) / C_i \tag{8}$$

The diffusion coefficient of water and ethanol were calculated and presented in Fig. 6. The results show that however the fluxes of the DN-PVAs is lower than the pristine membrane, yet the diffusivity of water inside the DN-PVAs is higher than through the PVA membrane. This is contributed to the high affinity of the fabricated membranes towards water compared to the pristine membrane. Additionally, for both membranes the ethanol diffusivity is almost obsolete compared to the water.

Arrhenius plots for temperature dependence on total permeation flux and total diffusion are shown in Fig. 7 (a) and (b), respectively.

The full results from the Arrhenius equation plots including the activation energies of the total and individual components are listed in Table 1.

From Table 1, it is noted that the activation energy values ethanol is remarkably high compared to those



Fig. 5 Influence of operating temperature on the intrinsic properties of the membrane, (a) selectivity, (b) water permeance and (c) ethanol permeance.



Fig. 6 Effect of temperature on diffusion coefficient in pervaporation of 5 wt% H₂O in ethanol.

of water (E_{PW}) indicating that DN-PVAs membrane has a higher separation efficiency towards water. That's why, the activation energy values for water permeation and total permeation (E_p) are closed to each other. Additionally, it is noticed that the activation energy needed both permeation and diffusion for both water and ethanol are higher for the DN-PVAs compared to the pristine membrane. This indicate that, however water require more energy to pass through the membrane, but also the ethanol energy is much higher. Hence, commonly, the feed component with higher sensitivity towards increasing temperature will have higher activation energy. This is assigned to

- 1. the narrow and compact structure of the fabricated DN-PVAs
- 2. the high affinity of this membrane towards water.

Using these activation energy values in Table 1, the heat of sorption can be calculated by Eq. (9) [21]

$$\Delta H_s = E_p - E_D. \tag{9}$$

The results are presented also in Table 1. The negative heat of sorption ΔH_s values indicates that the sorption process is controlled by Langmuir's mode.

4 Conclusions

In this work, thermal crosslinking is applied for DN-PVAs generation efficiently. The declination in the swelling degree of the DN-PVAs proves the increase in the crystallinity character of the PVA membranes.

Furthermore, ethanol dehydration performance is improved using DN-PVAs. The pervaporation dehydration of the water-ethanol mixture was investigated at three different feed compositions at 40 °C. The separation selectivity showed a significant enhancement, while the permeation flux declines due to the incorporation of the second PVA network with 95 % ethanol and at 40 °C. This was discussed due to the narrow network of the DN-PVAs membrane which allows only water to penetrate on the contrary to the loose PVA structure. Arrhenius equation has been used to investigate the influence of operating temperature on the pervaporation performance. The significantly lower activation energy values obtained for water permeation as compared to ethanol prove that the membranes developed in this work demonstrate excellent separation efficiency towards water. The close magnitudes of E_p and E_{D} indicate that both permeation and diffusion contribute almost equally to the pervaporation process.

The negative sorption heat values (ΔH_s) for the membranes suggest that the sorption process can be controlled by the Langmuir's theory.



Fig. 7 Arrhenius plot for both flux (a) and diffusion (b).

 Table 1 Activation energied for permeation and diffusion for both

pristine and DN membrane.		
Parameters (kJ/mol)	DN-PVAs	PVA
E _D	20.2495784	17.600738
E_{DE}	39.1614342	32.678177
E_{DW}	19.78732	17.2615268
E_p	20.0084724	17.3754286
E_{PE}	37.6674084	30.7277126
E_{PW}	19.770692	15.3110624
ΔH_s	-0.241106	-0.2253094
$\Delta H_{_E}$	-1.4940258	-1.9504644
$\Delta H_{_W}$	-0.016628	-1.9504644

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Nomenclature

DS	Degree of Swelling (%)
Ms	Mass of swollen membrane (g)
Md	Mass of swollen membrane (g)
J, J_i	Total and individual fluxes $(kg/m^2 \times h)$
W	Mass of collected permeate (g)
A	Effective membrane area (m ²)
t	Pervaporation operation time (h)
αPV	Separation Factor (-)
P_{w}, P_{eth}	Weight fractions of water and ethanol in perme-
	ate (-)
F_{w}, F_{eth}	Weight fractions of water and ethanol in feed (-)
Q_i	Permeance of component <i>i</i> (g/m ² × kPa × h)
P_i	Permeability of component <i>i</i> (Pa/m)
<i>L</i> , δ	Thickness of membrane (m)
x_i, y_i	Mole fraction of <i>i</i> in the feed and permeate (-)
γ_i	Liquid activity coefficient of component <i>i</i> (-)
P_i°	Pure component <i>i</i> vapor pressure (Pa)
β	Membrane selectivity (-)
D_i	Diffusion coefficient of i (m ² /s)
C_i	Concentration (kg/m ³)
E_{x}	Apparent activation energy (kJ/mol)
R	Universal gas constant (8314 kJ/(K×mol))
Т	Temperature (°C)
E_D	Diffusion activation energy (kJ/mol)
$E_{_{DE}}$	Ethanol diffusion activation energy (kJ/mol)
E_{DW}	Water diffusion activation energy (kJ/mol)
E_p	Permeation activation energy (kJ/mol)
\dot{E}_{PE}	Ethanol permeation activation energy (kJ/mol)
E_{PW}	Water diffusion activation energy (kJ/mol)
ΔH_s	Heat of sorption (kJ/mol)
$\Delta H_{_W}$	Water heat of sorption (kJ/mol)
$\Delta H_{_E}$	Ethanol heat of sorption (kJ/mol)

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