Chemical Engineering Journal 146 (2009) 71–78

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Crosslinked poly(vinyl alcohol) membranes for separation of dimethyl carbonate/methanol mixtures by pervaporation

Luying Wang, Jiding Li*, Yangzheng Lin, Cuixian Chen

Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:
Received 29 April 2007
Received in revised form 13 May 2008
Accepted 15 May 2008

Keywords:
Pervaporation
DMC/MeOH mixtures
PVA
Membrane

ABSTRACT

Novel polymer membranes were prepared mainly by poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), and glutaraldehyde (GA) for the separation of methanol (MeOH) from dimethyl carbonate (DMC)/MeOH mixtures by pervaporation. The membranes of different GA content were characterized by contact angle, Fourier transform infared spectra (FTIR), X-ray diffractometer (XRD), and dynamic mechanical analysis (DMA). Swelling experiments were tested in DMC/MeOH mixtures to evaluate the membranes of different GA content. Besides, the effects of GA content in membrane, operating temperature, and feed composition on pervaporation performances were observed: the flux increased but the separation factor increased first and then decreased with increasing the GA content in membrane; the flux increased but the separation factor decreased with increasing the operation temperature or the MeOH concentration in feed. The results demonstrated that the crosslinked PVA membrane prepared in this work had an excellent selectivity: the MeOH concentration in permeate side was always higher than 98.6 wt% for separating feed mixtures of 40–70 wt% MeOH at 50–70 °C.

1. Introduction

As an environmental benign chemical material, dimethyl carbonate (DMC) is gaining increasing importance in the chemical industry for its versatility in many fields. Because of its low toxicity and quick biodegradation, DMC can be applied in industrial manufacture to achieve SHE (safety, health and environment) compliance [1,2]. It has higher oxygen content (53%) than methyl ter-butyl ether (MTBE) and ter-amyl methyl ether (TAME) [3,4], and shows a potential possibility to act as an oxygenation agent in reformulated gasoline and an octane component. DMC is also used as a methylating, carbonylating, and methoxylating agent to replace the virulent carcinogen (such as phosgene, dimethyl sulphate (DMS), chloromethane and methyl chloroformate), because DMC molecule includes CH_3–, CH_3O–, and –CO– groups. Besides, DMC can be widely used in other fields, such as medicine, pesticide, solvent, composite material, dyestuff, flavoring agent of foodstuff and electronic chemical [5–7].

Up to now, there are mainly three methods for the synthesis of DMC: (a) phosgenation of methanol (MeOH) [8], (b) oxidative carbonylation of MeOH [9], and (c) transesterification of ethylene carbonate with MeOH [10]. However, in any of these methods, DMC is obtained as a mixture with MeOH, so purifying DMC is an indispensable step in DMC manufacturing. Under normal pressure, DMC and MeOH constitute an azeotrope at a composition of 30 wt% DMC and 70 wt% MeOH, which DMC/MeOH mixtures are difficult to be separated. It has been reported that some conventional methods of low temperature crystallization [11], high-pressure distillation [12], azeotropic distillation [13], extractive distillation [14], and adsorption [15] can be used for separating DMC/MeOH mixtures. But each of these conventional methods has some disadvantages, such as high capital investment, high-energy consumption, low efficiency, and complicated operation, etc.

Recently, pervaporation has gained much attention to separate organic mixtures, especially to separate azeotropis mixtures or close boiling point mixtures. Pervaporation is a membrane based process: the liquid mixtures contact with one side of the membrane and the permeates are removed from the other side, to achieve separation. Compared with other separation method, pervaporation have high separation efficiency, low energy consumption, less environmental pollution, and cost saving. It was reported that pervaporation coupled with distillation enables to simply break the DMC/MeOH azeotrope and to inject the corresponding mixture on a lower distillation plate to obtain purified DMC [16]. Jonquières et al. [17] compared this new hybrid process with distillation and concluded that the hybrid process could substantially save capital cost and operating cost, for example, the total cost for an annual

---

* Corresponding author.
E-mail address: lijiding@mail.tsinghua.edu.cn (J. Li).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.05.026

production of 907 t DMC is only 40% of that of the conventional distillation process.

In our previous studies [18], the poly(acrylic acid) (PAA)/poly(vinyl alcohol) (PVA) blend membrane of 70 wt% PAA showed high permeate flux and good selectivity for the separation of MeOH from DMC/MeOH azeotrope. Although the membrane was crosslinked through an esterafication reaction between the carboxylic groups in PAA and the hydroxyl groups in PVA, the membrane was brittle because of the high PAA content in the membrane. Reducing the PAA content in the membrane could improve the physical properties of the membrane, but at the same time the crosslinking degree of the membrane decreased resulting in a low selectivity. In order to improve the PVA membrane's selectivity to MeOH, crosslinking was a common way and a lot of crosslinking agents were reported [19]. Glutaraldehyde (GA) was a typical crosslinking agent for PVA membrane which had been studied many years [19–23].

In this study, crosslinked PVA membranes were prepared mainly by PVA, PAA, and GA for the selective separation of MeOH from DMC by pervaporation. In these membranes, the weight ratio of PVA to PAA was 90/10 but the GA content was varied. Contact angle, FTIR, XRD, DMA, and swelling experiments were carried out to characterize the crosslinked PVA membranes of different GA content. Furthermore, the pervaporation experiments were used to investigate the effects of GA content in the membrane, operation temperature and feed composition on pervaporation performances.

2. Experimental

2.1. Materials

PVA (hydrolyzed 99%) and PAA (35 wt% in water) were purchased from Beijing Organic Chemical Plant and Aldrich Co., respectively. GA (25 wt% in water), sulfuric acid, and MeOH were all from Beijing Bei Hua Fine Chemicals Co. DMC was supplied by Hebei Newchaoyang Chemical Stock Co. All chemicals were used without further purified.

2.2. Membrane preparation

PVA was dissolved in water by refluxing and stirring for about 6 h at 90–100 °C and the resulting clear solution was cooled to room temperature to form a homogeneous solution of 10 wt% PVA. Then the PVA solution and PAA solution were mixed in a weight ratio of 90/10. To this polymer solution, GA solution and sulfuric acid were added by slowly stirring at room temperature. After kept at vacuum oven to remove bubbles, the resulting solutions of different GA content were cast on a glass plate and on supported membranes, respectively. The membranes were dried at desired temperature by heating, and then were heated in a thermosetted oven at least 100 °C for 1 h. Homogeneous membranes prepared were used to carry out membrane characterization studies and swelling experiments, and the composite membranes prepared were used to carry out pervaporation experiments.

The GA content in the PVA membrane was usually presented by the term of the crosslinking ratio (X), which equaled moles of GA per mole of PVA repeating unit [24]:

$$X(\%) = \frac{m_{\mathrm{GA}}/M_{\mathrm{GA}}}{m_{\mathrm{PVA}}/44} \times 100 \tag{1}$$

where m_{GA} and m_{PVA} are the weights of GA and PVA (g), respectively, M_{GA} the mole weight of GA (g/mol), and 44 means the mole weight for a repeat unit of PVA (g/mol). The resulting crosslinked PVA membrane of different GA content was designated as PVA-GX. In this work, the PVA-G3 membrane, the PVA-G6 membrane, and the PVA-G9 membrane were prepared, respectively.

2.3. Membrane characterization

The contact angles for water on the surfaces of the membranes were measured at home temperature by Contact Angle System OCA20 (DataPhysics Co.). Fourier transform infared (FTIR) spectral of different membranes were scanned in a range of 4000–400 cm^{-1} on a FTIR spectrometer (Nicolet, IR560) to study the intermolecular interactions. The morphologies of the membranes were characterized by a Germany Bruker D8 Advance X-ray diffractometer (XRD) using Cu Kα, the angle of diffraction was varied from 5° to 60°. Dynamic mechanical analysis (DMA) was conducted using DMA 2980 instrument (TA Instruments), in the tensile mode, at a frequency of 1 Hz, with a 20 μm amplitude, and by heating from −20 °C to 160 °C at a rate of 5 °C/min in an air atmosphere.

2.4. Swelling experiments

The membranes were immersed in DMC/MeOH mixtures at home temperature for 48 h to reach swelling equilibrium, and then were taken out from the mixtures. The free liquid on the surface of the swollen membranes must be removed quickly by using absorbent paper, and then the swollen membranes were weighted using electronic balance (Sartorius, BP 210S).

The degree of swelling (DS) of the membranes was defined as

$$\mathrm{DS}\ (\%) = \frac{m_{\mathrm{t}} - m_0}{m_0} \times 100 \tag{2}$$

where m_0 and m_{t} are the weights of dry and swollen membrane (g), respectively.

2.5. Pervaporation experiments

The composite membranes were used in pervaporation experiments.

The pervaporation apparatus used in this study is showed in Fig. 1. The membrane was installed in a membrane cell, and the effective membrane area in this cell was 21.70 cm^2. The feeding solutions were continuously circulated from a feed tank to the upstream side of the membrane at the desired temperature by a pump. The pressure at downstream side was maintained at about 200 Pa. Upon reaching steady-state conditions which was obtained after about 3 h throughout the experiments, permeates were collected in liquid nitrogen traps with certain intervals (1–2 h), and weighted to calculate the permeate flux. The composition of collected permeate was determined by GC (SHIMADZU,GC-14C) to calculate the separation factor.

The separation factor (α) was defined as

$$\alpha = \frac{Y_{\mathrm{a}}/Y_{\mathrm{b}}}{X_{\mathrm{a}}/X_{\mathrm{b}}} \tag{3}$$

where X and Y represent the weight fraction in the feed and permeate, respectively; indices a and b refer to the more permeable component and the less permeable component, respectively.

The permeate flux (J) was calculated from

$$J = \frac{w}{At} \tag{4}$$

where w is the weight of permeate (g), A the effective area of membrane (m^2), and t is the time (h).

In this study, the operation temperature was 50 °C, 55 °C, 60 °C, 65 °C and 70 °C, respectively. The MeOH concentration in feed mixtures was varied from 40 wt% to 70 wt%.

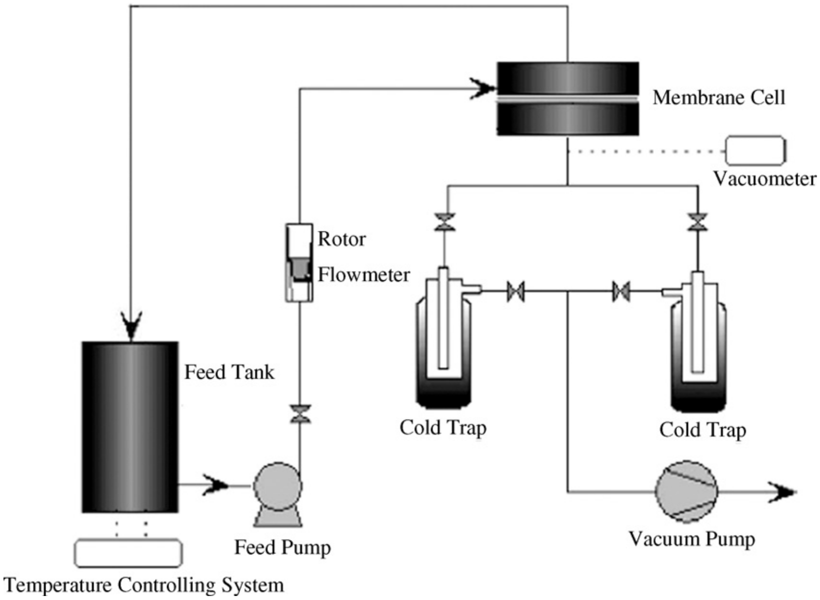

Fig. 1. Schematic diagram of pervaporation apparatus.

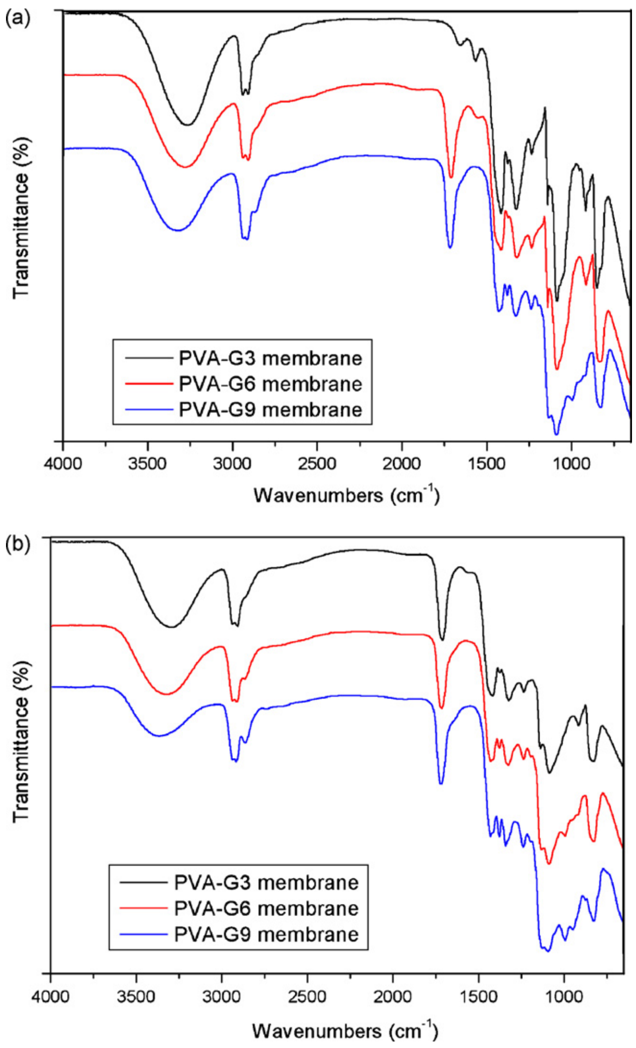

Fig. 2. FTIR spectra of different membranes.

3. Results and discussions

3.1. Membrane characterization

3.1.1. Contact angle results

The results are summarized in Table 1, where the contact angle of the membranes increases with increasing the GA content in the membranes. It means that the membrane of higher GA content has a lower hydrophilicity, mainly because more hydroxyl groups in PVA react with GA.

3.1.2. FTIR results

Fig. 2a illustrates the FTIR spectra of pure PVA membrane, PVA/PAA membrane, and PVA-G6 membrane. The FTIR spectra of the pure PVA membrane shows the main characteristic peaks: 3260 cm^{-1} of the O–H stretch and 914 cm^{-1} of the O–H bend. A new characteristic peak of the PVA/PAA (90/10 of weight ratio) membrane is found at 1692 cm^{-1} corresponding to the C=O stretching band in PAA. It can be seen from the FTIR spectra of the PVA-G6 membrane that the peaks of the O–H stretch and the O–H bend both decrease, the peaks between 970 cm^{-1} and 1385 cm^{-1} all increase attributed to acetal ring group and ether linkage formation, and a little peak at 2866 cm^{-1} corresponding to CO–H strech of GA arises. It is demonstrated that PVA is crosslinked with GA to form acetal rings and ether linkages, and there is some unreacted aldehyde groups of GA. The FTIR spectra of membranes containing different GA content are shown in Fig. 2b. As the GA content increases, three main changes take place: the peak of O–H stretching band and the O–H bend decreases, the peaks of acetal ring group and ether linkage formation increase, and the peak of CO–H stretching band increases. These changes indicate that the crosslinking degree of the membrane and the number of the unreacted aldehyde groups

Table 1
Contact angle of crosslinked PVA membranes

	Contact angle (°)
PVA-G3	30.2
PVA-G6	61.1
PVA-G9	63.2

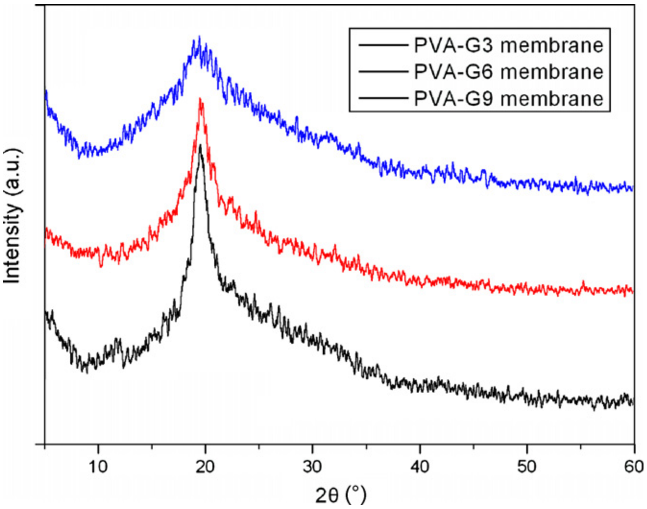

Fig. 3. X-ray diffraction pattern of crosslinked PVA membranes with different GA content.

in the membrane both increase with increasing GA content in the membrane.

3.1.3. XRD results

The XRD patterns of the PVA-GX membranes are presented in Fig. 3, where it is clear that the peak intensity of the typical diffraction peak at $2\theta = 20^\circ$due to mixture of $\langle 1\,0\,1\rangle$ and $\langle 2\,0\,0\rangle$ crystalline planes [25] decreases with increasing the GA content in the membranes. This illustrates that the crystallinity of the membrane decreases with increasing the GA content in the membranes because of the crosslinking reaction between PVA and GA. The increased amorphous region makes the permeates easily diffusing in the membrane, resulting in an increasing flux.

3.1.4. DMA analysis

In DMA studies, the glass transition temperature (T_g) is estimated from the $\tan\delta$ as a function of temperature, is generally associated with the temperature of $\tan\delta$ peak position. From the DMA spectra (Fig. 4), the $\tan\delta$ peak position both shift to a considerably higher temperature with increasing the GA content in the membranes. The increasing T_g can be explained by the fact that the crosslinked reaction reduces the flexibility of the polymer chains. It is concluded again that the crosslinking degree of the membrane increases with increasing the GA content in the membranes.

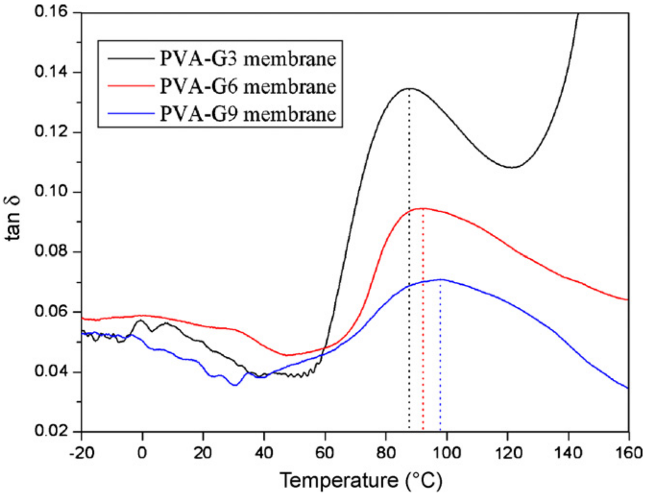

Fig. 4. DMA spectra of crosslinked PVA membranes with different GA content.

3.2. Swelling measurement

The swelling degree of PVA/PAA membrane and PVA-GX membranes are investigated at home temperature in DMC/MeOH azeotropic mixtures. Fig. 5a exhibits the swelling degree of PVA/PAA membrane is higher than that of PVA-GX membrane, and the swelling degree of PVA-GX membrane increases with increasing the GA content in the membrane. It is clear that PVA-GX membrane has a higher crosslinking degree than PVA/PAA membrane because of the crosslinking reaction between PVA and GA. So the PVA-GX membrane has a more compact structure, resulting in a lower swelling degree. Generally, the membrane with higher crosslinking degree has a more compact network resulting in a lower swelling degree. In this case, more crosslinks make PVA-GX membrane more swollen in DMC/MeOH azeotrope. This phenomenon can be explained by the effect of unreacted aldehyde groups on swelling behavior of the membranes. It has been concluded through FTIR spectra that there are more unreacted

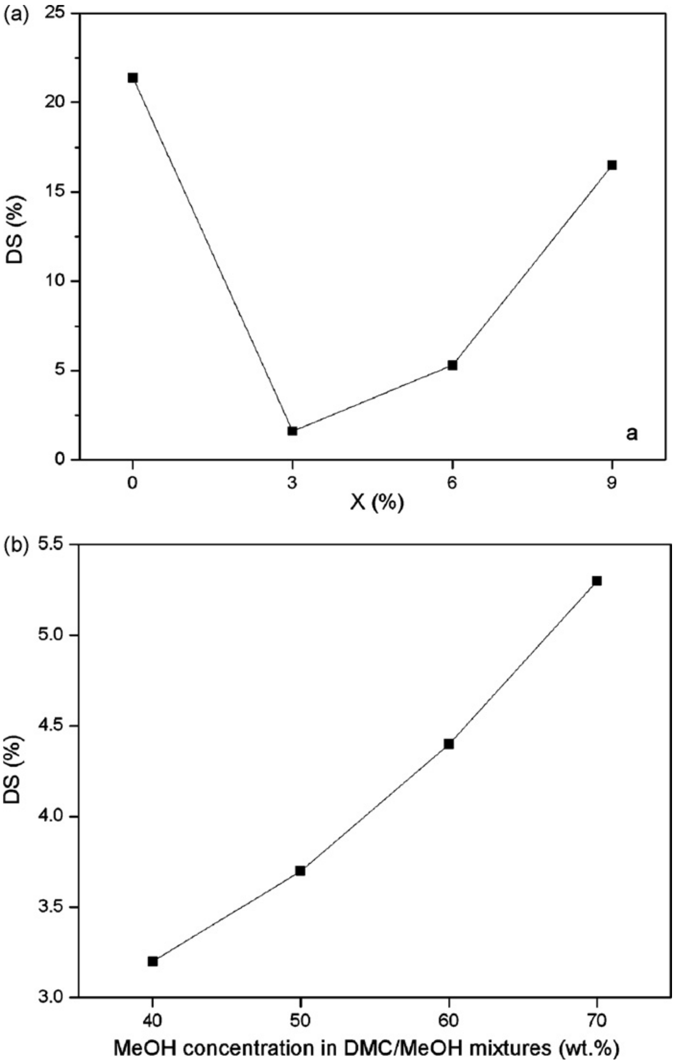

Fig. 5. Effect of (a) GA content and (b) MeOH concentration on swelling degree of crosslinked PVA membranes.

Table 2
Solubility parameters calculated by group contribution with Hansen method [26,27]

	δ_d ($cal^{1/2}\,cm^{-2/3}$)	δ_p ($cal^{1/2}\,cm^{-2/3}$)	δ_h ($cal^{1/2}\,cm^{-2/3}$)	δ_{sp} ($cal^{1/2}\,cm^{-2/3}$)
PVA	7.8	13.0	11.7	19.2
PAA	9.9	4.7	7.4	13.2
GA	9.0	7.2	5.8	12.9
MeOH	7.4	6.0	10.9	14.5
DMC	7.7	3.7	5.3	10.1

aldehyde groups in membranes of higher GA content. Shown in Table 2, the solubility parameter (δ_{sp}) of GA is closer to that of MeOH than to that of DMC, which means that GA has a good affinity with MeOH. Thus, as the unreacted aldehyde groups of GA in membrane increase, the affinity of the membrane to MeOH is enhance and then the number of MeOH molecules adsorbed into the membrane increases, which consequently contributes to the increasing swelling degree of the membrane. Similar results have been reported in the literature [31]. The effect of MeOH concentration in the mixtures on the swelling degree tested by using PVA-G6 membrane is showed in Fig. 5b, where the swelling degree increases with increasing MeOH concentration in the mixtures. The chemical structures of the polymer and the solvent control the swelling of the membrane, and MeOH shows a better affinity to the membrane than DMC. As the MeOH concentration increases from 40 wt% to 70 wt%, the membrane contacts more MeOH and then swells more.

3.3. Pervaporation results

3.3.1. Effect of GA content in membranes on pervaporation performances

The pervaporation results for separating DMC/MeOH azeotropic mixtures (30 wt% DMC, 70 wt% MeOH) at 70 °C by using different PVA membranes is given in Table 3, where the PVA membrane crosslinked with PAA has a little higher flux but a lower separation factor than the PVA membrane crosslinked with GA, whereas the PVA-GX membrane crosslinked simultaneously with PAA and GA shows a much better selectivity than the other two membranes. It is clear that the PVA-GX membrane has a complex polymer network which makes this membrane show excellent selectivity to MeOH.

It also can be seen in Table 3 that the flux increases gradually but the separation factor has a maximum of 37 when the *x* value is 6 with increasing the GA content in the membranes. The increasing flux results from the increasing swelling degree and the increasing amorphous region of the PVA-GX membrane. The results of membrane characterization experiments show that the membrane with a higher GA content has a more crosslinking degree and then has a more compact structure, leading to a less chain mobility and a better selectivity. Therefore, the MeOH selectivity of the PVA-G6 membrane is better than that of the PVA-G3 membrane, because of the crosslinked structure in membranes. But the separation factor of the PVA-G9 membrane is less than that of PVA-G6 membrane. It could be explained by the high swelling degree of the PVA-G9 membrane, which is almost three times the swelling degree of the PVA-G6 membrane (Fig. 5a). Although the PVA-G9 membrane has a higher crosslinking degree than the PVA-G6 membrane, the swelling effect overcomes the effect of crosslinked structure, leading to a lower separation factor of the PVA-G9 membrane.

Table 3
Pervaporation results of different PVA membranes (70 wt% MeOH in feed, 70 °C)

PVA membrane		Pervaporation results	
PVA/PAA (weight ratio)	*X* (%)	α	J ($g/(m^2\,h)$)
90/10	0	2.8	510
100/0	6	8.3	385
90/10	3	16	154
90/10	6	37	248
90/10	9	17	366

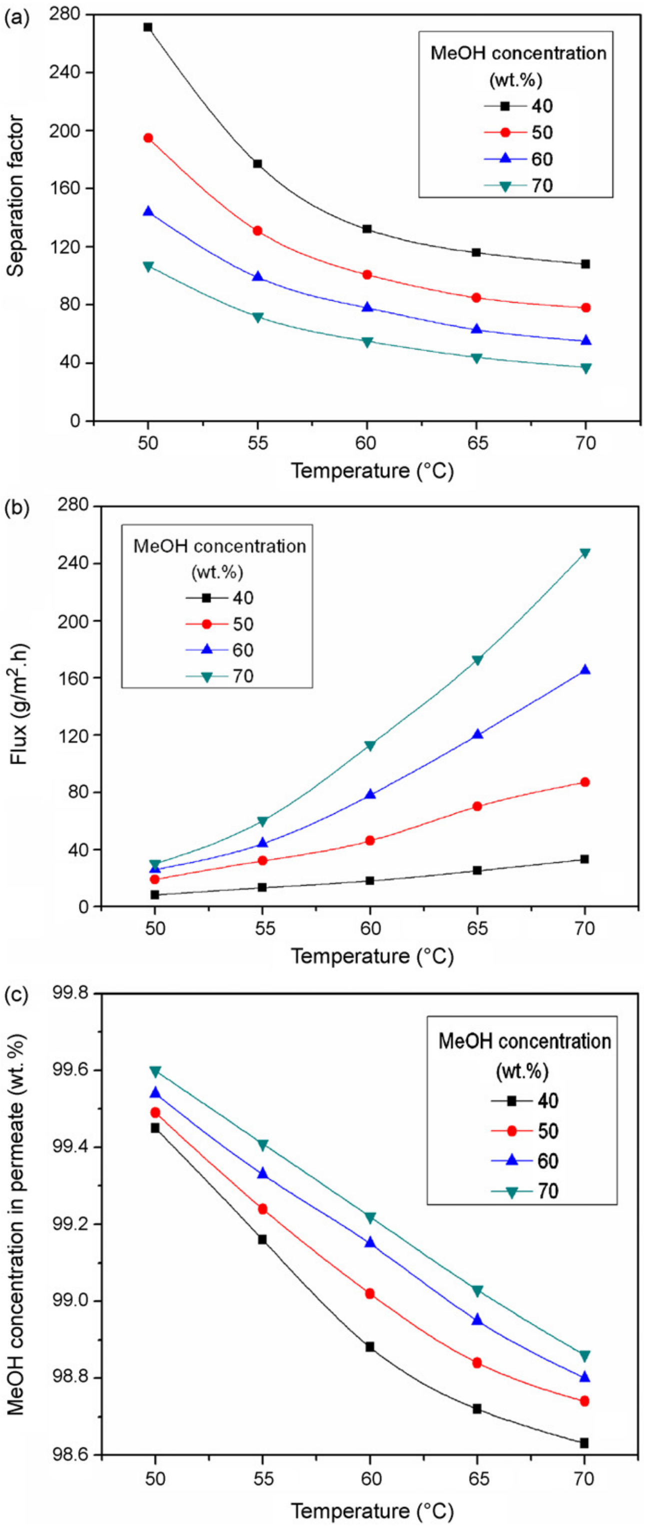

Fig. 6. Effect of operation temperature on (a) separation factor, (b) flux, and (c) MeOH concentration in permeate side.

3.3.2. Effect of operation temperature on pervaporation performances

The effect of operation temperature on pervaporation performances has been investigated by using PVA-G6 membrane. As shown in Fig. 6, the separation factors and MeOH concentration in permeate side both decrease but the fluxes increase with increasing the operation temperature from 50 °C to 70 °C. As the temperature increases, the thermal motion of polymer chains becomes more violent, leading to an increase in free volume within the membrane. In other hand, the increasing operation temperature enhances the diffusion of both MeOH and DMC molecules, resulting in more DMC molecules permeating to the membrane. Therefore, the fluxes increase but the separation factors decrease with increasing the operation temperature. It is worth while pointing out that the separation factors decrease sharply but the MeOH concentrations in permeate side decrease slightly (Fig. 6c).

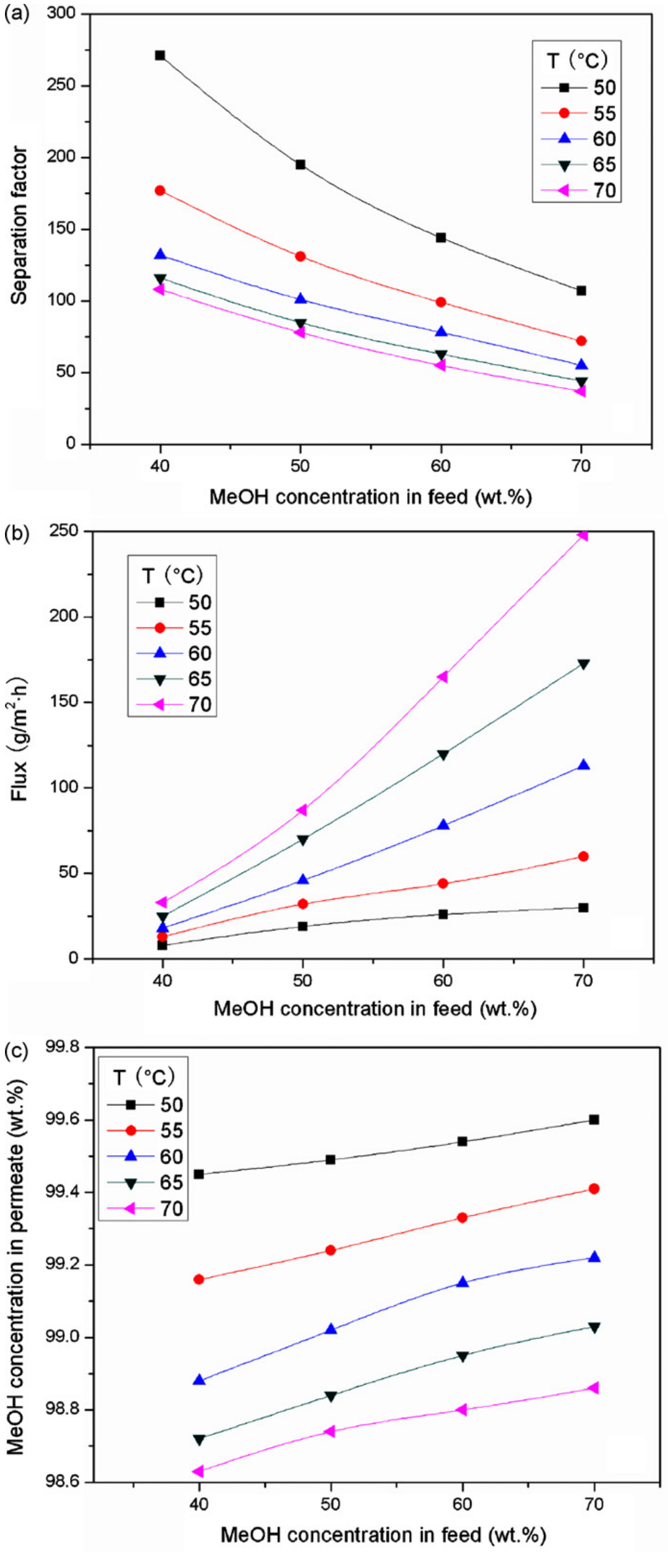

Fig. 7. Effect of MeOH concentration in feed on (a) separation factor, (b) flux, and (c) MeOH concentration in permeate side.

3.3.3. Effect of MeOH concentration in feed on pervaporation performances

The effect of feed composition by using the PVA-G6 membrane is showed in Fig. 7, where the separation factors decrease but the fluxes increase with increasing MeOH concentration in feed from 40 wt% to 70 wt%. This result can be explained by the MeOH plasticization effect toward the membrane. As the MeOH concentration in the feed increases, the membrane becomes more swollen because of a stronger affinity with MeOH. Consequently, the polymer chains are more flexible and the energy required for diffusive transport is less, resulting in an increasing in the flux. The decrease of separation factor with increasing MeOH concentration in feed can be explained that the increasing in free volume of the membrane allows more DMC molecules to pass through. In addition, it can be seen in Fig. 7c that the MeOH concentration in permeate side is also higher than 98.6 wt% when the feed contains only 40 wt% MeOH. Fig. 8 illustrates that the permeation selectivity of this membrane at 70 °C is compared with distillation separation based on vapor–liquid equilibrium. The MeOH concentration in the permeate side is much higher than that in the feed side. It means that this crosslinked PVA blend membrane can exhibit excellent potential to break the azeotropic balance, which shows the membrane prepared in this work may be used to separate DMC/MeOH mixtures by pervaporation.

3.4. Comparison of PVA-G6 membrane with literature data

In Table 4, it is presented that a comparison of pervaporation performences of different membranes for separating DMC/MeOH azeotrope (30 wt% DMC, 70 wt% MeOH) reported in the literatures and this work. Clearly, the PVA-G6 membrane has a best

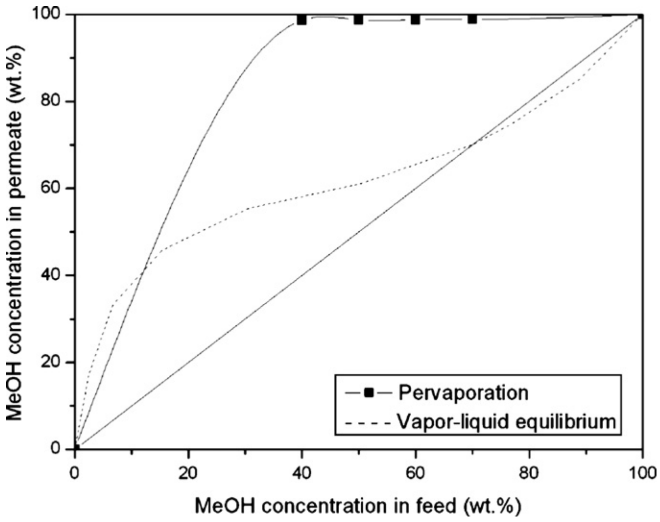

Fig. 8. Relationship of MeOH concentration in feed side and in permeate side.

Table 4
Comparison of pervaporation performances of different membranes for separating DMC/MeOH azeotrope

Membrane	Operation temperature (°C)	α	J (g/(m^2 h))	Reference
Crosslinked PVA membrane	70	18	100	[28]
Nafion-K membrane	70	3.3	130	[29]
Chitosan membranes	55	8	300	[30]
Crosslinked chitosan membranes	55	9	500	[31]
PVA/chitosan blend membrane	25	5	165	[32]
ZSM-5 zeolite-filled chitosan membranes	25	6.1	103	[33]
PAA/PVA blend membrane	60	13	577	[18]
PVA-G6 membrane	70	37	248	This work

Table 5
Comparison of pervaporation performances of different MeOH selectivity membranes

Membrane	Feed mixtures	Thickness (μm)	MeOH wt% in feed	Operation temperature (°C)	α	J (g/(m^2 h))	Reference
PVA/PAA membrane	MTBE/MeOH	20	20	35	45	610	[34]
Poly(phenylene oxide) membrane		5	21	40	7.7	640	[35]
CTA membrane		25	37.5	50	29	528	[36]
Silicalite membrane		460	50	50	4	150	[37]
Agarose membrane		15	50	30	45	400	[38]
Pervap 2255-60	Methyl acetate/MeOH	–	23.5	45	5.7	550	[39]
Cuprophane membrane		10 mm	41.4	30	4.3	490	[40]
PPy-PTS membrane	Toluene/MeOH	–	50	57.5	15	110	[41]
PPy-PF membrane		–	50	57.5	50	500	[41]
PPy-PF membrane	IPA/MeOH	–	50	57.5	8	35	[41]
PPy-PTS membrane	Acetonitrile/MeOH	–	50	50	2.2	1100	[41]
PVA-G6 membrane	DMC/MeOH	–	40	50	271	8	This work
		–	50	50	195	19	This work
		–	40	70	55	165	This work
		–	50	70	37	248	This work

selectivity to MeOH in these membranes; its separation factor is at least twice as many as other membranes' separation factor. Using PVA-G6 membrane for separating DMC/MeOH azeotrope at 70 °C, the separation factor is 37 and the permeate flux is 248 g/(m^2 h).

In addition, the selectivity of PVA-G6 membrane is compared with other MeOH selectivity MeOH membranes, shown in Table 5. These results, shown in Table 5, were tested at different feed temperature for separating different mixtures with different MeOH concentration. Although the fluxes of PVA-G6 membrane are not as high as the fluxes of other MeOH selectivity membranes, the PVA-G6 membrane's selectivity to MeOH is the best in these MeOH selectivity membranes. It means that our work shown in this manuscript makes some progress in separation of DMC/MeOH mixture and also in removing MeOH from other organic mixtures.

4. Conclusions

The PVA-GX membranes of a fixed PVA/PAA weight ratio (90/10) and a varied GA content were prepared mainly by PVA, PAA and GA. The results of characterized experiments indicated that the crosslinking degree of the membrane and the unreacted aldehyde groups in the membrane both increasing with increasing GA content. It was demonstrated by the swelling experiment that the membrane of higher GA content has a stronger affinity with MeOH. Pervaporation performances for separating DMC/MeOH azeotropic mixtures at 70 °C showed that the separation factor had a maximum value but the flux increased gradually with increasing GA content in the membrane. The effects of operation temperature and feed composition on pervaporation performances were also studied: the separation factors decreased but the fluxes increased as the operation temperature or the MeOH concentration in feed increased. The crosslinked PVA membrane prepared in this work had an excellent selectivity: the MeOH concentration in permeate side was always higher than 98.6 wt% for separating feed mixtures of 40–70 wt% MeOH at 50–70 °C. Therefore, it could be expected that the PVA-GX membranes prepared in this work should be used to separate DMC/MeOH mixtures in real application.

Acknowledgements

The authors greatly appreciate the financial supports of the Major State Basic Research Program of China (No. 2003CB615701), National Natural Science Foundation of China (Nos. 20736003 and 20676067), National High Technology Research and Development Program of China (No. 2007AA06Z317), Foundation of Ministry of Education of China (No. 20070003130), SINOPEC Foundation (No. X505002).

References

[1] D. Delledonne, F. Rivetti, U. Romano, Developments in the production and application of dimethyl carbonate, Appl. Catal. A: Gen. 221 (2001) 241–251.
[2] A.-A.G. Shaikh, S. Sivaram, Organic carbonates, Chem. Rev. 96 (1996) 951–976.
[3] M.A. Pacheco, C.L. Marshall, Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive, Energy Fuels 11 (1997) 2–29.
[4] K. Pan, C.S. Cheung, M.A. Liu, S.C. Lee, Performance of DMC blended diesel in reducing pollutant emissions, in: Paper presented at the conference: Better Air Quality in Asian and Pacific Rim Cities (BAQ 2002), Hong Kong SAR, December 16–18, 2002.
[5] D.D. Kanne, Air pollution reduction, US Patent 5,004,480 (1991).
[6] Y. Ono, Dimethyl carbonate for environmentally benign reactions, Catal. Today 35 (1997) 15–25.
[7] H.-C. Shiao, D. Chua, H.-P. Lin, S. Slane, M. Salomon, Low temperature electrolytes for Li-ion PVDF cells, J. Power Sources 87 (2000) 167–173.
[8] Société Nationale des Poudres et Explosifs FR Patent 2,163,884 (1973), Chem. Abstr. 80 (1973) 3112.
[9] S. Uchiumi, K. Ataka, T. Matsuzaki, Review: oxidative reactions by a palladium–alkyl nitrite system, J. Organomet. Chem. 576 (1999) 279–289.
[10] J.A. Gilpin, A.H. Emmons, Synthesis of dimethyl carbonate, US Patent 3,803,201 (1974).
[11] G.A. Passoni, Purification of dimethyl carbonate, DE Patent 2,450,856 (1973).

[12] U. Romano, Recovery of dimethyl carbonate from its azeotropic mixture with methanol, DE Patent 2,607,003 (1976).

[13] B.H. Josef, K. Heindrich, R. Hans, Ger. Offen, Process for separating off dimethyl carbonate, DE Patent 2,737,265 (1979).

[14] H.-J. Buysch, Separation of DMC from its azeotrope with methanol, DE 2,737,265 (1977).

[15] I. Janisch, H. Landscheidt, W. Struver, A. Klausener, Process for separating off methanol from a mixture of dimethyl carbonate and methanol, US Patent 5,455,368 (1994).

[16] V. Shah, C. Bartels, Engineering considerations in pervaporation applications, in: R. Bakish (Ed.), Proceedings of the Fifth International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corporation, Heidelberg, Germany, 1991, pp. 331–337.

[17] A. Jonquières, R. Clément, P. Lochon, J. Néel, M. Dresch, B. Chrétien, Industrial state-of-the-art of pervaporation and vapour permeation in the western countries, J. Membr. Sci. 206 (2002) 87–117.

[18] L. Wang, J. Li, Y. Lin, C. Chen, Separation of dimethyl carbonate/methanol mixtures by pervaporation with poly(acrylic acid)/poly(vinyl alcohol) blend membranes, J. Membr. Sci. 305 (1994) 238–246.

[19] J. Yu, C.H. Lee, W.H. Hong, Performances of crosslinked asymmetric poly(vinyl alcohol) membranes for isopropanol dehydration by pervaporation, Chem. Eng. Process. 41 (2002) 693–698.

[20] C.K. Yeom, K.H. Lee, Pervaporation separation of water–acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde, J. Membr. Sci. 109 (1996) 257–265.

[21] K.J. Kim, S.B. Lee, N.W. Han, Effects of the degree of crosslinking on properties of poly(vinyl alcohol) membranes, Polym. J. 25 (12) (1993) 1295–1302.

[22] L. Zhang, P. Yu, Y. Luo, Separation of caprolactam–water system by pervaporation through crosslinked PVA membranes, Sep. Purif. Technol. 52 (2006) 77–83.

[23] R. Guo, C. Hu, B. Li, Z. Jiang, Pervaporation separation of ethylene glycol/water mixtures through surface crosslinked PVA membranes: coupling effect and separation performance analysis, J. Membr. Sci. 289 (2007) 191–198.

[24] R.W. Korsmeyer, N.A. Peppas, Effect of the morphology of hydrophilic polymeric matrices on the diffusion and release of water soluble drugs, J. Membr. Sci. 9 (1981) 211–227.

[25] Y. Nishino, R.St.J. Manley, Cellulose/poly(vinyl alcohol) blends prepared from solutions in *N*,*N*-dimethylacetamide–lithium chloride, Macromolecules 21 (1988) 1270.

[26] D.W. Van Krevelen, Properties of Polymers, Elsevier, Amsterdam, 1990.

[27] A.F.M. Barton, Handbook of Solubility Parameters and Other Cohesion Parameters., CRC Press Inc., Boca Raton, FL, 1983.

[28] M. Pasternak, C.R. Bartels, J. Reale, Separation of organic liquids, US Patent 4,798,674 (1989).

[29] M. Pasternak, Separation of organic liquids, US Patent 5,238,573 (1993).

[30] W. Won, X. Feng, D. Lawless, Pervaporation with chitosan membranes: separation of dimethyl carbonate/methanol/water mixtures, J. Membr. Sci. 209 (2002) 493–508.

[31] W. Won, X. Feng, D. Lawless, Separation of dimethyl carbonate/methanol/water mixtures by pervaporation using crosslinked chitosan membranes, Sep. Purif. Technol. 31 (2003) 129–140.

[32] B. Liu, Y. Cao, X. Li, X. He, J. Lao, Z. Wu, Q. Yuan, Study on pervaporation for poly(vinyl alcohol)/chitosan blend membranes, Membr. Sci. Technol. (Chinese J.) 27 (2007) 37–41.

[33] B. Liu, Y. Cao, T. Wang, Q. Yuan, Preparation of novel ZSM-5 zeolite-filled chitosan membranes for pervaporation separation of dimethyl carbonate/methanol mixtures, J. Appl. Polym. Sci. 106 (2007) 2117–2125.

[34] H.C. Park, N.E. Ramaker, M.H.V. Mulder, C.A. Smolders, Separation of MTBE–methanol mixtures by pervaoration, Sep. Purif. Technol. 30 (1995) 419–433.

[35] F. Doghieri, A. Nardella, G.C. Starti, C. Valentini, Pervaporation of methanol–MTBE mixtures through modified poly(phenylene oxide) membranes, J. Membr. Sci. 91 (1994) 283–291.

[36] S. Cao, Y. Shi, G. Chen, Pervaporation separation of MeOH/MTBE through CTA membrane, J. Appl. Polym. Sci. 71 (1999) 377–386.

[37] T. Sano, M. Hasegawa, Y. Kawkami, H. Yanagishita, Separation of methanol/methyl-ter-butyl ether mixture by pervaporation using silicalite membrane, J. Membr. Sci. 107 (1995) 193–196.

[38] M. Yoshikawa, T. Yoshioka, J. Fujime, A. Murakami, Pervaporation separation of MeOH/MTBE through agarose membrane, J. Membr. Sci. 178 (2000) 75–78.

[39] S. Steinigeweg, J. Gmehling, Transesterification processes by combination of reactive distillation and pervaporation, Chem. Eng. Proc. 43 (2004) 447–456.

[40] S. Sain, S. Dinçer, Ö.T. Savaşçyi, Pervaporation of methanol–methyl acetate binary mixtures, Chem. Eng. Proc. 37 (1998) 203–206.

[41] M. Zhou, M. Persin, J. Sarrazin, Methanol removal from organic mixtures by pervaporation using polypyrrole membranes, J. Membr. Sci. 117 (1996) 303–309.