

Separation of caprolactam–water system by pervaporation through crosslinked PVA membranes

Lei Zhang, Ping Yu, Yunbai Luo*

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China

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Abstract

ϵ -Caprolactam (CPL) is usually crystallized from CPL–water mixtures by reduced pressure distillation through triple-effect evaporation sets. But high energy consumption and low heat transfer coefficient limit economic profit of this process. To improve or substitute the CPL aqueous solution dehydration process, pervaporation separation of caprolactam–water system was investigated using PVA crosslinked membranes. An in-depth study of sorption, swelling, pervaporation performances of caprolactam–water mixtures and crosslinked membrane had been conducted. The experimental data demonstrated that the PVA crosslinked with glutaraldehyde showed excellent dehydration performances. The novel separation technique is feasible for application to the dehydration of CPL–water mixtures.

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Keywords: CPL–water mixtures; Pervaporation; PVA crosslinked membranes; Glutaraldehyde; Novel separation technique

1. Introduction

Pervaporation is known as an effective process for separation of liquid mixtures, especially for separating of azeotropic, close boiling, isomeric or heat-sensitive liquid mixtures [1–8]. Compared to traditional separation processes such as distillation, pervaporation can offer high separation efficiency and low energy consumption. Currently, pervaporation separation of water–organic mixtures has been widely studied using hydrophilic membranes owing to their high water-permselectivity. Poly(vinyl alcohol) (PVA) membranes are widely used in dehydration pervaporation processes [4–11]. Because PVA has excellent characteristics such good selectivity towards water, chemical stability, film-forming ability in spite of poor physical stability in aqueous. The films must be insolubilized by crosslinking or heat treatment to improve the stability in aqueous solutions, for the crosslinked polymers have a net-like structure as compared to linear polymers. Thus, they are not easily dissolved. Hence they are used in preparing separation membranes materials with improved mechanical strength and durability.

CPL, as the monomer of nylon-6, is an important organic chemical material, which is used extensively in the manufacture of high quality nylon-6 fibers and resins. Worldwide capacities will reach above 4.5 million metric tonnes in the year 2005. Since CPL is very heat sensitive substance and has lower volatility than water, it is usually crystallized from CPL–water mixtures under reduced pressure distillation through triple-effect evaporation sets in the final CPL purification. But disadvantages, such as a large amount of middle pressure steam consumption, low heat transfer coefficient make researchers look for a new technique to improve or substitute the CPL aqueous solution dehydration process. Dehydration of CPL aqueous solutions in pervaporation has rarely been reported up to date. Therefore, the purpose of this article is to study the feasibility for application to dehydration of CPL aqueous solution with pervaporation. In this study, PVA membranes were chemically modified by crosslinking reaction with glutaraldehyde followed with a heat treatment.

2. Experimental

2.1. Materials

ϵ -Caprolactam (CPL) (chemical pure) was provided by Baling Petrochemical Co. Ltd. (SINOPEC, Yueyang, China); poly(vinyl alcohol) (hydrolyzed 99%, with average

* Corresponding author. Tel.: +86 27 6877 2263; fax: +86 27 6877 6726.
E-mail address: ybai@whu.edu.cn (Y. Luo).

Mw = 89,000–98,000 and glutaraldehyde (Gal, 25 wt.% in water, Aldrich) were obtained from Aldrich Chemicals (USA). All the chemicals were used as received. Deionized water was used in preparing the aqueous feed solutions for the pervaporation experiments.

2.2. Membrane preparation

The phase inversion method was used to prepare the membrane. The technique of membrane preparation follows a procedure reported in references [7,11–12,20]. The procedure for membrane preparation included four basic steps: film casting, partial evaporation of solvent, gelation and drying [13]. PVA was dissolved in water by refluxing and stirring for 6 h at 100 °C. Homogeneous solution of 10 wt.% polymer in water was obtained. To this solution, HCl (as a catalyst) and a certain amount of crosslinking agent (glutaraldehyde) were added. Slowly stir the solution continuously at room temperature for a desired amount of time, and then the reaction was stopped by neutralization with sodium hydroxide solution. Then the cooled and degassed solution was cast on a plexiglass by a gardener knife. The gelatination state was allowed to evaporate slowly till dried at room temperature. Finally, the crosslinked membranes were treated in an air-circulating oven at temperature 120–150 °C for 1 h for thermal crosslinking.

2.3. Characterization of membranes

Scanning electron microscopy (SEM, HITACHI X-650, Japan) was used for the investigation of the PVA membrane morphology. The crosslinking reaction of PVA with Gal was confirmed by the FTIR with a Nicolet AVATAR 360 FT-IR spectrometer. The WAXD was examined using x-ray diffraction of Cu K α radiation operated at 40 kV and 40 mA (XRD, Bruker AXS D8Advance). WAXD data were measured at room temperature. The diffraction angles (2 θ) were from 5° to 40° with the speed of 4° min⁻¹.

2.4. Sorption measurement

The sorption tests reflect the affinity between membrane materials and the permeating molecules. The equilibrium sorption of the feed mixture in the membrane was determined as follows: precisely weighed dry membranes sheets was immersed in a closed bottle containing the CPL–water mixture at 40 °C in a thermostatic bath for 48 h. After the swelling equilibrium state was reached, the strip was removed from the bottle and put into a closed tube after the surface liquid was quickly removed with tissue papers and the swollen membrane was weighed. The sorbed liquid was distilled out of the sample by the vacuum apparatus shown in Fig. 1. The evaporation of the liquid during the transfer step was always less than 2 wt.% of the total amount of liquid in the membrane [14]. The swollen membrane with excessive solvent removed was placed in the sample tube of the apparatus, and then the tube was heated with hot water, the released substances were condensed in a receiving tube, which was cooled

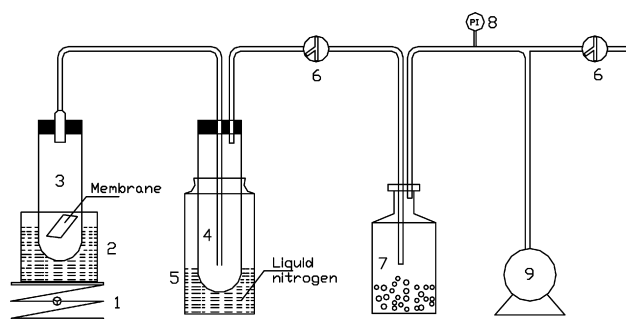


Fig. 1. Schematic of sorption and desorption equipment. 1, elevator; 2, heater; 3, sample tube; 4, receiver tube; 5, cold trap; 6, T-valve; 7, desiccator; 8, pressure gauge; 9, vacuum pump.

in liquid nitrogen. The composition of this condensate was analyzed by a SP3400 gas chromatography with a FID detector (made in China) under the following conditions: PEG-20M capillary column: 2 m \times 6 mm i.d., temperature: 170 °C, carrier gas: nitrogen, flow rate: 30 ml min⁻¹.

The degree of swelling S was calculated by the following equation:

$$S(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where W_{dry} and W_{wet} are the weights of the dry membrane and the swollen membrane, respectively.

The selectivity of sorption (S_{sorp}) was calculated by:

$$S_{\text{sorp}} = \frac{Y_{\text{water}}/Y_{\text{CPL}}}{X_{\text{water}}/X_{\text{CPL}}} \quad (2)$$

where X_{water} , X_{CPL} and Y_{water} , Y_{CPL} are the weight fractions of water and CPL in the feed and condensate, respectively.

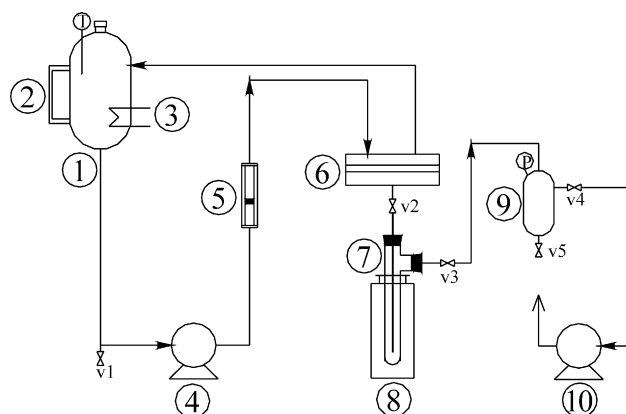


Fig. 2. Schematic diagram of pervaporation apparatus. 1, feed tank; 2, liquid level meter; 3, heater; 4, circulation pump; 5, rotary flow meter; 6, membrane cell; 7, collecting bottle; 8, liquid nitrogen cold trap; 9, buffer vessel; 10, vacuum pump; V1–5, valves; T, temperature control; P, vacuum pressure gauge.

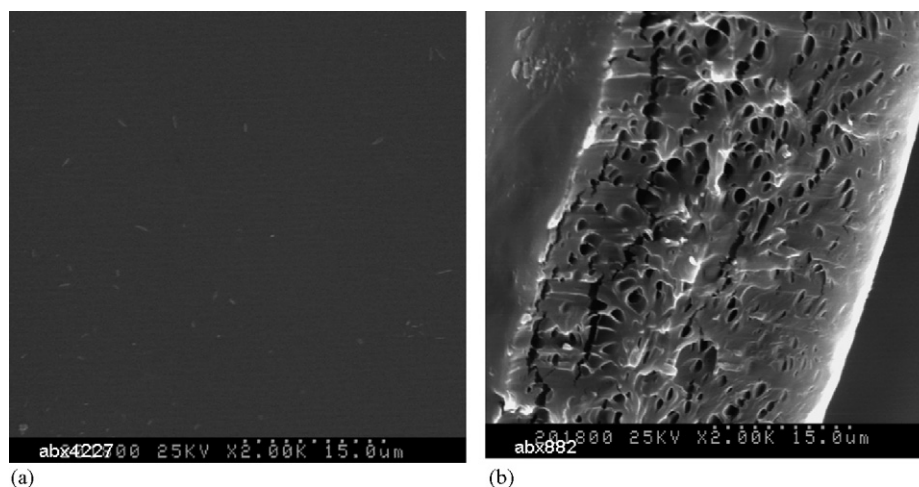


Fig. 3. The morphology of the crosslinked PVA membrane. (a) Top surface and (b) cross-section.

2.5. Pervaporation measurements

The PV experiments were performed in an apparatus developed in this laboratory. A schematic layout of the experimental set-up used in this study is presented in Fig. 2. The liquid feed was circulated through the pervaporation cell from a feed tank by a pump with a rate of 200 l h^{-1} . The pressure at the downstream side was kept about 10 mbar within ± 1 mbar by a vacuum pump. Permeate was condensed in liquid nitrogen traps. Pervaporation flux was determined by weighing penetrant collected by a liquid nitrogen trap during a given amount of time. Steady state was obtained after 2 h throughout the experiments. The feed solution temperature maintained in the range of $30\text{--}65^\circ\text{C}$ and the area of the membrane in contact with the liquid was 72.35 cm^2 . The composition of the liquid feed mixture was analyzed by measuring the refractive index of the permeate within an accuracy of ± 0.0001 units using high-precision Abbe Refractometer (Atago NAR-3T, Japan) and using standard graph of refractive index versus known compositions of water–CPL mixtures. The refractometer prisms were maintained at $20 \pm 0.1^\circ\text{C}$. The results from refractive index measurements can compare well with those from gas chromatography, for all tested membranes the variation of flux from different batches was less than 10% [15,16]. The vapor penetrant collected mixture was analyzed with the same GC as used in the sorption measurement.

The permeation flux (J_t) was calculated from the following equation:

$$J_t (\text{g}/(\text{m}^2 \text{ h})) = \frac{W (\text{g})}{A (\text{m}^2) \times t (\text{h})} \quad (3)$$

where W is the weight of penetrant, A the effective membrane area (m^2) and t is the measuring time.

The separation factor α_{PV} was calculated by:

$$\alpha_{\text{PV}} = \frac{Y_{\text{water}}/Y_{\text{CPL}}}{X_{\text{water}}/X_{\text{CPL}}} \quad (4)$$

where X_{water} , X_{CPL} and Y_{water} , Y_{CPL} are the weight fractions of water and CPL in the feed and permeate, respectively.

3. Results and discussion

3.1. Characterization of the crosslinked PVA membranes

3.1.1. Scanning electron microscopy

Scanning electron micrographs of the crosslinked PVA membranes are presented in Fig. 3. Fig. 3a and b shows the top surface and cross-section of the crosslinked PVA membrane prepared by phase inverse technique. The crosslinked PVA membrane have a dense skin layer from Fig. 3a and the thickness of membrane was found about $25\text{--}35 \mu\text{m}$ from Fig. 3b.

3.1.2. FTIR analysis

Yeom and Lee [17] have studied the crosslinking reaction between PVA solution and Gal crosslinking agent, HCl as a catalyst. The crosslinking reactions involved in the process are shown in Fig. 4.

Based on the above related two kinds of crosslinking reaction, the results of crosslinked PVA networks can be analyzed by FTIR spectra. Fig. 5 shows the infrared absorption spectra of

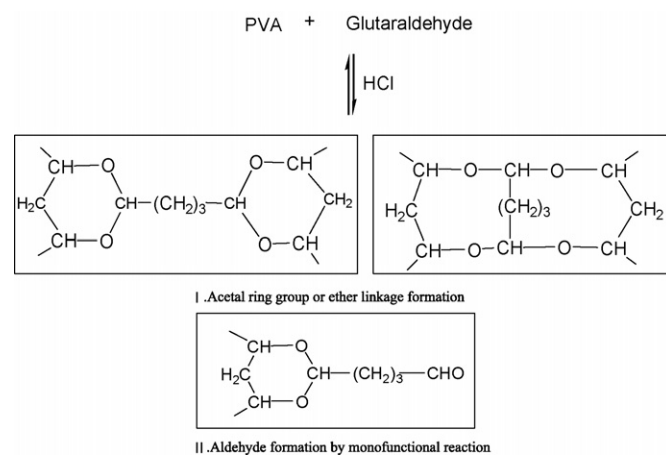


Fig. 4. The crosslinking reaction between PVA and Gal [17]. (I) Acetal ring group or ether linkage formation and (II) aldehyde formation by monofunctional reaction.

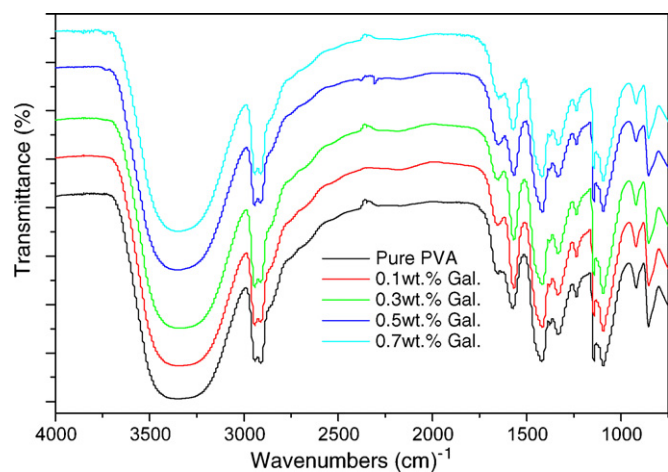


Fig. 5. FTIR spectra of PVA crosslinked membranes with different Gal contents in the crosslinking agents.

the PVA crosslinked with different Gal contents in crosslinking agents. It can be seen from these spectra that the main characteristic absorption peaks are: one distinct broad absorption bands at $3000\text{--}3600\text{ cm}^{-1}$, which is attributed to stretching of the O–H hydroxyl group; 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; 1620 cm^{-1} , stretching of C=C group or the O–H group of trace amount water; $1200\text{--}1480\text{ cm}^{-1}$, maybe corresponding to variable deformation vibrations of the CH_2 or C–H groups; 1094 and 1200 cm^{-1} , which are attributed to C–O and C–O–C groups due to acetal or ether linkage formation (see Fig. 4). The intensity of the O–H bands observed in membranes decreasing considerably with the Gal contents increasing in the crosslinking agent indicates that the degree of crosslinking in the PVA film is increased. In addition, the intensity of the absorption band at 1720 cm^{-1} does not increase, indicating that hydroxyl groups and free aldehyde groups in Gal reacted completely via acetal reaction [5,17]. Similar results have been reported in literatures [18,19].

3.1.3. X-ray diffraction of PVA membranes

The X-ray diffraction patterns of the PVA membranes are shown in Fig. 6. The typical diffraction peak is observed at $2\theta = 20^\circ$. From these patterns, it is clear that the uncrosslinked PVA membranes exhibit more crystalline domains than the crosslinked ones. The crystallinity has decreased with increasing Gal contents in the crosslinking agents. This result implies that the increase in the crosslinking of the PVA membrane decreases the crystallinity of the membrane, which results in a compression of the amorphous region [15,20].

3.2. Effects of crosslinking agents loading and feed composition on membrane swelling and sorption selectivity

Swelling measurement was performed to determine the degree of crosslinking and the sorption selectivity of the crosslinked membranes. The effect of the crosslinking agents

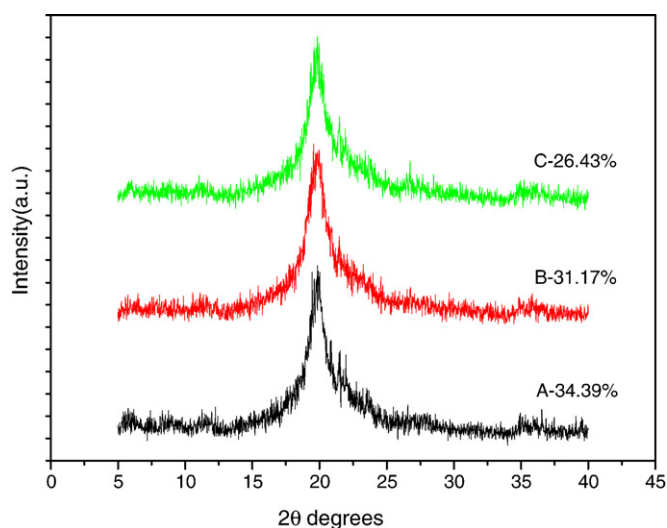


Fig. 6. X-ray diffraction pattern of (A) pure PVA; (B) PVA crosslinked with 0.5 wt.%; (C) PVA crosslinked with Gal 0.7 wt.% Gal contents in the crosslinking agents.

on the degree of swelling and the sorption selectivity of PVA membranes for 30 wt.% CPL aqueous solution is shown in Fig. 7. From this plot it can be observed that crosslinked PVA membrane shows a good affinity to water and both the degree of swelling and the sorption selectivity decrease with increasing Gal concentration in crosslinking agent on the membrane. This can be explained from the formation of the membranes [17,20]. XRD results confirm that the more crosslinking agent concentration, the more compact amorphous region of the membranes is (see Fig. 6). That is to say, the more compact structure of polymeric chains results in less chain mobility. High sorption selective usually can be obtained by introduction into a macromolecule of active centers which are capable of specific interactions with penetrate, such as hydrogen bond or ion–dipole interactions [21]. FTIR results show that the intensity of the O–H bands observed

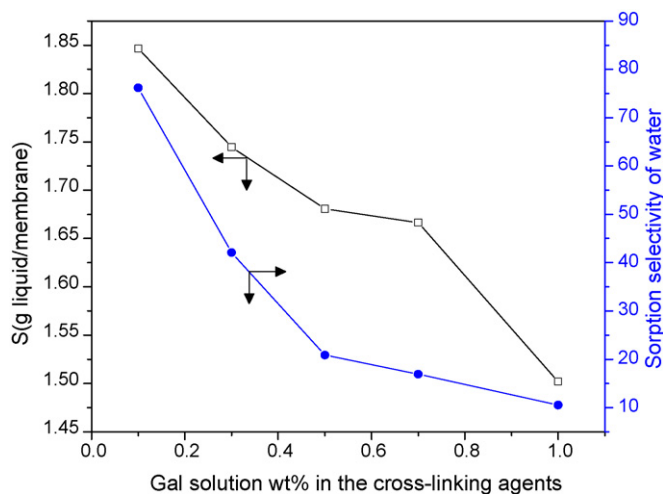


Fig. 7. The degree of swelling and sorption selectivity for 30 wt.% aqueous solution in crosslinked PVA membranes with different Gal contents in the crosslinking agent at 40°C .

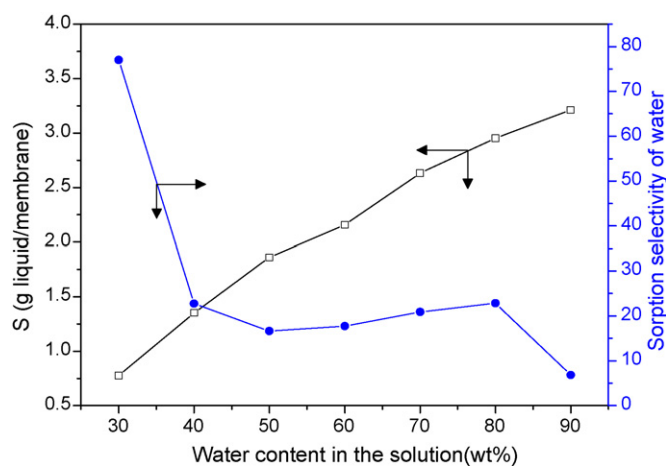


Fig. 8. The degree of swelling and sorption selectivity for different water concentration in the feed in crosslinked PVA membrane with 0.5 wt.% Gal contents in the crosslinking agent at 40 °C.

in membranes gradually weakened with the Gal concentration in the crosslinking agents increasing, which means that hydrogen bonds have been destroyed, leading to the sorption selectivity of the membranes decrease (see Fig. 5). Hence, we can draw a conclusion that hydrogen-bonding interaction is the important factor controlling the selectivity toward water in the sorption process. From Fig. 8, it can be observed that the degree of swelling increases and the sorption selectivity decreases for the crosslinked PVA membranes with increasing water concentration. Since water has a better affinity towards the membranes than CPL, this means that the more selective component water increases in the mixtures, the more swollen membrane is. As the water concentration increases, sorption selectivity first decreases sharply due to its swelling induced plasticisation and stays comparatively constant from 40 to 80 wt.% water in the solution, then sorption selectivity decreases because of the excessive swelling action of water.

3.3. Pervaporation characteristics

3.3.1. Effect of operating temperature

The effect of operating temperature on pervaporation properties is shown in Fig. 9. It can be observed that the total permeation flux increased significantly and separation factor decreased when temperature increased from 313 to 338 K. Generally speaking, as temperature increases, the rotating frequency and amplitude of the chain increase and free volume becomes larger. Hence, the mobility of permeating molecules is enhanced both by the temperature and the higher mobility thus the weaker interaction between the penetrants and the membranes at higher temperature facilitates the transport of penetrants, which leads to the decrease of the separation factor towards water.

The temperature dependence of the permeation flux can be expressed by an Arrhenius type relationship:

$$J_t = J_0 \exp\left(\frac{-E_0}{RT}\right)$$

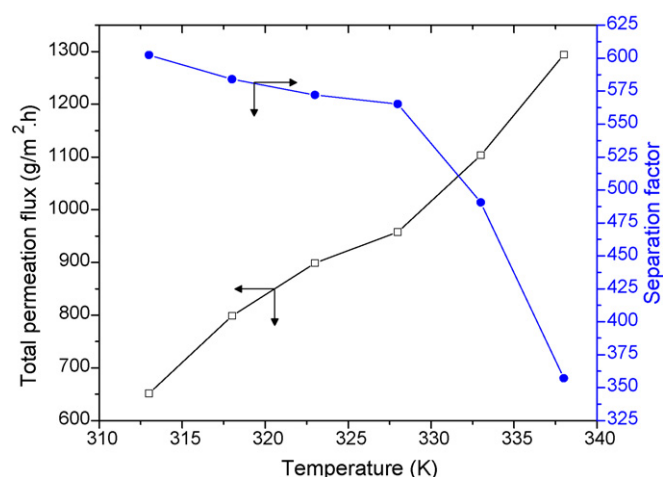


Fig. 9. Effect of operating temperature on pervaporation characteristics with PVA membrane crosslinked with 0.5 wt.% Gal in the crosslinking agent for 50 wt.% CPL in the feed.

where J_t is the total permeation flux, J_0 and E_0 are the pre-exponential factor and the apparent activation energy of permeation, respectively. Arrhenius plots of total permeation flux are illustrated in Fig. 10. The apparent activation energy at 50 wt.% CPL in the feed is significantly higher than that at 40 wt.% CPL in the feed, indicating the membrane is less swollen at higher CPL concentration and more penetration energy is needed for the permeate to transport through the membrane.

3.3.2. Effects of water feed concentration

Pervaporation performances of CPL–water mixtures with PVA membrane crosslinked with 0.5 wt.% Gal in the crosslinking agent was carried out over a range of 30–70 wt.% water in the feed at 323 K. The results are shown in Fig. 11. It is generally observed that the permeation rate increases as the feed concentration of the preferentially selective component increases but selectivity decreases due to high swelling of the

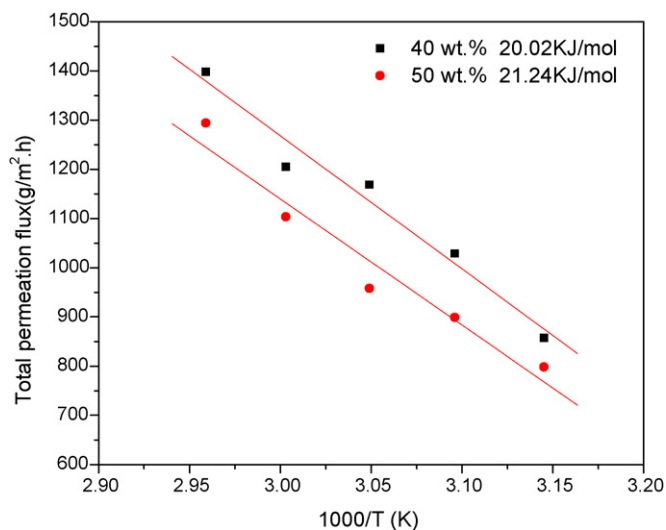


Fig. 10. The curve between total permeation flux and temperature reciprocal.

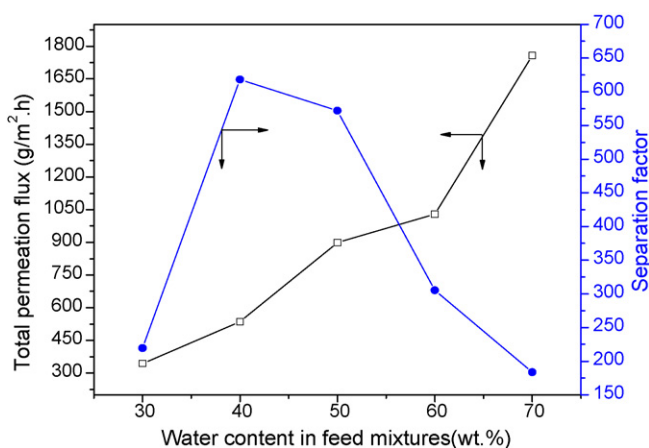


Fig. 11. Effect of water concentration on pervaporation characteristics with PVA membrane crosslinked with 0.5 wt.% Gal in the crosslinking agent at 323 K.

membrane [22]. The total permeation flux was found to increase with water increasing in the feed; this can be explained in terms of the plasticising effect of the water on membranes. With higher water concentration in the feed mixture, the amorphous regions of the membrane are more swollen and the polymer chains become more flexible. This makes both water molecules and CPL molecules more easily penetrate through membranes, so the total permeation flux increases. According to the solution–diffusion theory [23], the separation mechanism in pervaporation is based on the difference in sorption and diffusion properties of the feed compounds, instead of on the difference in relative volatilities. Sorption selectivity can be obtained by using sorption data. From the plot, it can be seen that the separation factor towards water initially increases up to a maximum and then decreases with an increase in weight fraction water in the feed. Since the sorption selectivity decreases sharply (see Fig. 8), the only explanation for the sharp increase in separation factor would have to be diffusion properties of the feed compounds. Because the size of the water molecule sorbed into the membranes is smaller than that of the CPL, the water molecule can be more easily diffused in the moderately swollen membranes, thus the separation factor initially ascends; then the separation factor decreases due to the combined effects of the breakdown of hydrogen-bonds between permeant constituents and the polymer because of excessive swollen of the membranes and the strong polar–polar interaction of CPL and water.

4. Conclusions

A detail study of sorption and permeation of water–CPL mixture was carried out by using PVA membranes crosslinked by Gal. Pervaporation and sorption characteristics of CPL–water mixtures were studied with membranes prepared under different conditions. The feed composition and crosslinking agents loading had an important impact on the degree of swelling and sorption selectivity. The effects of operating conditions on pervaporation properties were also studied. The results showed

that crosslinked PVA membranes had excellent dehydration performances for CPL–water mixtures. However, due to the poor durability and mechanical strength, we thought that a composite membrane with PVA as the active skin layer would be more suitable for this application.

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