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Pervaporation separation of dimethyl carbonate/methanol azeotrope through cross-linked PVA–poly(vinyl pyrrolidone)/PAN composite membranes

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ABSTRACT

Pervaporation (PV) separation of dimethyl carbonate/methanol azeotrope was investigated using composite membranes consisting of Poly(vinyl alcohol) (PVA)/poly(vinyl pyrrolidone) (PVP) blend membrane as active layer and a polyacrylonitrile ultrafiltration membrane as substrate. The active layer was physically blended and cross-linked with glutaraldehyde (GA). The chemical and physical properties of the blend membranes with different proportions of PVA/PVP were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), X-ray diffraction, thermogravimetric analysis, and contact angle measurement. The PV properties of the membranes were investigated by the separation of azeotrope. The effects of PVP, GA content, and operating temperature on PV performances were investigated. Permeation flux increased with increasing PVP content and feed temperature, while separation factor decreased. However, the separation factor increased with increasing GA content, whereas the flux decreased. The results showed that the membrane containing 70 wt% PVP and 0.5 wt% GA exhibited excellent PV properties with a flux of 955.77 $g\,m^{-2}\,h^{-1}$ and separation factor of 68.00 at 50°C.

Keywords: Pervaporation; Composite membranes; PVA/PVP; Dimethyl carbonate/methanol azeotrope

1. Introduction

Pervaporation (PV) is a cost effective and eco-friendly clean membrane separation technology. It is considered as a prospective industrial separation process. As its separation efficiency relies on the differences in sorption and diffusion properties of the permeating molecules, PV has gained much attention to separate organic mixtures, especially to separate azeotropic mixtures or close boiling point mixtures [1,2].

Dimethyl carbonate (DMC) is a nontoxic, good biodegradable, and environmentally benign methylating, carbonylating, and methoxylating agent that can replace hazardous chemicals like phosgene, dimethyl sulfate, chloromethane, and methyl chloroformate in

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many chemical processes [3]. Up to now, three methods of nontoxic DMC synthetic processes have been suggested: (a) phosgenation of methanol (MeOH), (b) oxidative carbonylation of MeOH, and (c) transesterification of ethylene carbonate with MeOH [4,5]. The use of excess MeOH, however, causes a purification problem because MeOH forms an azeotrope with DMC at a composition of 30 wt% DMC and 70 wt% MeOH under normal pressure. This azeotrope was difficult to be separated by simple distillation. Some conventional methods of low temperature crystallization, high-pressure distillation, azeotropic distillation, and extractive distillation have been thoroughly investigated and used for the purification. But, these processes suffer from high capital investment, high energy consumption, low efficiency, and complicated operation.

For the separation of the azeotropic composition (30 wt% DMC and 70 wt% methanol), the single PV is used to destroy azeotropic point and then separated by traditional rectification. The high flux is important in the section of PV. Therefore, the choice of membrane material is the key to the success of PV by giving high flux. Its purification by PV has been reported in the literatures using various membranes materials, such as Poly(vinyl alcohol) (PVA)–poly(acrylic acid) (PAA) blend membrane [6], cross-linked PVA membrane [7], ZSM-5 zeolite-filled chitosan (CS) membrane [8], CS–silica [9] and silicotungstic acid hydrate (STA) –CS hybrid membranes [10]. PV composite membranes consist of the thinner skin layer coated on a porous support layer to achieve a higher permeation rate and sufficient mechanical strength, which are often widely used in industry.

In this paper, porous polyacrylonitrile (PAN) ultrafiltration (UF) membrane as support layer is selected for its hydrophilic character. It is widely used as support layer for dehydration applications in PV technology [11,12]. PVA/Poly(vinyl pyrrolidone) (PVP) blend membranes with different proportions through the cross-linking with glutaraldehyde (GA) are selected as separating layer. PVA membranes are widely used in PV processes as it has excellent characteristics such as high selectivity towards water, chemical stability, and film-forming ability [13–17]. PVP is an idea hydrophilic membrane material, which can easily blend with other organic or inorganic compounds. PVP is chosen as the additive to blend with PVA, with the aim of hindering the PVA crystallization by the hydrogen bonds between the two polymers and making the membranes more permeable to molecular species [18]. Moreover, the miscibility between PVP and methanol is much stronger than that between PVP and DMC, which makes it reasonable to suppose that the PV performance of pure PVA membrane may be enhanced by incorporating PVP [19]. To reduce excessive swelling, polymer blending is accompanied by cross-linking and annealing which can all strongly influence permeability or selectivity [20–22]. The PVA/PVP membranes loaded with phosphomolybdic acid and the cross-linked PVA/PVP blend membranes have been successfully used for dehydration of ethanol and THF, respectively [23,24]. The GA crosslinked PVA/PVP blend membrane for separation of MeOH/DMC mixture has been explored to a very limited extent [25]. So, an in-depth study of separation of MeOH/DMC azeotropic mixture in composite-type PV membrane was investigated in the present study.

2. Experimental

2.1. Material

PVP (K–30, Mw ≈ 30,600) was purchased from Sinopharm Chemical Reagent Co., Ltd. PVA (hydrolyzed 99%, with average Mw = 89,000–98,000) and GA (25 wt % in water) was both supplied by Aldrich Chemicals (USA). DMC and MeOH were purchased from Shanghai Petrochemical Co. Ltd (SINOPEC, China). Porous UF membrane of PAN (PAN) (Cut–off M_W 5×10^4) with pure water flux of 500 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ was obtained from the Development Center of Water Treatment Technology (China). All the chemicals were used without further purification.

2.2. Preparation of cross-linked PVA/PVP composite membranes

The technique of PVA/PVP composite membrane preparation follows a procedure reported in references [26]. PVA (5 g) was dissolved in 100 ml water by refluxing and stirring for 6 h at 100℃. PVP particles were dispersed in water, sonicated for 30 min, and added to the previously prepared PVA solution. The blend solutions were prepared by varying composition of PVA/PVP weight ratio from 90/10 to 10/90. To this polymer solution, HCl as a catalyst and a certain amount of cross-linking agent (GA) was added and the reaction stirred for 24 h at room temperature. PAN porous UF membranes as supported membranes, which had been treated with about 4 wt % 1 N sodium hydroxide solution for 24 h, were washed and rinsed by about 4 wt% 1 N hydrogen chloride solution and deionized water till neutrality and air-dried. The resulting solutions were cast on a clean Plexiglas and on PAN-supported membranes using a casting knife, respectively. The membranes in the gelatination state were allowed to evaporate slowly till dried at room temperature. Finally, the membranes were annealed in vacuum at temperature 100℃ for 1 h for thermal cross-linking. Homogeneous membranes with the average thickness of 50 μm were used to carry out membrane characterization and swelling experiments. The composite membranes were used to carry out PV experiments with the average thickness of 100 μm.

2.3. Characterization of membranes

2.3.1. Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis

The interaction between PVA and PVP, the cross-linking reaction of blend membrane with GA were both confirmed using the Nicolet AVATAR 360 FTIR Spectrophotometer. FTIR spectra were recorded within the range of 4,000–400 cm^{-1}.

SEM (FEI Quanta 200, Holland) was used to study the morphology of the cross-linked PVA–PVP composite membranes. All specimens were coated with a conductive layer of sputtered gold.

The thermal stability of the cross-linked PVA–PVP membrane active layer was analyzed with Setaram SETSYS Evolution 16 thermogravimetric analyzer by heating from room temperature to 650℃ at a rate of 10 $℃\,\mathrm{min}^{-1}$ under nitrogen gas.

The XRD patterns of the membrane samples were characterized by a Germany Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. The angle of diffraction was varied from 8° to 50° using a step size of 0.02°.

2.3.2. Contact angle measurements

The relative hydrophilicity was determined by measuring the contact angle of a water drop (2 μl) deposited onto the dry membrane surface. Contact angle was measured by DSA100 instrument using static sessile drop method with gonio meter (Germany, Kruss Company). To reduce evaporation effect, measurements were made as quickly as possible (less than 10 s). The average contact angle data were taken for each membrane from five parallel experiments.

2.4. Swelling experiments

The dry PVA–PVP blend membranes with different mass ratios were weighed before being immersed in DMC–MeOH (70 wt%) azeotropy mixture at 30℃ in a thermostatic bath for 48 h. The swollen membrane sample was taken out from the solution, wiped with filter paper to remove the surface liquid, and then quickly weighed. All experiments were repeated at least three times. The results were averaged.

The degree of swelling (DS, %) was calculated by

$$\mathrm{DS}\ (\%) = \frac{W_s - W_d}{W_d} \times 100\% \tag{1}$$

where W_d and W_s were the weights of the dried and swollen membranes, respectively.

2.5. Pervaporation experiments

The experimental PV setup was used as reported in our previous article [25]. The membrane was installed in a stainless-steel membrane cell with the effective surface area of 51.53 cm^2 in contact with feed mixture. The feed solution was continuously circulated from a feed tank at a relatively high flow rate 200 L/h to the upstream side of the membrane in the cell at the desired temperature by a pump. The feed temperature in the range of 40–60℃ was monitored by a digital vacuometer. PV experiments were carried out by maintaining atmospheric pressure on the feed side while on the permeate side about 10 mbar within ± 1 mbar with a vacuum pump. Upon reaching steady-state conditions which was obtained after about 1 h throughout the experiments, permeate vapor was collected in liquid nitrogen traps with certain intervals (1 h), and weighted to calculate the permeate flux. The concentration of both the feed and permeate was measured by gas chromatography (SP 6890 with an FID detector, SE30 1.5 M, id = 0.25 mm column temperature 20℃, injector temperature 180℃, and FID temperature 180℃, Lunan Ruihong of China) to calculate the separation factor.

The permeation flux (J, $\mathrm{g\,m^{-2}\,h^{-1}}$) was defined as follows:

$$J(\mathrm{g\ m^{-2}\ h^{-1}}) = \frac{W(\mathrm{g})}{A(\mathrm{m}^2) \times t(\mathrm{h})} \tag{2}$$

where W is the weight of penetrant, A is the effective membrane area, and t is the measuring time.

The separation factor α was calculated by:

$$\alpha = \frac{y_{\mathrm{MeOH}}/y_{\mathrm{DMC}}}{x_{\mathrm{MeOH}}/x_{\mathrm{DMC}}} \tag{3}$$

where x_{MeOH}, x_{DMC} and y_{MeOH}, y_{DMC} are the mole fraction of MeOH and DMC in the feed and permeate, respectively.

3. Results and discussion

3.1. Membrane characterization

3.1.1. FTIR analysis: interaction

The homopolymer solutions of PVA, PVP, and their blend solutions were optically clear. No phase separation or precipitation was observed even after keeping the mixture for a longer time at ambient temperature. Fig. 1 represents the interaction between the blended polymers and the cross-linking mechanism of PVA with GA as reference [25,27].

Based on the above related reaction, GA cross-linked PVA/PVP blend membranes can be analyzed by FTIR spectra. As shown in Fig. 2, the FTIR spectra of cross-linked pure PVA (e) shows the main characteristic bands: 3,200–3,600 cm^{-1} of the –OH stretching vibration peaks, 2,888–2,931 cm^{-1} of the C–H stretching vibration peaks, 1,024 cm^{-1}, 1,062 cm^{-1} of the C–O–C asymmetric stretching vibration peaks, and 1,150 cm^{-1} of the C–O–C bond stretching vibration with the crystallization. The main characteristic bands of pure PVP (a) membrane are located at 1,613 cm^{-1} due to the stretching band of C=O, 1,385 cm^{-1} for the stretching band of C–N. Spectra of GA cross-linked PVA/PVP blend membranes (b, c, d) show peaks that come from both PVA and PVP. At higher PVP contents in the blend, the peaks of C=O become intensified and move to 1,662 cm^{-1} owing to C=O bond of PVP formation of hydrogen bonds with the O–H of PVA. These phenomena suggested that PVA and PVP are perfectly compatible

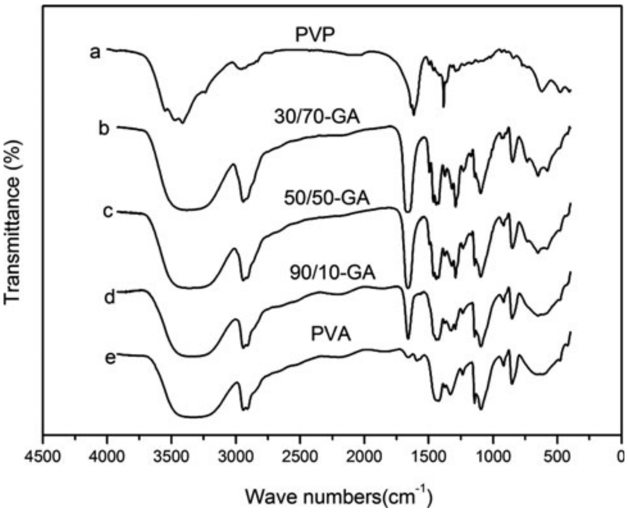

Fig. 2. FTIR of PVA membrane, PVP powder and GA (0.5 wt%) cross-linked PVA/PVP blend membranes.

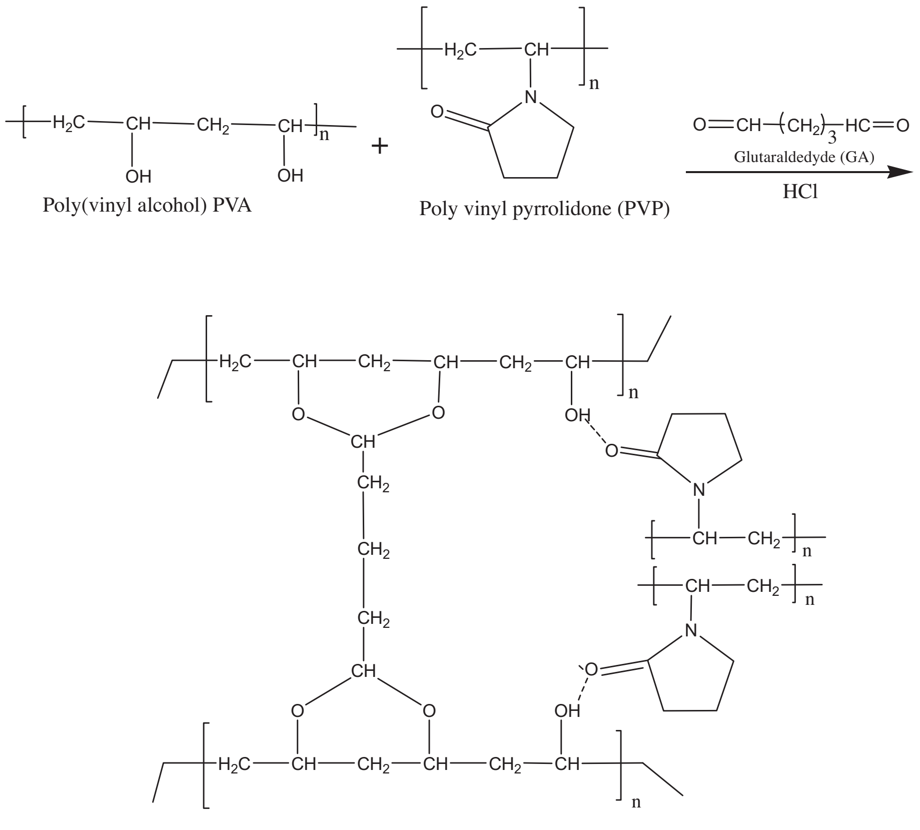

Fig. 1. Interaction between the blended polymers and the cross-linking mechanism of PVA with GA.

polymers because of the hydrogen-bond interactions between PVP CO-groups and PVA OH-groups. The small amounts of GA do not significantly change the polymer compatibility. Similar results were found in the previous studies [28–30].

3.1.2. SEM analysis: morphology

SEM images of the cross-linked PVA–PVP/PAN composite membranes are shown in Fig. 3. Fig. 3(a) presents the top surface of the cross-linked PVA–PVP membrane. Both flaws and phase separation were not observed from the surface of the PVA–PVP blend membrane. From Fig. 3(b), the typical asymmetric structure of composite membrane is observed very clearly: a very thin active layer (skin layer), a supported porous layer, and a nonwoven fabric. The total thickness of dry composite membrane PVA–PVP/PAN for PV is found to be about 110 ± 5 µm. It is observed that a uniform PVA–PVP thin dense layer with thickness of about 5–10 µm is properly cast on the top of the PAN substrate in the Fig. 3(c) and (d).

3.1.3. XRD analysis: crystallinity

Fig. 4 presents XRD patterns of cross-linked PVA–PVP blend membranes along with PVA and PVP membranes. It is clear that the peak intensity of the typical diffraction peak at $2\theta = 20^\circ$ due to the PVA crystalline planes [24] decreases with increasing the PVP content in the membranes indicating that the crystallinity decreases, which is expected for PVP is less crystalline than PVA. This indicates that the amorphous regions increases, thereby making it easier for small molecules to transport through and possibly resulting in an increase in permeation flux of the PVA–PVP blend membranes over the PVA membrane.

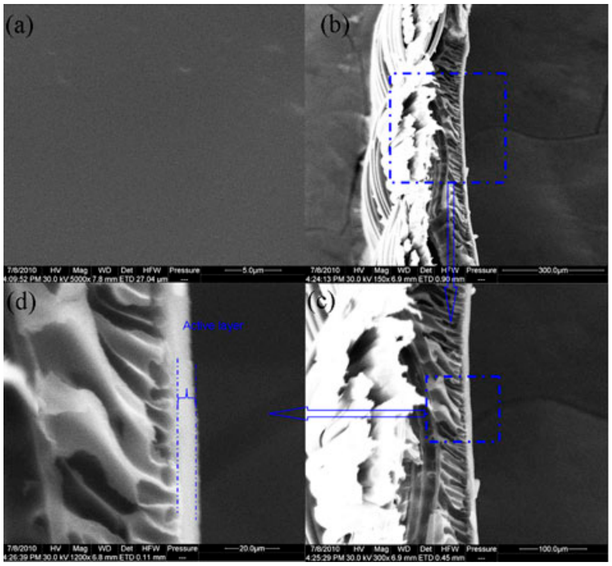

Fig. 3. Morphology of PVA–PVP/PAN composite membranes (a) top surface, (b), (c), and (d) cross section of membrane.

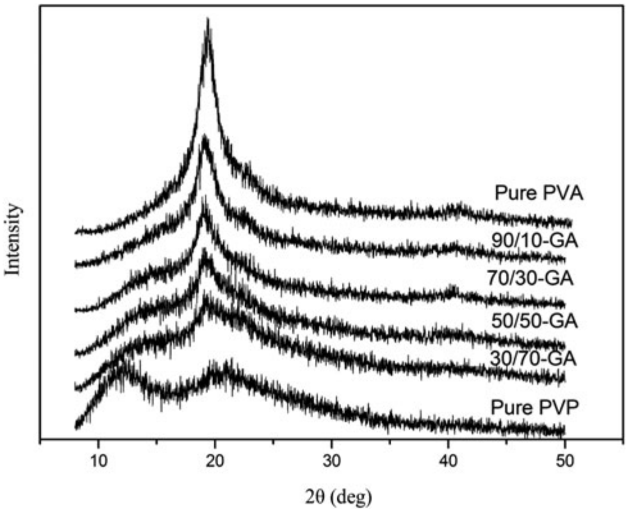

Fig. 4. XRD of pure PVA membrane, PVP powder, and GA (0.5 wt%) cross-linked PVA/PVP blend membranes with different proportions.

3.1.4. TGA analysis: thermal stability

The thermal decomposition expressed in terms of weight loss as a function of the temperature for the plain PVA, PVP membrane, and the PVA–PVP blend membranes are shown in Fig. 5. The weight loss of ~10% before 200°C was observed for all samples. This weight loss was considered to be corresponding to the absorbed water in the membranes. PVA membrane

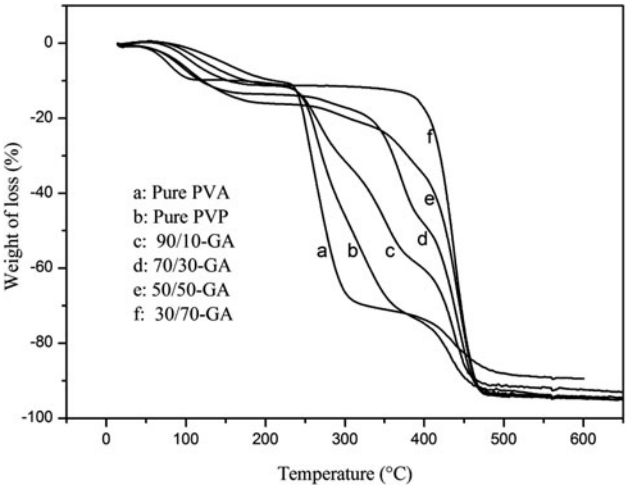

Fig. 5. TG of pure PVA membrane, PVP powder, and GA (0.5 wt%) cross-linked PVA/PVP blend membranes.

exhibits two major weight loss regions. The weight loss in the first stage between 250 and 360℃ is attributed to splitting of the main chain, followed by the final decomposition of the polymer around 530℃. It is observed that the extent of major weight loss gradually increased from 250 to 400℃ for PVA–PVP blend membranes, since the decomposition temperature of both plain PVA (at around 250℃) and PVP (around 400℃) was in this temperature range [31]. It was also worth noting that the thermal stability of the PVA–PVP blends was higher than plain PVA and was enhanced with the addition of PVP.

3.1.5. Contact angle analysis: surface hydrophilicity

The PV performance of a composite membrane is related to the hydrophilicity of the separation layer. As shown in Fig. 6, the water contact angle of these membranes gradually decreases with increasing PVP content. It means that the membrane of higher PVP content has a higher relative hydrophilicity, mainly because of more polar groups of the unreacted CO-groups in blend membrane (shown in FTIR). These free CO-groups form hydrogen bonding with H_2O.

3.2. Swelling characteristic

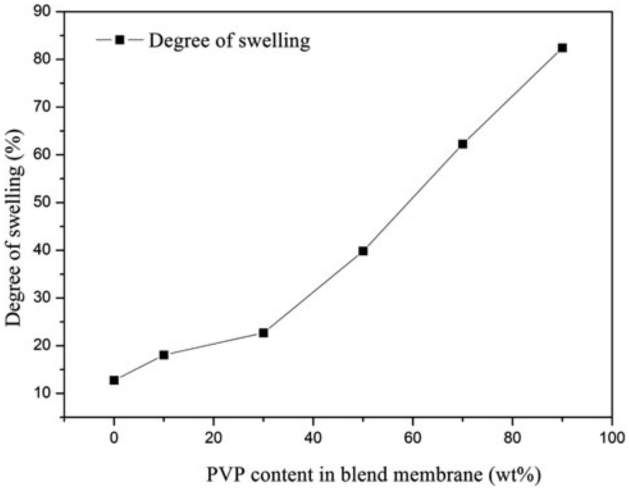

Fig. 7. Effect of PVP content on the degree of swelling of GA (0.5 wt%) cross-linked PVA/PVP blend membranes in the DMC/MeOH (30/70) azeotropic mixture.

The sorption experiments were performed to reveal the sorption and diffusion characteristics based on the theory of solution–diffusion. In PV, the permeation flux and selectivity of a membrane are dependent on the degree of swelling of the permselective layer. So, studying the degree of swelling may gain an insight into the membrane characteristics. The swelling results of different blend membranes in mixture of 70 wt% MeOH are given in Fig. 7. The degree of swelling increases with the increase of the PVP content. This can be explained by the hydrophilic character of PVP. As for MeOH/DMC mixtures, MeOH is more hydrophilic and polar than DMC due to dipole moment of hydroxyl group. These free CO-groups form hydrogen bonding with MeOH.

3.3. Effect of composition on pervaporation performance

3.3.1. Effect of PVP content on pervaporation performance

Polymer blending is an efficient method for membrane modification. In this paper, PVP was introduced to modify the PVA membranes (PVP alone could not be used to form films). Fig. 8 shows the effect of PVP content in blend membranes on permeate flux and

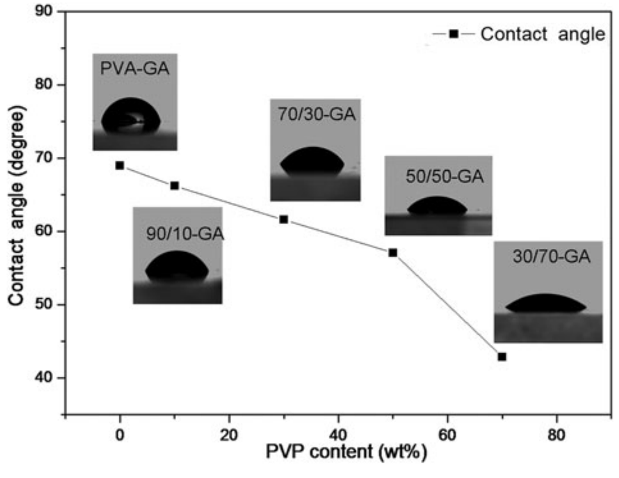

Fig. 6. Effect of PVP content on the contact angle of GA (0.5 wt%) cross-linked PVA/PVP blend membranes.

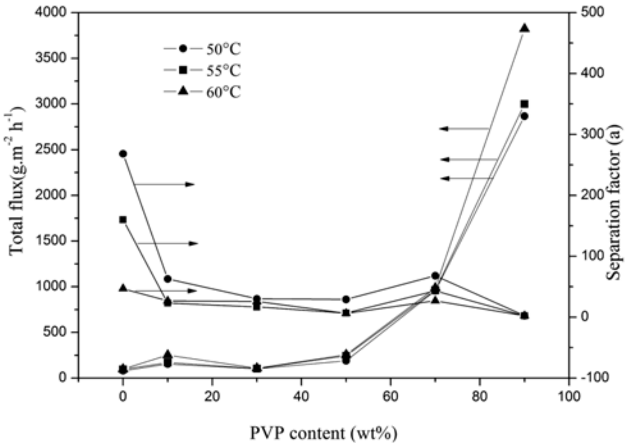

Fig. 8. Effect of PVP concentration in the PVA–PVP coating solution on PV performances with 0.5 wt% GA for 30 wt% DMC.

separation factor for DMC/MeOH azeotropic mixture. It was obvious that the permeation flux increased with increasing the PVP content, whereas the separation factor first dropped with addition of 10 to 50 wt% PVP for the plain PVA membrane. When the PVP content increased from 50 to 70 wt%, the separation factor increased and then dropped sharply when the PVP content reached 90 wt%. The highest separation factor of 68.01 (99.4 wt% MeOH in permeate) was obtained for the blend membrane containing 70 wt% PVP. On the one hand, introduction of PVP could significantly enhance the hydrophilicity of the membranes which was confirmed by the contact angle measurement, as shown in Fig. 7. The formation of hydrogen bonding between the membranes and MeOH was hence promoted. Therefore, the affinity between azeotropic mixture and membranes increased accordingly, which was confirmed by the swelling of degree measurement. On the other hand, introduction of PVP into PVA can disorder the arrangement of the PVA chains; as a result, the degree of the crystallinity of the PVA decreased, and the amorphous regions of the membranes increased with increasing the PVP loading (Fig. 5). As a result, separation factor first decreased, and then reached a maximum and dropped down. The permeation flux increased with increasing PVP content for the higher swelling degree.

3.3.2. Effect of GA content on PV performance

The PV performance is related to the structure of membranes, while cross-linking is an efficient way to modify the structure of membranes. Fig. 9 displays the effect of GA content on PV performance for DMC/MeOH azeotropic mixture with the membrane of 50 wt% PVP at 55°C. The flux decreases gradually but the separation factor has a maximum of 6.76 when the GA content is 0.5 wt% with increasing the GA content in the range of 0–0.8 wt%. The decreasing flux results from the more compact structure of polymeric chains, leading to a less chain mobility and a better selectivity.

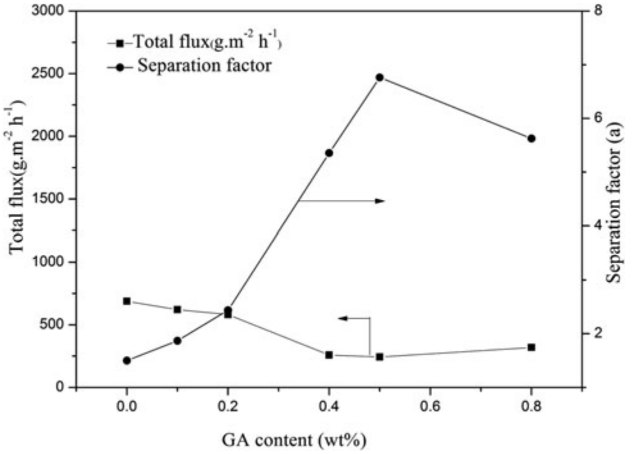

Fig. 9. Effect of GA concentration on the PV performances with the membrane of 50 wt% PVP at 55°C.

3.3.3. Effect of feed composition and temperature

Temperature has a significant effect on permeation flux and separation factor. The effect of feed temperature on the PV performances is investigated in Fig. 10 (a) and (b). From the Fig. 10(a), the separation factors decrease but the fluxes increase with increasing the operation temperature from 45 to 60°C. Generally speaking, an increase in temperature increases thermal mobility of the polymer chains, which leads to an increase in both the free volume of the membrane and an easier transport of both methanol and DMC molecules. In addition, the vapor pressure of MeOH and DMC in the feed mixture increased with increasing of the feed temperature, and the vapor pressure at the permeate side was not affected. These lead to an increase of the driving force for mass transfer. As a result, the diffusion of both permeating molecules increased, and this led to higher flux but lower separation factor.

Also, Fig. 10(b) indicates that the flux and the separation factor are strongly dependent on the feed composition. With the MeOH concentration increasing from 50 to 70 wt%, the total flux increased from 168.62 to 243.26 $\mathrm{g\,m^{-2}\,h^{-1}}$ while the selectivity decreased from 9.93 to 6.76. This trade-off was generally observed in PV processes. With higher MeOH concentration in the feed mixture, the amorphous regions of the membrane are more swollen and the polymer chains become more flexible. This makes both MeOH molecules and DMC molecules more easily penetrate through membranes. Furthermore, the size of the MeOH molecule is smaller than that of the DMC. The MeOH molecule can be more easily diffused in the moderately swollen membranes. So, the total permeation flux increases while the separation factor decreases a little.

3.3.4. Comparison of present membranes with literature data

The total flux and selectivity from the present study (for separating DMC/MeOH azeotrope at 50°C) were compared with other different composite membranes reported in literatures and presented in Table 1. Although the membrane are made from different material and preparation techniques, the performance of the cross-linked PVA–PVP composite membrane prepared in this study shows significantly improved for a good flux and better selectivity.

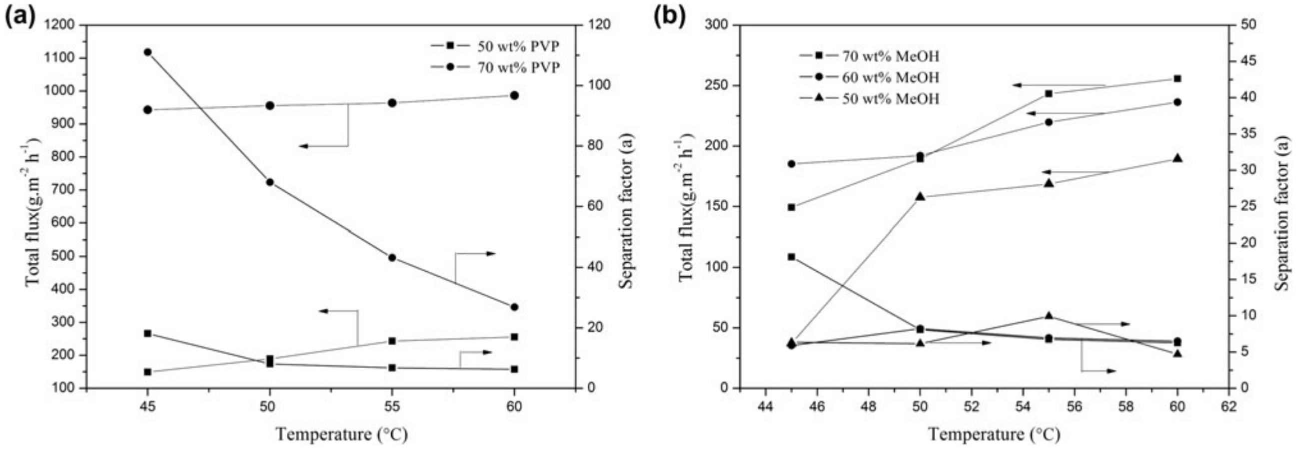

Fig. 10. Effect of the feed temperature on the PV performances (a) at 30 wt% DMC and (b) at 50 wt% PVP.

Table 1
Comparison of composite membrane separation performance with literatures

Membrane	Thickness (±μm)	Temperature (℃)	Mass% of MeOH in feed	Flux ($g\,m^{-2}\,h^{-1}$)	Separation factor	Reference
PAA/PVA	–	60	70	577	13.0	[6]
GA cross-linked PVA/PAA	–	50	70	248	37.0	[7]
ZSM-5 zeolite–filled chitosan	35 ± 2	25	70	263	9.2	[8]
Chitosan cross-linked with APTEOS	20	50	70	1,275	29.8	[9]
STA/CS	13	50	50	1,362	41.5	[10]
Chitosan	–	55	70	291	8	[32]
GA cross-linked PVA–PVP/PAN composite membrane	110 ± 5	50	70	956	68.0	Present work

4. Conclusions

The PVA–PVP/PAN composite membranes were successfully prepared. The morphologies and properties of the resulting membrane were characterized by SEM, FTIR, XRD, TGA, and contact angle measurement, respectively. Furthermore, these membranes were applied in the separation of the MeOH/DMC azeotropic mixture by the single PV to destroy azeotropic point. These membranes have higher flux and selectivity. The effects of PVP, GA content in membranes, and the feed temperature on PV performances were investigated. The main conclusions are as follows:

(1) The FTIR spectra indicated that PVA and PVP are perfectly compatible and miscible polymers via the hydrogen-bond interactions between the –CO groups of PVP and –OH groups in PVA. Compared with unmodified PVA membrane, the cross-linked PVA–PVP blend membranes as active layer have higher the thermal stability, lower crystallinity and higher hydrophilicity, which benefited to enhance the membrane performances.

(2) The PVA–PVP/PAN composite membrane was employed for the PV separation of DMC/MeOH azeotrope. The membranes showed good performance in PV separation azeotrope. Cross-linking by GA and annealing can efficiently control the swelling of the membranes to ensure a high separation factor. In addition, the permeation flux also increased with increasing feed temperature, whereas the separation factor decreased accordingly. It was demonstrated that introducing PVP could enhance the hydrophilicity of the membranes and is in favor of increasing permeation flux. Of all the blend membranes prepared, the membrane of 70 wt% PVP was the best one since it exhibited both high permeation flux and separation factor. The experimental results also indicated that the PVA–PVP composite membrane had superior performances for separation DMC/MeOH azeotrope.

List of symbols

DS — degree of swelling (%)

W_s, W_d — weight of the swollen and dry membrane (g)

J — PV permeation flux ($\mathrm{g\,m^{-2}\,h^{-1}}$)

W — weight of penetrant (g)

A — effective membrane area ($\mathrm{m^2}$)

t — permeation measuring time (h)

α — separation factor

x_{MeOH}, x_{DMC} — the mole fraction of MeOH and DMC in the feed

y_{MeOH}, y_{DMC} — the mole fraction of MeOH and DMC in the permeate

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