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Pervaporation performance of crosslinked PVA and chitosan membranes for dehydration of caprolactam solution

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ABSTRACT

ε-Caprolactam (CPL) is the monomer of nylon-6 used extensively in the manufacture of high quality nylon-6 fibers and resins. But high energy consumption, high wastage and condensate pollution have restricted the wide-scale production of CPL and the commercial profit of this process. To improve a new dehydration process, pervaporation separation of CPL solution was investigated using composite membranes. The selective layer was formed with poly(vinyl alcohol) and Chitosan matrix through the cross-linking reaction with glutaraldehyde. Films were characterized by scanning electron microscope (SEM), Fourier transform-infrared (FT-IR) and X-ray diffraction (XRD). The pervaporation results have revealed that separation performances of CS/PVA composite membranes are strongly related to the ratio between PVA and CS as well as its hydrophilic nature and the operating parameters. The membrane of the ratio (CS/PVA=1:3) exhibited the most conformable separation performance with a total flux of 757 g/(m^2 h) and separation factor of 443 at 50°C for 50 wt% CPL aqueous solution. Data showed that the composite membranes had superior separation performances for dehydration of CPL solution, which provided a new way for CPL dehydration.

Keywords: ε-Caprolactam; Pervaporation; Poly(vinyl alcohol); Chitosan; Cross-linking

1. Introduction

ε-Caprolactam ($C_6H_{11}NO$, CPL) is the monomer of nylon-6 and an industrially important organic chemical material, used extensively in the manufacture of high quality fibers and engineering plastics. Dehydration is the most important process in the final CPL purification, and several traditional separation techniques [1], such as thin-film distillation, crystallization, melt crystallization by suspension, have some disadvantages, such as low heat transfer coefficient, a large amount of middle pressure steam consumption and coagulation from steam containing considerable CPL. Therefore, a high-efficiency dehydration process operation for the concentrate of CPL solution is required.

Pervaporation (PV) is considered to be an effective process, which is also an energy efficient alternative and eco-friendly clean technology for separation of liquid mixtures. In general, it is used for separating of azeotropic, close-boiling, isomeric or heat-sensitive liquid mixtures [2–5], and makes it possible to utilize waste-heat as the heat of vaporization to separate volatile organic compounds from water in the chemical industry [6]. Unlike distillation process, the separation mechanism in PV is not based on the relative volatility of the components, but on the difference in sorption and diffusion properties of the feed components as well as perm-selectivity of the membrane.

In membrane-based PV separation, different types of polymers have been used for a variety of aqueous–organic mixtures. However, the key is the development of novel membranes resistant to liquids or their mixtures

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under test conditions, giving high selectivity and flux to water. Blending and/or formation of composites are one of the attractive means of tuning the performance of a membrane to achieve the desired flux and/or selectivity. In particular, the development of blend membranes has been an attractive area of PV study because one component of the blend provides the desired permeability characteristics and the other improves the mechanical strength properties [7–11].

Poly(vinyl alcohol) (PVA) has been the most widely used membrane in pervaporation [12–15]. It is a hydrophilic polymer with semi-crystalline molecular structure. Due to the good chemical stability, film-forming ability and high hydrophilicity, nontoxicity, the studies on diffusive permeabilities of solutes in PVA gel membranes and the application for separation have been reported [16,17]. Because of recent environmental concern and awareness in public sectors, new trends are moving in the direction of using environment-friendly polymers that can easily be degraded after their intended applications. Chitosan (CS), a naturally occurring carbohydrate polymer [(1–4)-2-amino-2-deoxy-b-D-glucan] is found in all arthropods, in some invertebrates (e.g., squid and cuttlefish), and in some microorganisms. It can be readily prepared from chitin by *N*-deacetylation with alkali treatment. An effort has been made primarily to enhance the flux of this PVA membrane by suitably interposing CS in the membrane matrix in different proportions using the same sol–gel method. The CS was selected in view of its significant affinity towards water, good film forming ability, and functional groups that can be easily modified apart from its good mechanical strength and chemical stability. It has been widely used in PV separation of aqueous–organic mixtures [18–21]. In the present study, advantages was taken of the hydrophilic nature of both PVA and CS polymers, in order to prepare blend membranes [22] that were not only hydrophilic but also exhibited a good combination of flux and selectivity, and at the same time were environmentally friendly.

The preparation of CS/PVA blended hydrogel membranes treated with glutaraldehyde (GA) was reported in this study. It was to use PVA as the base polymer and to prepare its blends by adding CS, the proportion was CS: PVA = 1:1, 1:3 and 1:5, and then crosslink the membrane with GA. The characteristics of the CS/PVA membrane were studied with scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analysis. The pervaporation experiments were studied. Due to the excellent properties of CS/PVA membranes for pervaporation dehydration applications, further investigation to produce a promising membrane for industrial applications will come along.

2. Experimental details

2.1. Materials

ε-Caprolactam(CPL) (industrial grade) was supplied by Baling Petrochemical Co. Ltd (SINOPEC, China); Chitosan (CS) with an *N*-deacetylation degree of 90%, Poly(vinyl alcohol) (PVA) with degree of polymerization of 1750 ± 50 and degree of hydrolysis of 98%, and glutaraldehyde (GA, 25 wt% in water) were purchased from Guoyao Chemicals Co., Ltd (Si Chuan, China). Ultrafiltration membrane of polyacrylonitrile (PAN) (Cut-off MW 5×10^4) was supplied by the Development Center of Water Treatment Technology (China). All the chemicals were used without further purification. Deionized water was used in preparing the aqueous feed solutions for the pervaporation experiments.

2.2. Preparation of crosslinked composite membranes

2.5 wt% CS solutions were prepared by dissolving CS in 2wt% acetic acid solution at ambient temperature with stirring for 5 h. PVA was dissolved in water by refluxing and stirring for 6 h at 100°C. Homogeneous solution of 5 wt% polymer in water was obtained. Then the mixture of CS and PVA solution were stirred in different wt% ratios (CS: PVA =1:1, 1:3 and 1:5). To this solution, a certain amount of cross-linking agent (glutaraldehyde, GA) was added and the reaction last for 24 h. The resulting homogenous solution was used for the sequent process after degassing.

The coated membranes, Hydrolyzed PAN membranes, were prepared by immersing PAN ultrafiltration membrane in 5 wt% NaOH aqueous solution at 50°C for 1 h, washed thoroughly with deionized water until neutral and then immersed in 1N HCl aqueous solution for 20 min, and washed with water until neutral [23]. Then, the prepared solution was cast on the PAN substrate membranes held on a glass plate with the aid of a casting knife made in our laboratory. The composite membranes in the gelatination state were allowed to evaporate slowly in a dust-free atmosphere till dried at ambient temperature. Finally, the composite membranes were treated in an air-circulating oven at 80–100°C for 1 h to effect thermal cross-linking structure. The crosslinked membranes in different CS/PVA mass ratio (1:1, 1:3 and 1:5) were designated as CS/PVA-1, CS/PVA-2 and CS/PVA-3, respectively.

2.3. Swelling experiments

Equilibrium swelling experiments on all membranes were performed in feed mixtures of water/CPL with compositions ranging from 30 to 90 wt% water at 40 ± 0.5°C. The masses of dry membranes were first determined and these were equilibrated by soaking in different compositions of feed mixture in a sealed vessel at 40°C for 48 h. The swollen membranes were weighed as quickly as possible after careful wiping off the surface water with a piece of filter paper on a digital microbalance (Mettler B204-S, Toledo, Switzerland) within an accuracy of ±0. 1 mg. All the experiments were performed at least three times and the results were averaged. The percent degree of swelling (S) was calculated by the following equation:

$$S(\%) = \frac{W_s - W_d}{W_d} \times 100\%, \qquad (1)$$

where W_d and W_s are the weight of the dry membrane and the swollen membrane, respectively.

2.4. Membrane characterization

2.4.1. Scanning electron microscopy (SEM)

The morphology of the various composite membranes was examined by scanning electron microscopy (SEM). All specimens were coated with a conductive layer of sputtered gold. The morphologies of the CS/PVA composite membranes were observed with SEM (FEI Quanta 200, Holland).

2.4.2. Fourier transform infrared (FT-IR) spectroscopy

The cross-linking reaction of CS/PVA with GA was confirmed by the FT-IR. The FT-IR spectra of various composite membranes were scanned using Nicolet AVATAR 360 FT-IR spectrometer.

2.4.3. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) measurements were carried out on a Shimadzu XRD-6000 diffractionmeter equipped with graphite monochromatized Cu K_α radiation ($\lambda = 1.540\,60$ Å). The angle of diffraction was varied from 10° to 35° to identify any changes in the crystal structure.

2.5. Pervaporation experiments

PV experiments were performed using an indigenously designed apparatus as shown in Fig. 1. This apparatus consisted of a stirred stainless-steel cell around which water was circulated to maintain the desired high flow rate of 200 L/h from the feed tank through the membrane cell. The membrane cell was designed to allow high fluid velocity parallel to the membrane surface and the effective surface area of the membrane contact with the feed mixture was 72.35 cm^2. The temperature of the feed mixture was kept constant using a thermostatically thermocouple. The vacuum in the downstream side of the apparatus was maintained about 10 mbar ±1 mbar.

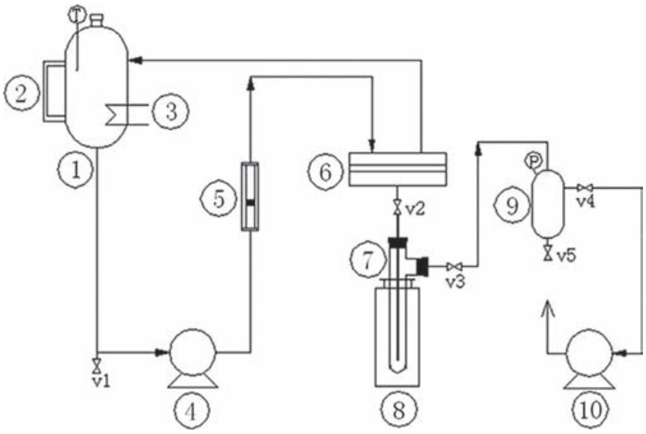

Fig. 1. Diagram of pervaporation apparatus.

The test membrane was allowed to equilibrate for about 1–2 h at the corresponding temperature before performing the PV experiment with fixed compositions of feed mixture. This is done in order to achieve the equilibrium condition for the membranes. After establishment of a steady state, the permeate vapor was collected in a trap immersed in the liquid nitrogen jar on the downstream side at a fixed time of intervals. The feed mixtures composed of the water and CPL was varied from 10 to 70 wt% CPL. Pervaporation experiments for CPL solution having different concentrations of CPL were conducted in the range of 40–60°C. During the pervaporation apparatus runs, the compositions of the liquid feed mixtures were analyzed every 1 h by measuring the refractive index and comparing it with a standard graph of refractive index versus mixture composition. The composition was determined at 20°C by measuring the refractive index of the liquid mixture using a high-precision Abbe Refractometer (Atago NAR-3T, Japan). The trap filled with condensed permeate was warmed up to ambient temperature, and weighed to calculate the permeation flux. The compositions of permeates were determined with gas chromatography (GC). For the separation of the impurities in CPL solution by GC, columns packed with polyethylene glycol (PEG) 1000, PEG 20 M, PEG 4000 and BP20 capillary column with a conventional detector have been employed [24]. Here the composition of the condensed liquid was analyzed by a SP3400 gas chromatography with a FID detector (made in China) under the following conditions: PEG-20M capillary column, 2 m × 6 mm i.d. temperature: 170°C, carrier gas: nitrogen, flow rate: 30 mL/min.

From the PV data, separation performance of the membranes was assessed in terms of flux (*J*) and separation factor (α). These were calculated respectively using the following equations:

$$\alpha = \frac{y_w}{y_{cpl}} \Big/ \frac{x_w}{x_{cpl}} \tag{2}$$

$$J = \frac{W}{At}, \tag{3}$$

where in Eq. (2) x_w, y_w are the mole fraction of water in the feed and permeate, and x_{cpl}, y_{cpl} are the mole fraction of CPL in the feed and permeate; in Eq. (3), W (g), A (m^2) and *t* (h) are weight of permeates, effective membrane area and time, respectively.

3. Results and discussion

3.1. Membrane characterization

3.1.1 SEM analysis

The microscopic analyse of CS/PVA composite membrane is shown in Fig. 2. It is obvious that the multilayer structure of composite membrane is observed very clearly: an active layer, a supported porous layer, and a substrate. It can be seen that PVA and CS thin dense layer was properly cast on the top of the PAN substrates, especially the aperture of supported porous layer is arranged very regularly, which is benefit for the osmosis of the membranes and improvement of the flux. It is also shown that the active layer of the composite membrane is about 10 µm, and the total thickness is about 100 µm.

3.1.2 FT-IR analysis

Fig. 3 shows the FT-IR spectra of the active layer coated on the PAN substrates crosslinked with GA at different CS/PVA proportion, along with the CS or PVA crosslinked with GA, respectively.

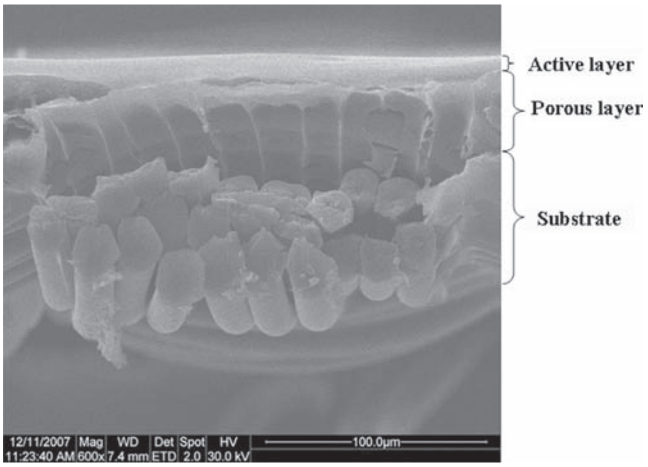

Fig. 2. The morphology of CS-PVA composite membrane01.

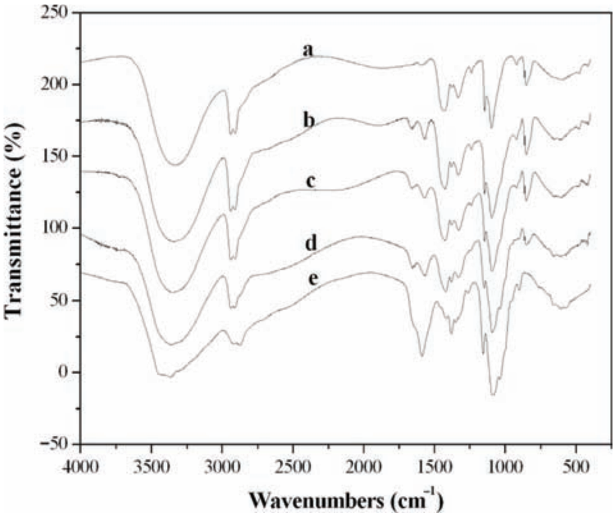

Fig. 3. FTIR spectra of (a) PVA-GAL; (b) CS/PVA-3 (c) CS/PVA-2; (d) CS/PVA-1; (e) CS-GAL.

In the FTIR spectrum of CS (Fig. 3e), the absorption bands of carbonyl stretching vibration in O=C–NHR groups and N–H bending vibration in amine groups were observed at 1500^{-}–$1700 cm^{-1}$ [25]. The absorption bands of O–H and N–H stretching vibrations appeared at 3000–3600 cm^{-1} [25,26]. The two sharp band at 2900 cm^{-1} corresponding to asymmetric and symmetric stretching of the CH; 1720 cm^{-1}, corresponding to stretching of C=O group of aldehyde; 1094 and 1200 cm^{-1}, which are attributed C–O and C–O–C groups due to acetal or ether linkage formation after the crosslinking took place [26].

With the existing of PVA, the absorption bands at 3000–3600 cm^{-1} in the FTIR spectra of the CS/PVA membranes became sharp (Fig. 3(b)–(d)) and shifted to the lower wave numbers. The absorption peak at 1593 cm^{-1} of amino gradually decreased and finally disappeared due to the decreasing amount of CS in membranes as well as the interaction between PVA and CS macromolecules. It suggested that hydrogen bonds between hydroxyl groups in PVA and amino groups or hydroxyl groups in CS could possibly come into play. Therefore, the addition of PVA could moderate the interaction between CS macromolecules.

3.1.3 XRD analysis

The X-ray diffraction patterns of the CS/PVA membranes are given in Fig. 4. As can be seen, XRD patterns of all the membranes indicate semicrystalline behavior. The typical diffraction peak is observed at about $2\theta = 20°$. From these patterns, it is clear that the crystallinity has increased with increasing PVA contents in the

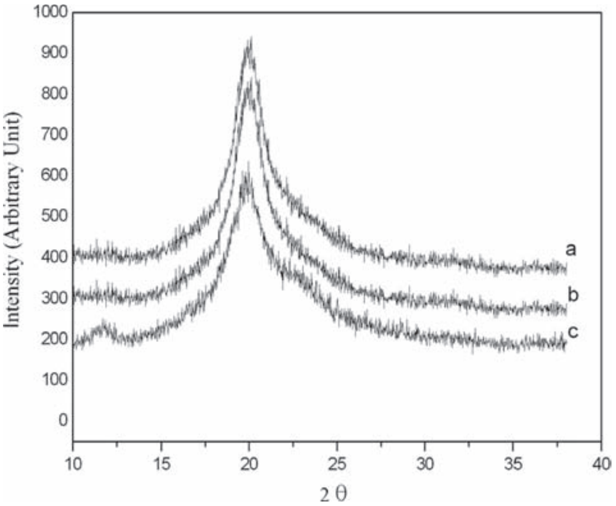

Fig. 4. XRD diffractograms of (a) CS/PVA-3 (b) CS/PVA-2; (c) CS/PVA-1.

composition membranes. This result implies that the change the ratio of PVA and CS content changed the crystallinity of the membrane after crosslinking [18,19].

3.2. Pervaporation characteristics

3.2.1 Effect of operating temperature

The PV process is known to be temperature dependent [27,28] as both flux and selectivity are influenced by the change in temperature. Effect of operating temperature on the PV performance for water/CPL mixtures has been studied for all the membranes at 50 wt% of water in the feed, and the resulting values are presented in Fig. 5. The operating temperature range was chosen from 40 to 60°C [20]. As is reflected from the Fig. 5a, it could be due to the fact that the increase of feed temperature makes the partial fluxes increase for all the membranes, and this phenomenon may be traditionally explained by the increase in frequency and amplitude of polymer chain thermally induced. The other source of this behaviour is the change of penetrants' diffusivities [7] and the expansion of the free volume. Increasing temperature brings about higher molecular diffusivity [29–31]. While the increase of the partial fluxes following the temperature rising, the separation factor decreases synchronously (Fig. 5(b)). It is because that high temperature not only decreases the intermolecular interaction between permeants, but also decreases within the membrane material, resulting to increase free -OH and -NH_2 groups on the membrane [32]. These are responsible for predominating the plasticizing effect on the membrane due to greater swelling. Therefore, the permeation of diffusing molecules and the associated molecules through the membrane becomes easier, leading to an increase of total permeation flux, while suppressing the separation factor. In addition, with increasing feed temperature, the vapor pressure in the feed compartment increases, but the vapor pressure at the permeate side is not affected. These result in an increase of driving force with increasing temperature.

The alignment of polymer chains in the polymer network also plays a crucial role in the separation performance (Fig. 5(b)). It is absolutely because it is the consideration of the entire membrane property not the structure of one component polymer. The morphological structures of polymer network highly influence the free volume in the matrix and eventually affect the solubility and diffusivity of feed components through the membranes [7].

From Fig. 5(a) and (b), water flux of CS/PVA-2 membrane is higher than it of CS/PVA-3 with separation factor in reverse. It could be due to the fact that CS is more water permselective than PVA under the treatment conditions in this study and the insertion of small amount of CS could make certain parts of PVA compact network distorted and lead to higher free volume in the network. The further increase of CS in the membrane

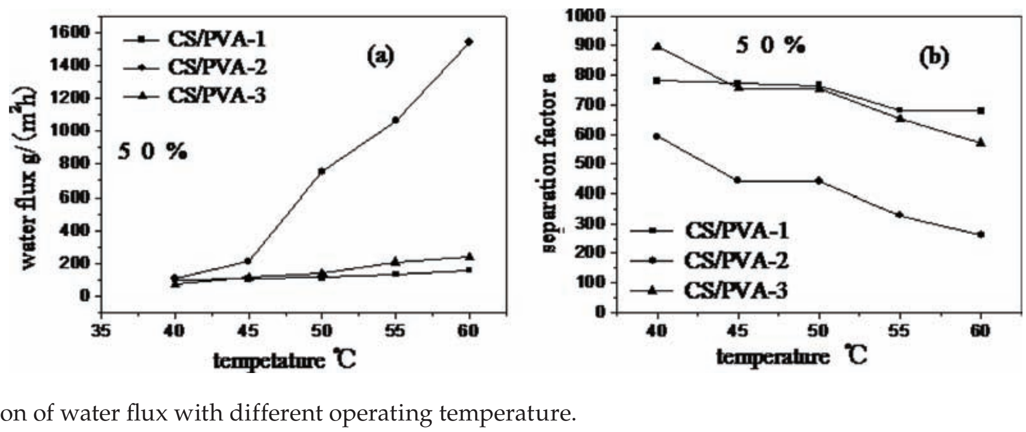

Fig. 5. Variation of water flux with different operating temperature.

CS/PVA-2 allows higher mass transport of water across membrane [7]. Due to the higher free volume in the network, separation factor decreases compared with CS/PVA-3. When the CS content increases at a certain proportion in the CS/PVA-1 membrane, it can be seen that the flux decreases obviously. It may be because of the fact that polymer matrix of the CS/PVA-1 membrane becomes more condensed than that of the CS/PVA-2 membrane. It is possible that the further increase of CS in CS/PVA-1 fill in free volume amongst PVA chains and this leads to higher density of polymer network in the CS/PVA-2 membrane. So the flux and separation factor of CS/PVA-1 membrane has a conflicting change from the trend of CS/PVA-2 and CS/PVA-3.

The apparent activation energy (ΔE_a) of water and CPL permeates through the CS/PVA-1 membrane, the CS/PVA-2 membrane and the CS/PVA-3 membrane with 70% CPL concentrations are calculated on the basis of the Arrhenius formula as shown in Fig. 6, and their results are summarized in Table 1.The Arrhenius relationship is expressed in Eq. (4):

$$J = J_0 \exp(-E_p/RT). \tag{4}$$

E_t values for CS/PVA-1, CS/PVA-2 and CS/PVA-3 membranes were found to be 17.43, 137.44 and 63.39 kJ mol/L, respectively. E_w values for CS/PVA-1, CS/PVA-2 and CS/PVA-3 membranes were 17.42, 137.37 and 63.37 kJ mol/L, respectively. It could be found that activation energies of total and water permeations were very close on three membranes in this study. It suggests that water flux has a control of total flux. In addition, activation energy for CPL permeation was higher than that for water permeation. It implies that water consumes less amount of energy for permeation and has higher permeability than CPL. Totally the apparent activation energy ranged from the maximum to the minimum is CS/PVA-2 > CS/PVA-3 > CS/PVA-1. It suggests that higher separation factor needs lower energy.

Table 1
Apparent activation energy (ΔEa) of water and CPL for CS-PVA composite membranes with 70 wt% CPL in feed solution.

Membrane type	ΔEa Activation energy (kJ/mol)		
	E_T	E_W	E_{cpl}
CS/PVA-1	17.43	17.42	26.26
CS/PVA-2	137.45	137.37	169.54
CS/PVA-3	63.39	63.37	79.70

3.2.2 Effect of feed composition

Fig. 7(a) shows the effect of feed composition on the total permeation flux at 50°C for all the membranes and concentrations of 10–70 wt% of CPL in the feed mixtures [26]. It is observed that the total permeation flux increased for all the membranes with respect to mass percent of water in the feed. This behavior is consistent with the previous reports in the dehydration of aqueous organic mixture through hydrophilic polymeric membranes [33–36]. It is mainly because of -OH in PVA and the introduction of -NH_2 groups and further increase of -OH groups by the incorporation of CS.

In Fig. 7(a) it can be seen that CS/PVA-2 membrane has obvious superiority in total flux and the largest reached 2551 g/(m^2 h) in 10wt% feed, which were 938 g/(m^2 h) and 228 g/(m^2 h) for CS/PVA-1 and CS/PVA-3, respectively. For rest concentration of feed mixtures the total flux for CS/PVA-1 and CS/PVA-3 were similar and the values were much lower than it for CS/PVA-2. The superiority of flux for CS/PVA-2 was quite visible.

From CS/PVA-3 membrane to CS/PVA-2 membrane, total flux increased gradually with increase of the CS content in the membrane. It confirmed the explanation previously about the effects of CS composition that the higher CS in the membrane, the higher the total permeation flux [7]. But when the CS content increases as it in CS/PVA-1 membrane, total flux decreases. The trend in

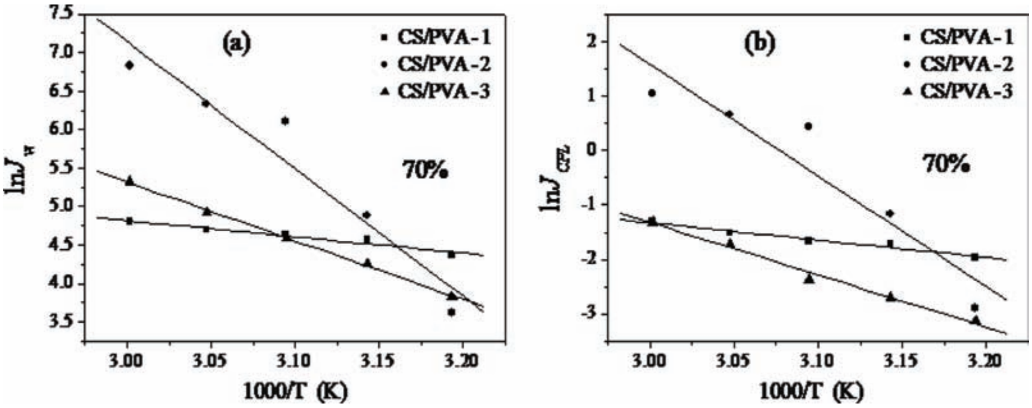

Fig. 6. Variation of ln JW with temperature.

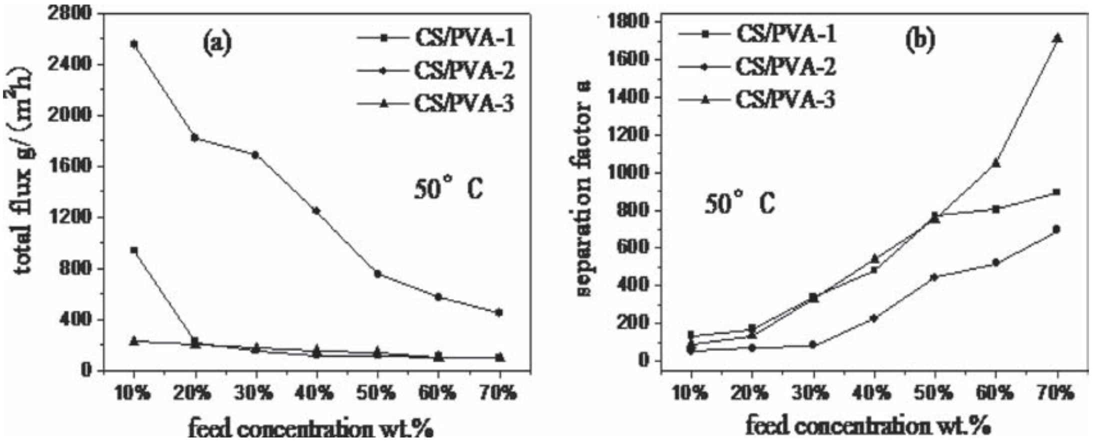

Fig. 7. Effect of feed concentration on the PV performances.

effect of CS content is the same as that in effect of operating temperature. It also could be due to higher density of polymer network in the CS/PVA-1 membrane than that of the CS/PVA-2 membrane which may be caused by the further increase of CS in CS/PVA-1 filling in free volume amongst PVA chains. As described before, it is believed the least compact structure of polymer blends from the CS/PVA-2 membrane enhances the mass transport across the membrane.

At higher concentration of water in the feed, the membranes swell greatly because of the formation of a strong interaction between the membrane and water molecules, while suppressing the interaction within the membrane material (i.e., between CS and PVA). As a result, selectivity decreases gradually at higher concentration of water in the feed, irrespective of the amount of the CS in the membrane matrix (Fig. 7(b)). The trend of total flux and separation factor from CS/PVA-3 to CS/PVA-2 is accordant with Wu *et al*. [36,37] study. But when the CS content in the membrane increased further (CS/PVA-1), the change of water permeate content upon CPL feed concentration was different. At this situation the morphological structures of polymer network influences the most important part. Due to the highest density of CS/PVA-1 membrane, it can be seen that the trend has a theatrically change: the total flux decreases and separation factor happens in reverse and both of the value are similar with those from CS/PVA-3.

3.3 Swelling experiments

Sorption mechanism is an important factor for membrane swelling in PV process, as it controls the transport of permeating molecules under the chemical potential gradient. This section is to determine the influences of sorption in pervaporation performance. Therefore, to study the effects of feed composition and proportion of CS/PVA on membrane swelling, the percent degree of swelling was plotted with respect to different mass percent of CPL from 30% to 70% in the feed at 40°C as shown in Fig. 8.

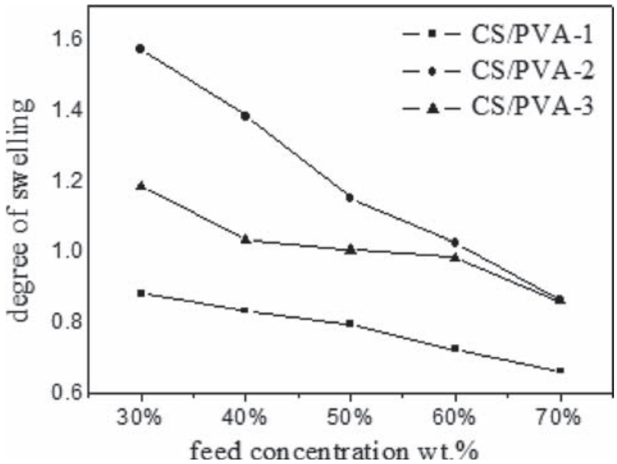

Fig. 8. The swelling ratio for 30~70 wt% CPL aqueous solution.

It is noticed that the swelling degree of the membrane increased when the CPL content in the solution decreased. This is due to the fact that all membranes are highly hydrophilic and have an increase of strong interaction between water molecules and the membrane containing -NH_2 and -OH groups [32].

It also can be seen that the percent degree of swelling increases from CS/PVA-3 to CS/PVA-2 membrane under every concentration in feed and then decreases on CS/PVA-1 membrane. This is in accordance with the results observed in the effect of feed composition study. The reason is also the two-tier parts and complicated.

4. Conclusions

PVA was used to prepare blend membranes by adding different amounts naturally available CS of the proportion. Results of XRD and FTIR indicated CS could possibly have interactions with PVA through hydrogen bonding. Therefore, the pervaporation characteristics of blend membranes were greatly improved.

Pervaporation dehydration of CPL solution through CS/PVA/PAN composite membranes was investigated in this article. Results of this study indicated that total flux increases with the increase of both feed water concentration and feed temperature in all membranes. It is found that the composite membrane CS/PVA-2 has the best separation performances, and the largest permeation flux is under the condition of 10 wt% CPL–water mixtures at 60°C and the values are 3397.37 g/(m^2 h). When the condition was 70 wt% and 40°C, it gained the largest separation factor of 1101.24.

In short, the membrane of CA and PVA hydrogel membranes treated with glutaraldehyde has also been realized with an excellent pervaporation performance, and CS to PVA ratio of 1:3 performs the best pervaporation dehydration. It confirms that composite membrane of CS/PVA is feasible for application to the CPL dehydration integrating with triple-effect evaporation sets partly or wholly in future. Due to all above, further investigation to produce a promising membrane for industrial applications will come along.

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