

Dehydration of caprolactam–water mixtures through cross-linked PVA composite pervaporation membranes

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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. Since CPL is a very heat-sensitive substance and water is the most important impurity in the final CPL purification, reduced pressure distillation through triple-effect evaporation sets is widely adopted by chemical industry. But high energy consumption, high wastage and condensate pollution have restricted the wide-scale production of CPL and the commercial profit of the manufactures. To improve or develop a new CPL dehydration process, pervaporation separation of CPL–water mixtures was investigated using composite membranes consisting of a selective poly(vinyl alcohol) (PVA) membrane as top layer and a porous polyacrylonitrile (PAN) substrate. The selective layer was formed by PVA matrix followed by the cross-linking reaction of PVA with glutaraldehyde. The membranes were characterized by SEM, FTIR and TGA. Due to the formation of more compact cross-linked structure, cross-linked PVA composite membranes exhibited enhanced thermal stability. Through evaluating the pervaporation performance, we introduced a pervaporation transport equation to normalized permeation fluxes in terms of water permeance, CPL permeance and selectivity. The evaluated results have revealed that the separation performances of PVA composite membranes are strongly related to its hydrophilic/hydrophobic nature as well as the operating parameters, such as feed concentration and operating temperature. Experimental data showed that the PVA composite membranes had superior pervaporation separation performances for dehydration of caprolactam–water mixtures, which provided a new way for CPL dehydration.

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Keywords: Dehydration; Caprolactam–water mixtures; Glutaraldehyde; Pervaporation; Normalized permeation fluxes; Composite membranes

1. Introduction

ϵ -Caprolactam ($C_6H_{11}NO$, CPL) is an industrially important organic chemical material, which is used extensively in the manufacture of high quality fibers and engineering plastics. CPL is produced by the Baling Petrochemical Co. Ltd. (SINOPEC, China), which has adopted the HPO process developed by DSM Corporation (Dutch). The monomer of CPL is synthesized via the cyclohexanone oximation and Beckmann rearrangement route using highly concentrated sulfuric acid, followed by neutralization with ammonia; the scheme was shown in Fig. 1. The industrial processes utilized for fiber production are sensitive to quality fluctuations; so high purity of commercial CPL (>99.8%) is most often required by artificial fiber industry, especially in the production of high quality nylon fibers and

resins. Because certain trace level contamination in CPL directly influences the polymerization and the quality of fiber produced.

Water is the most important impurity in the final CPL purification, several traditional separation techniques, such as thin-film distillation, crystallization, melt crystallization by suspension, have been suggested [1,2]. Especially, crystallization under a reduced pressure distillation through triple-effect evaporation sets is often widely adopted in manufacture of high quality nylon-6 fibers and resins. However, since CPL is very heat-sensitive substance, traditional techniques have the disadvantage, such as high operating costs, high energy consumption and the pollutants are transferred to a second phase, where a further separation problem still remains and so on. Therefore, it is necessary to develop a new dehydration process for the concentrate of CPL–water mixtures.

In the recent years, pervaporation (PV) is rapidly emerging as an energy efficient alternative and eco-friendly clean technology. Moreover, pervaporation can be operated at lower temperatures than other separation methods, such as distillation,

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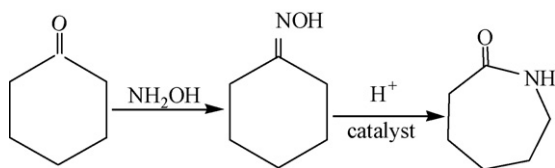


Fig. 1. The synthetic scheme of CPL.

which makes it possible to utilize waste-heat as the heat of vaporization to separate volatile organic compounds (VOCs) from water in the chemical industry [3]. Over the past several decades, research in pervaporation was mainly focused on separation of azeotropic, close boiling, isomeric, water/organic mixtures and organic/organic mixtures [3–18]. Among them, Bruschke and co-workers at GFT company (now Sulzer Chemtech) first commercialized PV technology for ethanol dehydration using composite membranes based on cross-linked poly(vinyl alcohol) (PVA) on micro-porous polyacrylonitrile substrate [4,5,9,18].

In PV, pervaporation composite membranes are widely used in industry. The thin “active” membrane layer is coated on a porous support layer to achieve high membrane performance and sufficient mechanical strength. In this paper, we have developed PVA composite membranes on homogeneous PVA membranes and modify them by chemical cross-linking method as separating layer material and porous polyacrylonitrile (PAN) ultrafiltration membranes as supporting layer to fabricate composite pervaporation membranes. PAN ultrafiltration (UF) membrane as support layer has been selected for this reason: PAN UF membranes, owing to its hydrophilic character, are widely used for dehydration applications in PV technology [4,5,9,11,18]. The selection of PVA was also due to such reasons: poly(vinyl alcohol) (PVA) can readily form thin films and having high hydrophilicity and good chemical resistance, which make it as an attractive polymer to be used as a pervaporation membrane for the dehydration of aqueous–organic mixtures [4–10,12–14]. Since PVA has poor stability and solubility in aqueous solution, the membrane must be insolubilized by modification reactions such as cross-linking to improve the stability of the membrane in aqueous solutions [4–9,11–13]. PVA cross-linked with glutaraldehyde has been widely used for water–ethanol, acetic acid–water and other system separation [4–7,11–13]; while its potential for separation of water–CPL mixtures has been explored to a very limited extent [19]. So an in-depth study of dehydration of CPL–water mixtures in composite-type pervaporation membrane was investigated in the present study.

2. Theory

In pervaporation process, there are two different but thermodynamically equivalent representations of pervaporation process [20]. One is the conventional representation that a liquid solution contacts the feed side of a membrane and a low pressure is withdrawn on the permeate side. For dehydration of solvents by pervaporation the performance of a membrane is usually expressed in terms of permeation flux (J) and separation factor (α_{pv}).

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

$$J \text{ (g/(m}^2 \text{ h))} = \frac{W \text{ (g)}}{A \text{ (m}^2 \text{)} \times t \text{ (h)}} \quad (1)$$

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

The separation factor α_{pv} was calculated by:

$$\alpha_{pv} = \frac{y_{\text{water}}/y_{\text{CPL}}}{x_{\text{water}}/x_{\text{CPL}}} \quad (2)$$

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

The other one is assumed that there is a vapor phase that exists between the feed solution and the feed side of the membrane. The driving force for pervaporation can be expressed as a vapor pressure difference. Although the performance of a pervaporation membrane is usually expressed in terms of the flux and separation factor, it is worth noting that these two parameters are a complex combination of the effect of the driving forces, the effect of interaction between permeants and the intrinsic membrane property [8,18,20]. In order to distinguish between intrinsic membrane properties and the influence of the experimental operation conditions further, normalized permeation flux (permeance) and membrane selectivity were proposed and evaluated to clarify the contribution by the nature of the membrane to separation performance.

When the driving forces are taken into account, a transport equation for the pervaporation process is defined as follows according to the solution-diffusion model [20–22]:

$$J_i = Q_i(x_i\gamma_i p_{i,\text{feed}}^0 - y_i p_{\text{permeate}}) \quad (3)$$

where J_i is the partial permeate flux of component i , Q_i the pressure-normalized permeation flux of i through the membrane (the permeance, which equals the partial flux divided by the partial pressure difference over the membrane), x_i , y_i the mole fraction of i in the feed and the permeate, respectively, γ_i the activity coefficient of i in the feed liquid and can be calculated by using Van Laar equations and $p_{i,\text{feed}}^0$ the saturation vapor pressure of pure i in the feed liquid temperature, is determined from the Antoine equation and p_{permeate} is the permeate pressure. The membrane selectivity (α_{mem}) is an intrinsic property of the membrane material, which is defined as the ratio of the water permeance over the CPL permeance.

$$\alpha_{\text{mem}} = \frac{Q_w}{Q_{\text{cpl}}} \quad (4)$$

In this paper, the vapor–liquid equilibrium data required for these calculations were obtained by using the coefficients for the Antoine and Van Laar equations as tabulated by Gmehling and Onken [23]. The coefficients are given in Tables 1 and 2.

Table 1

Coefficients for the Antoine equation used in the calculations: $\log(p_i^0) = A_0 - B_0/(T + C_0)$, with p_i^0 in 1.333224×10^2 Pa (mmHg) and T in degree celsius ($^{\circ}\text{C}$)

	A_0	B_0	C_0
Water	8.07131	1730.630	233.426
CPL	6.78000	2344.000	273.150

Table 2

Coefficients for the Van Laar equation used in the calculations: $\ln(\gamma_1) = A_{12}[A_{21}x_2/(A_{12}x_1 + A_{21}x_2)]^2$, $\ln(\gamma_2) = A_{21}[A_{12}x_1/(A_{12}x_1 + A_{21}x_2)]^2$

	A_{12}	A_{21}
CPL (1)/water (2) at 40°C	−1.0429	−1.5810

3. Experimental

3.1. Materials

ϵ -Caprolactam (CPL) (chemically pure) was supplied by Baling Petrochemical Co. Ltd. (SINOPEC, China); poly(vinyl alcohol) (PVA) (hydrolyzed 99%, with average $M_w = 89,000$ – $98,000$) and glutaraldehyde (GA, 25 wt.% in water) were obtained from Aldrich Chemicals (USA). Porous ultrafiltration membranes of polyacrylonitrile (PAN) (cut-off $M_w 5 \times 10^4$) 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.

3.2. Preparation of cross-linked PVA composite membranes

The technique of PVA composite membrane preparation follows a procedure reported in references [5,11,12]. The casting procedure is as follows: firstly, formulation of casting solution, 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 cross-linking agent (glutaraldehyde) was added and the reaction was started. Continuing to slowly stir the solution at room temperature for 20 h, the reaction was stopped by neutralization with sodium hydroxide solution.

Secondly, the preparation of composite membranes was done. The coated membranes, which had been treated with about 4 wt.% 1N sodium hydroxide solution for 24 h, were washed and rinsed by about 4 wt.% 1N hydrogen chloride solution and deionized water till neutrality and air-dried. Then, the prepared solution was cast on the porous 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 till dried at room temperature. Finally, post-treatment of the composite membrane, the composite membranes were treated in an air-circulating oven at temperature 120 – 150°C for 1 h for thermal cross-linking.

3.3. Characterization

3.3.1. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to study the morphology of the various composite membranes. All specimens were coated with a conductive layer of sputtered gold. The morphologies of the PVA composite membranes were observed with SEM (FEI Quanta 200, Holland).

3.3.2. Fourier transform infrared (FT-IR) spectroscopy

The cross-linking reaction of PVA with GA was confirmed by the FT-IR. The FT-IR spectra of uncross-linked and cross-linked membranes were scanned using Nicolet AVATAR 360 FT-IR spectrometer.

3.3.3. Thermogravimetric analysis (TGA)

The thermal stability of the PVA active layer was analyzed with Setaram SETSYS Evolution 16 thermogravimetric analyzer by heating from room temperature to 650°C at a rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen gas.

3.4. Sorption experiments

A precisely weighed dry membrane sheet was immersed in a closed bottle containing binary feed mixtures for a period at 40°C . It is necessary to indicate that only the PVA part of the membrane (considered to be the active layer) was tested for sorption in the chemicals used in this study. The sorption data thus obtained, indicated the sorption behaviour of only the active membrane layer. After the swelling, equilibrium state was reached; the strip was subsequently blotted between tissue paper to remove excess solvent and weighed as soon as possible before drying started. After complete drying, the weight of dry strips was measured once again.

Degree of swelling (S) was calculated by the following equation:

$$S(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (5)$$

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

3.5. Pervaporation experiments

PV experiments were carried out using an apparatus as shown in Fig. 2. Feed tank was maintained at constant temperature by a resistance controlled by a thermocouple. The membrane cell was designed to allow high fluid velocity parallel to the membrane surface. The membrane with an effective area of 72.35 cm^2 in contact with feed liquid was supported by a porous titanium plate. After the feed solution in the reservoir tank was reached at a desired temperature, feed solution was circulated with a relatively high flow rate of 200 l/h from the feed tank through the membrane cell by a feed pump. The vacuum in the downstream side of the apparatus was maintained about 10 mbar within ± 1 mbar. Steady state was attained after running 1–2 h in the feed tank at desired temperature before performing

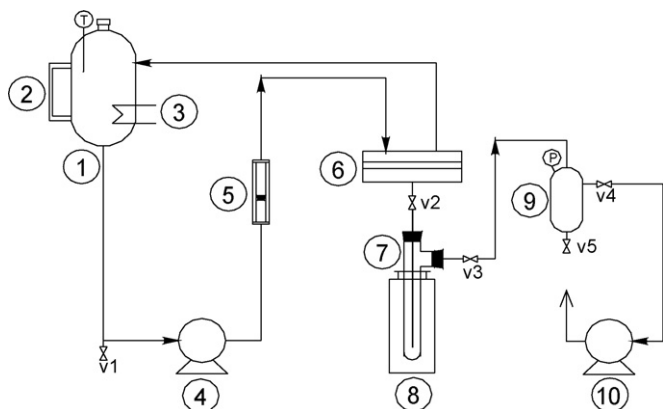


Fig. 2. Schematic diagram of pervaporation apparatus: (1) feed tank; (2) liquid level meter; (3) heater; (4) circulation pump; (5) rotary flow meter; (6) membrane cell; (7) collecting bottle; (8) liquid nitrogen cold trap; (9) buffer vessel; (10) vacuum pump; (V1–5) valves; (T) temperature control; (P)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

the PV experiment with a known volume of feed mixture; this is done in order to achieve the equilibrium condition for the membranes. Permeate vapor was collected and condensed in the collecting bottle immersed in liquid nitrogen. Pervaporation experiments for CPL–water mixtures having different concentrations of CPL were conducted in the range of 40–60 °C. During the pervaporation runs, the compositions of the liquid feed mixtures were analyzed every 1 h by measuring the refractive index within an accuracy of ± 0.0001 units using high-precision Abbe Refractometer (Atago NAR-3T, Japan), which can be calculated through using previously established standard graph of refractive index versus known mixture composition. The refractometer prism was maintained at 20 ± 0.1 °C. The trap filled with condensed permeate was warmed up to ambient temperature, and weighed to calculate the permeation flux. The compositions of the 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 \times 6 mm i.d.; temperature, 170 °C; carrier gas, nitrogen; flow rate, 30 ml min⁻¹.

4. Results and discussion

4.1. Membrane characterization

4.1.1. SEM analysis

SEM photographs of the PVA composite membranes are presented in Fig. 3. The multilayer structure of composite membrane is observed very clearly: an active layer, a supported porous layer and a substrate. It is observed that a uniform PVA thin dense layer was properly cast on the top of the PAN substrates, and that it had a thickness of about 5–10 μ m, slightly thicker than 3–5 μ m of the GFT membrane PVA layer. The total

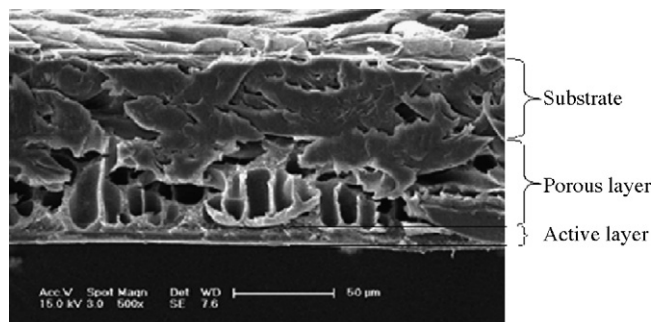


Fig. 3. The morphology of PVA composite membrane.

thickness of the dry composite membranes is found to be about 80–100 μ m.

4.1.2. FT-IR analysis

Fig. 4 shows the FT-IR spectra of the PVA active layer coated on the PAN substrates cross-linked at different GA contents in the cross-linking agents. The two main characteristic absorption peaks are: one distinct broad absorption bands at 3000–3600 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 CH₃; 1720 cm⁻¹, corresponding to stretching of C=O group of aldehyde. 1200–1480 cm⁻¹ may be corresponding to variable deformation vibrations of the CH₂ or C–H groups; 1094 and 1200 cm⁻¹, which are attributed C–O and C–O–C groups due to acetal or ether linkage formation after the cross-linking took place. Those spectral changes, an increase in the absorbance of the peaks between 1000 and 1386 cm⁻¹ and the weakening of the relative intensity of the O–H bands over the C–H bands gradually, arise from the formation of an acetal ring and ether linkage as a result of the reaction between the hydroxyl groups and the aldehydes and hydroxyl groups consumption. From the above spectral changes, it can be seen that as the GA contents in the cross-linking agents increases, more hydroxyl groups are consumed and more acetal rings and ether linkages are formed in

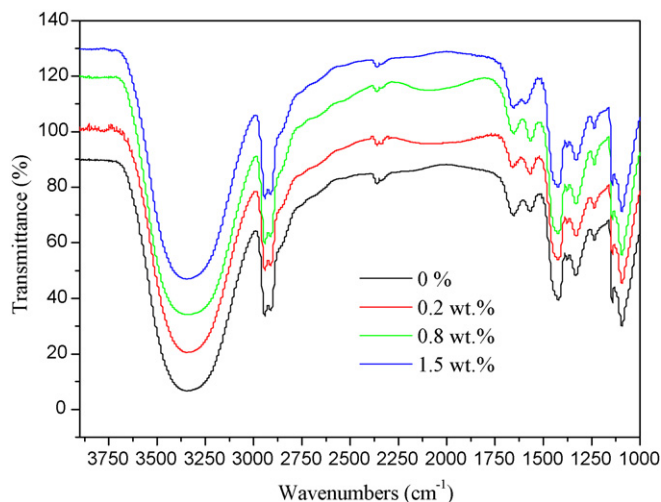


Fig. 4. FT-IR spectra of PVA composite membranes.

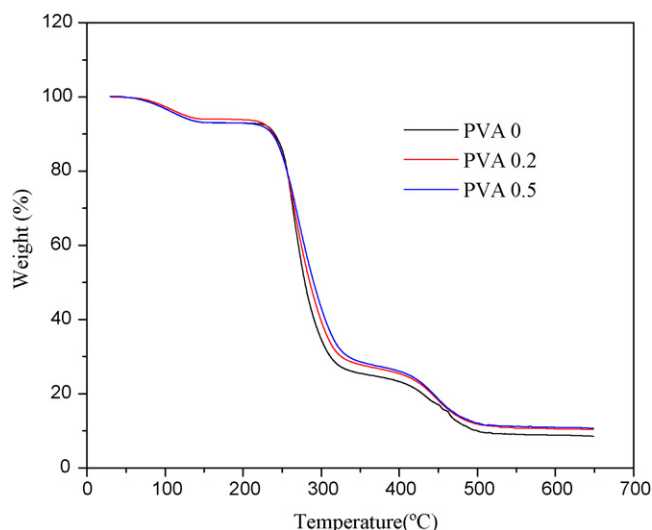


Fig. 5. TGA thermograms of PVA composite membranes cross-linked at different GA contents in the cross-linking agents.

the reaction between PVA and GA [13]. The absorption bands at 1720, 2731 and 2866 cm^{-1} are attributed to the characteristics of aldehyde. The intensities of the absorption bands at 1720, 2731 and 2866 cm^{-1} do not increase, indicating that hydroxyl groups and free aldehyde groups in GA reacted completely [7,13,25].

4.1.3. Thermal analysis

Thermal analysis is necessary to investigate the thermal stability of PVA thin membranes in aqueous solution. Fig. 5 compares the thermal stability and decomposition curves of the cross-linked PVA composite membranes. A weight loss before 220°C was observed for all samples. This weight loss was considered to be corresponding to the absorbed water in the membranes. The recorded thermograms for all samples showed two degradation steps: PVA composite membranes decomposition starts to decompose at 230°C and decomposes completely around 530°C . Compared with uncross-linked PVA composite membranes (PVA 0), less weight loss is observed for the cross-linked PVA membranes (PVA 0.2/0.5), this implies that the more formation of acetal rings and ether linkages complex would have higher thermal stability and decrease the hydrophilicity of the membranes.

4.2. Effect of the cross-linking density of the PVA composite membranes on the degree of swelling

The sorption experiments were performed to reveal the sorption and diffusion characteristics based on the theory of solution-diffusion. In pervaporation, the permeation flux and selectivity of a membrane are dependent on the degree of swelling of the permselective layer because of the interactions between the membrane and the contacting liquid and also the mutual interaction among permeates. So studying the degree of swelling may gain an insight into the membrane characteristics in various liquid mixtures.

Fig. 6 displays swelling behaviour of the composite membranes cross-linked with different GA solution in the cross-

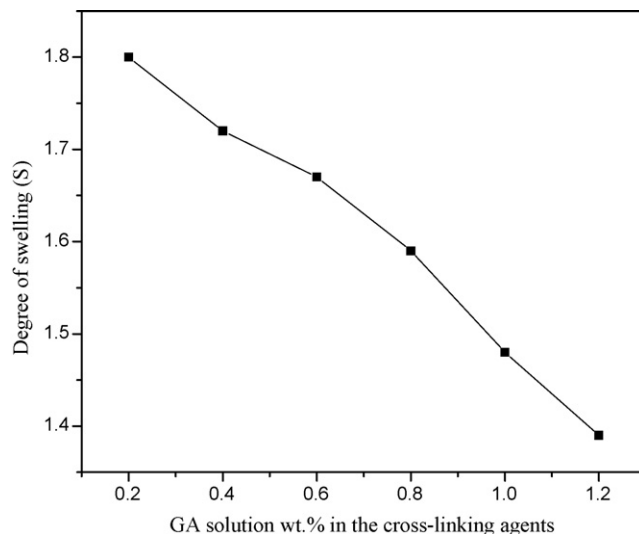


Fig. 6. The swelling ratio for 30 wt.% CPL aqueous solution in PVA composite membranes cross-linked with different GA solution in the cross-linking agent at 40°C .

linking agent on the degree of swelling in 30 wt.% CPL aqueous solution at 40°C . It is noticed that more the GA contents in the cross-linking agent, more the degree of cross-linking, i.e. the cross-linking density is higher and we know that PVA hydrophilic property is a strong driving force for water affinity and its sorption. Therefore, more the degree of cross-linking, lower the degree of hydrophilicity owing to the reason that more aldehyde groups (CHO) could penetrate to the membrane and react with the hydroxyl groups (OH) of the PVA to form more acetal or ether linkage [6,13], such cross-linking network may help to stabilize the structure from swelling; moreover, the increase in the cross-linking density usually leads to a decrease in the free volume of the membranes [13]. That is to say, the more compact structure of polymeric chains results in less chain mobility, thus the degree of swelling decreases.

4.3. Pervaporation characteristics

4.3.1. Effect of operating temperature

The composite membrane showed excellent thermal stability when pervaporation tests were carried out from 40 to 60°C . The effect of operating temperature on pervaporation performance of PVA composite membranes for 60 wt.% of CPL in the feed was studied and results are presented in Fig. 7. The operating temperature range was chosen from 40 to 60°C by considering the two major reasons: first, the color of CPL–water mixtures changed from white to slightly light brown with an increase in temperature. The system was executed for 24 h at the higher temperature investigated ($>65^\circ\text{C}$), a light brown material was produced. The slightly brown color was probably due to oxidative degradation at the higher temperature even though minor amounts of oxygen present in the surface of the feed liquid or adsorbed on crystalline CPL; second, CPL is very heat-sensitive substance, when temperature is high, ring-opening polymerization easily occurs and oligomer produced in the reaction will be deposited and is not soluble in water. As is reflected from

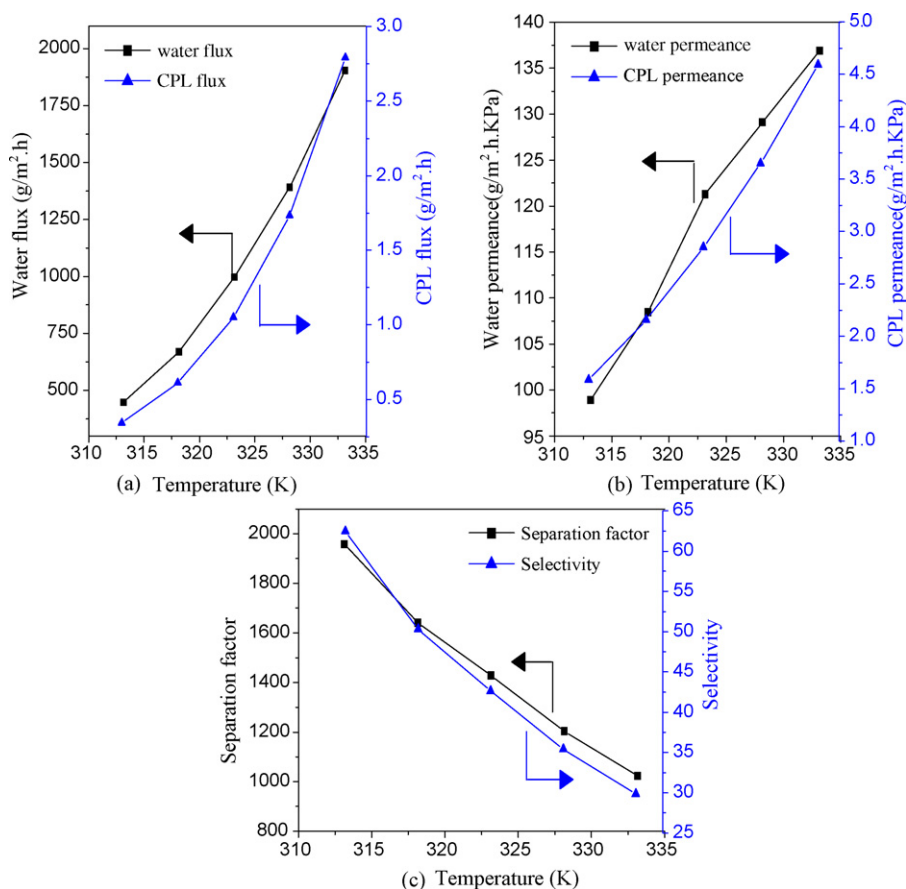


Fig. 7. Effect of the operating temperature on the pervaporation performances in terms of (a) flux, (b) permeance and (c) selectivity and separation factor through PVA composite membranes cross-linked with 0.6 wt.% GA contents in the cross-linking agent at 60 wt.% CPL aqueous solution.

Fig. 7(a), when the temperature increases, the partial fluxes increase, this phenomenon may be traditionally explained by the increase in frequency and amplitude of polymer chain thermally induced and the expansion of the free volume. In addition, at higher temperatures, diffusion rates of individual permeating molecules increase leading to high permeation flux [26]. However, the above explanation seems not to indicate a full agreement with the permeances versus feed temperature as illustrated in Fig. 7(b). Because the temperature effect on permeance is complicated. The reason may arise from the fact that permeance is defined as permeant flux divided by permeant driving force. The driving force combines two temperature dependent factors: γ_i and $p_{i,\text{feed}}^0$. When temperature increases, the activity coefficients (γ_i) of penetrates are quite close at different temperatures but the saturation vapor pressure ($p_{i,\text{feed}}^0$) of the penetrates also increases; since the downstream pressure is very low compared with the upstream pressure, it can be neglected; thus, the saturation vapor pressure ($p_{i,\text{feed}}^0$) of the feed composition contributes more to the driving force. Consequently, the increase in permeances is due to the combination of fluxes and the driving force effects mentioned above. Both separation factor and selectivity reveals decreasing trend with the rising temperature from Fig. 7(c). An increase in temperature reduces the interactions between permeating molecules and membrane and the increase of swelling of the membrane matrix at higher tem-

perature also facilitates the transport of CPL along with water molecules, thereby the separation factor decreases. Comparing with the partial fluxes versus partial permeances, and separation factor versus selectivity as well as their mutual relationship (see Fig. 7) indicates that the feed temperature has stronger effects on partial fluxes and separation factor than on their corresponding permeances and selectivity. These phenomena can be explained by the fact that the flux and separation factor parameters depend on both intrinsic membrane properties and influence of the experimental operating conditions, and permeance and selectivity exclude the effect of experimental operating conditions [8]. Consequently, the permeance and selectivity can reflect true membrane performance.

The temperature dependence of the pervaporation flux and permeance can be expressed by Arrhenius equations [20,27]:

$$J_i = J_0 \exp\left(-\frac{E_J}{RT}\right) \quad (6)$$

$$Q_i = Q_0 \exp\left(-\frac{E_Q}{RT}\right) \quad (7)$$

where J_0 , Q_0 , E_J and E_Q are the pre-exponential factor, apparent activation energy of the permeation flux and the membrane permeance, respectively. R indicates the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is absolute temperature (K).

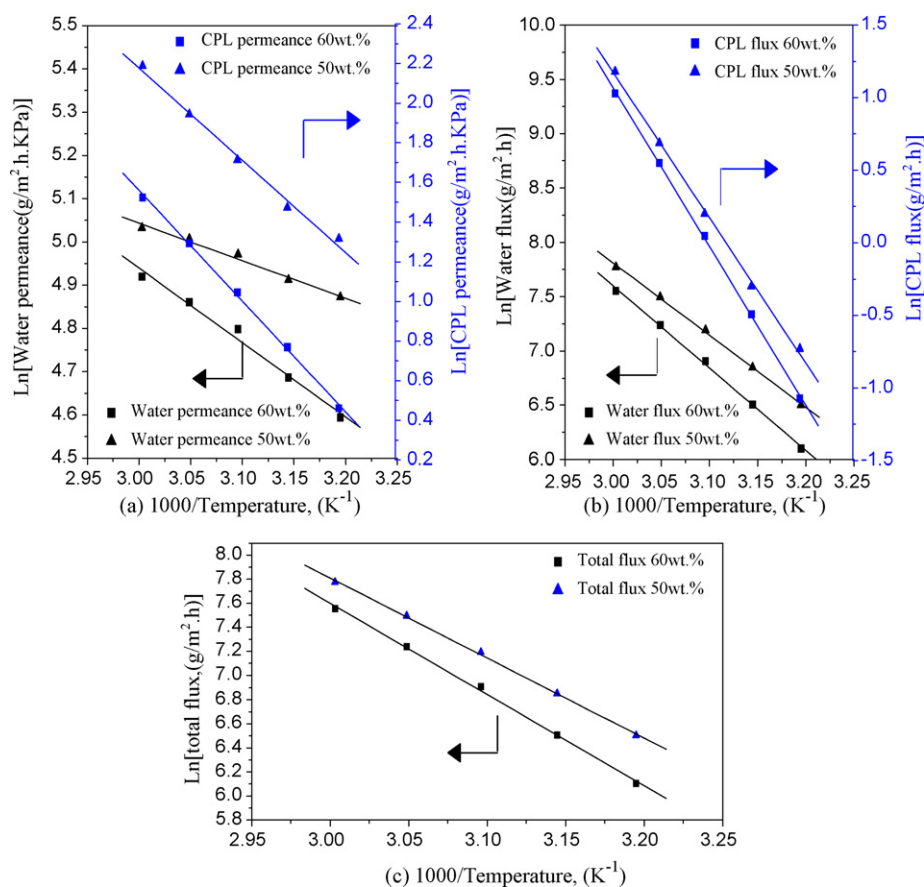


Fig. 8. Temperature dependence of (a) permeance, (b) flux and (c) total flux for 60 and 50 wt.% CPL aqueous solution.

The apparent activation energies of permeates through the composite membrane can be estimated by measuring the slope of the lines in the diagrams and the difference between E_J and E_Q is the molar heat of vaporization ΔH_v , expressed as follows [27,28]:

$$\Delta H_v = E_J - E_Q \quad (8)$$

From Fig. 8, it can be found that the temperature dependence of the pervaporation flux and permeance agrees well with the Arrhenius relationship. It is observed that the permeation flux and permeance increase with an increase in temperature, due to the changes in permeability of the polymer and the driving force. The evaluated values ($\ln(E_J)$, $\ln(E_Q)$ vs. $1/T$) are presented in Table 3. The total activation energies calculated from total fluxes of water and CPL for 60 and 50 wt.% CPL in the feed are 62.98 and 55.26 kJ/mol, respectively. The former is distinctly

higher than the latter, this is due to the membrane swelling, and thus results in a lowered permeation activation energy for the permeates to transport through the membrane material [29,30]. Table 3 shows a comparison that the activation energies of CPL calculated from either the flux (E_J) or the permeance (E_Q) are much higher than those of water, correspondingly. That is to say, more energy is required for CPL molecules to transport across the membrane at the same conditions. The lower activation energies of water than CPL are reflected by the intrinsic properties of hydrophilic PVA membrane materials. By comparing the activation energies (E_J) obtained from the flux with those (E_Q) from the permeance, it can be found that the former are remarkably higher than the latter, which in turn indicates that the fluxes of penetrates, and the separation factor are more strongly dependent on the feed temperature than the permeances of penetrates and selectivity. These behaviors can be explained that permeance and selectivity only depend on membrane intrinsic

Table 3
Evaluated activation energy data for PVA composite pervaporation membranes investigated

CPL in feed (wt.%)	Activation energy (kJ/mol)					ΔH_v (kJ/mol)	
	Total	E_J		E_Q		Water	CPL
		Water	CPL				
60	62.98	62.95	90.85	14.32	46.04	48.63	44.81
50	55.26	55.24	83.17	7.21	38.35	48.03	44.82

sic properties but flux and separation factor are also dependent on experimental operating conditions. Under the same circumstances, as shown in Table 3, the estimated ΔH_v values for water or CPL are almost the same between the two different CPL concentrations investigated, which is consistent with the previous reports in the dehydration of aqueous alcohol systems through filled-hydrophilic polymeric membranes [28].

4.3.2. Effect of feed composition

The effect of the feed concentration on the pervaporation performances is shown in Fig. 9, for concentrations of 30–70 wt.% of water in the feed mixtures. The feed concentration range from 30 to 70 wt.% of water in the feed solutions was chosen by considering the concentration changes from the triple-effect evaporation sets; in addition, CPL aqueous solution becomes stiff and saturated when the CPL content in feed solution is above 70 wt.% at room temperature. From Fig. 9(a), it is observed that the membrane exhibits increases in the permeation fluxes with the weight fraction of water in the feed increasing, this behavior is consistent with the previous reports in the dehydration of aqueous organic mixture through hydrophilic polymeric membranes [8,12,31,32]. This can be explained in terms of the plasticizing effect of the water on membranes. This is due to an increase of selective interaction between water molecules and

membranes. Generally, the hydrophilic membrane has a strong interaction with water through highly polar groups, e.g. hydroxyl group. With higher water concentration in the feed mixture, the amorphous regions of the membrane are more swollen and the polymer chains become more flexible, thereby, resulting in the diffusion coefficients of CPL and water to increase. Fig. 9(b) shows that the permeances of both CPL and water increase with increasing water feed concentration. This implies the hydrophilic character of the membrane. The higher the water feed concentration is, and the higher activity of water on both the feed and permeate side; and this result in the higher degree of swelling and thus, the sorption of the feed liquid into the PVA composite membrane increases, corresponding to increases in the permeances of water; though the activity of CPL on both the feed and permeate side decreases with feed water concentration increasing, it is interesting that CPL permeance also increases; this may be explained by the coupling effects [18]. That is to say, membrane swelling or plasticization effects changes the membrane properties and results in the facilitation of transport of the CPL component through the membrane. Fig. 9(c) shows both separation factor and selectivity decrease with an increase in feed water composition. The decreases of both separation factor and selectivity is easily explained by the membranes excessive swelling, owing to increased selective interaction between

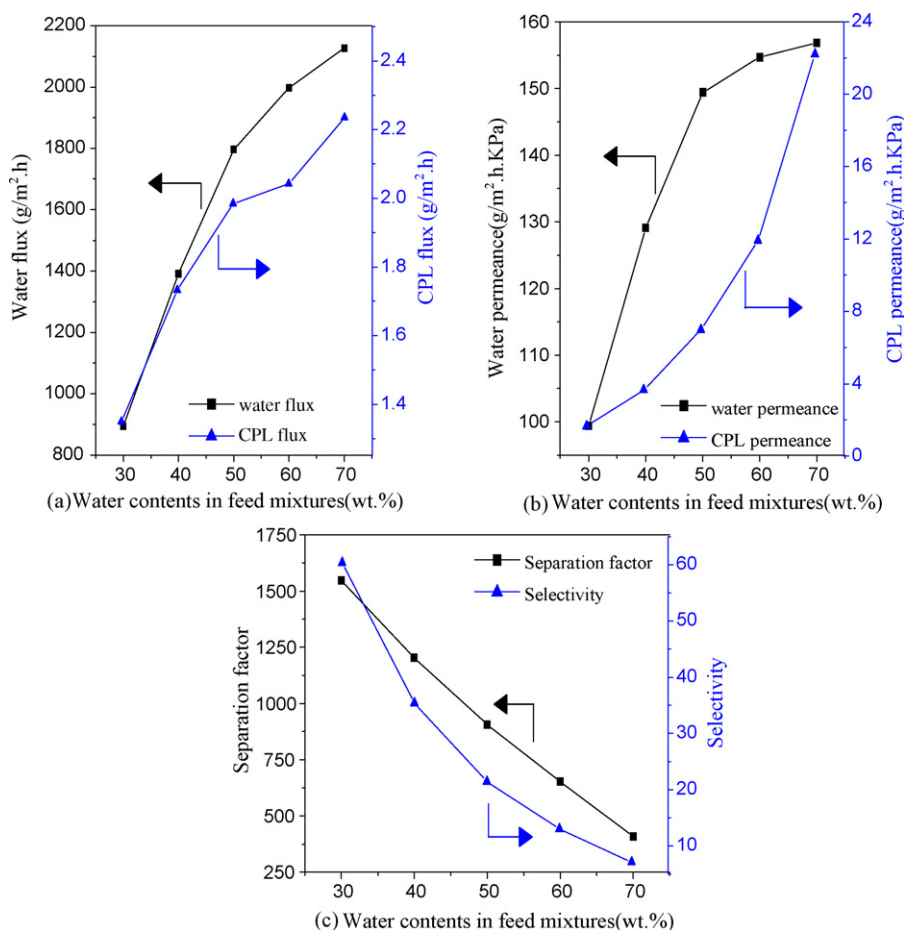


Fig. 9. Effect of the feed concentration on the pervaporation performances in terms of (a) flux, (b) permeance and (c) selectivity and separation factor through PVA composite membranes cross-linked with 0.6 wt.% GA contents in the cross-linking agent at 55 °C.

water molecules and the membrane, this results in an enlarged interstitial space between polymer chains, and declines separation performance [9]. Fig. 9(c) also suggests that the separation factor versus feed water content plots tend to have bigger negative slopes than that in the selectivity versus feed water content plots, which in turn indicates that the selectivity only depend on membrane intrinsic properties but separation factor are also dependent on the experimental operating conditions.

5. Conclusions

Pervaporation separation of CPL–water mixtures through PVA/PAN composite membranes were investigated in this article. The membranes were prepared using GA as a cross-linking agent on PAN supports. We are encouraged by the high flux and selectivity. With the aid of permeances, we find that the normalized permeation flux (permeance) exclude the effect of operating conditions on performance evaluation and clarify the contribution of the nature of membrane to separation performance more easily rationalized. The experimental results also indicate that the PVA composite membrane has superior dehydration performances for CPL–water mixtures. Furthermore, this study displays that applications of pervaporation for removal of water from CPL aqueous solutions have also been realized with an excellent pervaporation performance. This confirms that membrane based pervaporation (PV) technique is feasible for application to the CPL dehydration integrating with triple-effect evaporation sets partly or wholly in future. Evaluation of the treatment cost and energy consumption procedure will be discussed in further details.

Nomenclature

A	effective membrane area (m^2)
A_0, B_0, C_0	coefficients used in Antoine equation
A_{12}, A_{21}	coefficients used in Van Laar equation
CPL	ϵ -caprolactam
E_J	apparent activation energy of the permeation flux from the Arrhenius equation (kJ/mol)
E_Q	apparent activation energy of the permeance from the Arrhenius equation (kJ/mol)
GA	glutaraldehyde
ΔH_v	molar heat of vaporization of component i (kJ/mol)
J	pervaporation permeation flux ($\text{g}/(\text{m}^2 \text{ h})$)
J_i	permeation flux of component i ($\text{g}/(\text{m}^2 \text{ h})$)
J_0	pre-exponential factor of the permeation flux from the Arrhenius equation ($\text{g}/(\text{m}^2 \text{ h})$)
p_i^0	saturation vapor pressure of pure component i calculated from Antoine equation ($1.333224 \times 10^2 \text{ Pa}$ (mmHg))
$p_{i,\text{feed}}^0$	saturation vapor pressure of pure i in the feed liquid temperature (kPa)
p_{permeate}	permeate pressure (kPa)

PAN	polyacrylonitrile
PVA	poly(vinyl alcohol)
Q_0	pre-exponential factor of the permeance from the Arrhenius equation ($\text{g}/(\text{m}^2 \text{ h kPa})$)
Q_i	membrane permeance component i ($\text{g}/(\text{m}^2 \text{ h kPa})$)
R	gas constant ($\text{J}/(\text{mol K})$)
S	degree of swelling (%)
t	permeation measuring time (h)
T	temperature ($^\circ\text{C}$)
W	weight of penetrant (g)
$W_{\text{dry}}, W_{\text{wet}}$	weight of the dry and swollen membrane
x_i	mole fraction of component i in the feed
y_i	mole fraction of component i in the permeate

Greek letters

α_{mem}	membrane selectivity
$\alpha_{\text{w/cpl}}^{\text{P}}$	pervaporation selectivity
γ_i	activity coefficient of component i in the feed

Subscript

i	component i , either water or CPL
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