

PPMS composite membranes for the concentration of organics from aqueous solutions by pervaporation

Ying Luo, Shujuan Tan, Hui Wang, Fawen Wu, Xiaoming Liu,
Lei Li*, Zhibing Zhang

*Department of Chemical Engineering, School of Chemistry and Chemical Engineering, Nanjing University,
Nanjing 210093, PR China*

Received 12 October 2006; received in revised form 16 April 2007; accepted 2 May 2007

Abstract

In this study, polyphenylmethylsiloxane (PPMS)-CA and polydimethylsiloxane (PDMS)-CA membranes were prepared and used for the concentration of volatile organic compounds such as methanol, ethanol and acetone from aqueous solutions by pervaporation. The measurement of contact angles and swelling degree has indicated that the hydrophobicity of PPMS membranes is stronger than that of PDMS. Total fluxes for all three mixtures increase separately with increasing temperature while separation factors change little. Total fluxes also keep increasing with organic concentration. Separation factors of ethanol and methanol are nearly independent of feed concentration, but that of acetone/water mixture ascends sharply. PPMS membranes have better pervaporation performance than PDMS for acetone/water mixture. Total flux of acetone/water mixture by PPMS at 5 wt.% feed concentration and 40 °C is 2799 g m⁻² h⁻¹, and separation factor reaches 49.6. It can be attributed to the introduction of more hydrophobic and rigid phenyl groups.

© 2007 Elsevier B.V. All rights reserved.

Keywords: PPMS; PDMS; Pervaporation; Organics

1. Introduction

Pervaporation is an effective concentration method to extract volatile organics from dilute aqueous solutions [1,2]. The separation of organic components from an aqueous solution by pervaporation is achieved by selective partition into and diffusion through a polymeric membrane, followed by recovery as condensed vapor on the permeate side [3].

Silicone rubber membranes not only have strong hydrophobic property, but also excellent mechanical strength, thermal stability and film-forming properties due to their semi-organic and semi-inorganic structure. By far they have been widely used to remove Volatile Organic Components (VOCs) from water solutions by pervaporation, especially polydimethylsiloxane (PDMS) and its modified membranes [4]. However, their unsatisfactory selectivity of organics versus water has yet limited their applications to some extent [5–7].

Research reports have indicated that despite of its strong hydrophobicity, PDMS rubbery membrane shows high water permeation, which may be ascribed to higher diffusion rate of water molecules with smaller size than most of the organic molecules through soft PDMS polymer chains. Thus the poor selectivity of organics versus water through PDMS is obtained [8]. For the improvement of separation behavior, the modification of PDMS membrane by the introduction of rigid organophilic groups should be paid more attention to in pervaporation field.

In this paper, polyphenylmethylsiloxane (PPMS)-CA membranes were prepared and used for separation of organic/water mixtures such as ethanol/water, methanol/water and acetone/water at different temperature and concentration. The pervaporation capabilities of PPMS were compared with those of PDMS in detail. Due to the introduction of more hydrophobic and rigid phenyl group, the solubility of organics into PPMS membrane increases and the free volume of the membrane are diminished [9]. The former can increase the total flux, while the latter has significantly negative influence on the mass transfer of the smaller water molecules, which will make

* Corresponding author. Tel.: +86 25 83596665 808; fax: +86 25 83593772.
E-mail address: ll-nju@163.com (L. Li).

separation factor through PPMS membranes improved to some extent.

2. Experimental

2.1. Materials

α,ω -Dihydroxypolydimethylsiloxane (DMS) with an average molecular weight of 5000 was purchased from Shanghai Synthetic Resin Company, China. Phenylmethylsiloxane (PMS) (25 wt.% phenyl groups) was provided by Dalian Yongyuan Organic Silica Company, China. The molecular structures of PDMS and PPMS are both indicated in Fig. 1. Tetraethyl orthosilicate (TAOS), dibutyltin dilaurate, *n*-heptane, methanol, ethanol, and acetone were obtained as analytical reagents from Shanghai Chemical Reagent Company, China. Distilled and deionized water was used. Cellulose acetate (CA) microfiltration membranes, with an average pore size of 0.45 μm , were from Shanghai Filter Company, China and used as supports in this paper.

2.2. Membrane preparation

PMS, cross-linking agent TAOS and catalyst dibutyltin dilaurate were mixed according to a 1:1:0.2 weight ratio in *n*-heptane. Prior to coating, the CA support was laid and spread out on the surface of water in a basin. Excess water on the CA support surface was wiped off quickly with a filter paper. Directly afterwards, the PPMS solution was pored over the surface of support and the basin was put under a hood. The membrane system containing partly cross-linked PPMS, after kept under ambient temperature for 2 h, was introduced into a vacuum oven at 60 °C for 4 h to complete the cross-linking. With this technique, mass transfer resistance due to the intrusion of the PPMS solution into the porous substrate during fabrication of the composite membrane could be reduced. PDMS composite membrane was prepared in the same way [10].

The composite membranes with skin layers of variable thickness could be achieved by controlling the concentration of the casting solution or the coating amount. In this way, PPMS-CA and PDMS-CA composite membranes with skin layer thickness of 1–2 μm were prepared for this study, respectively.

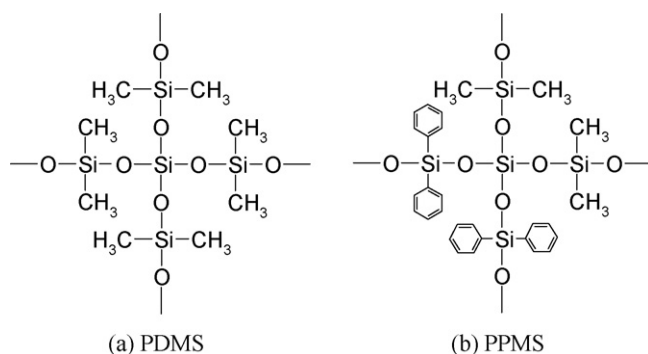


Fig. 1. Molecular structures of PPMS and PDMS.

2.3. Characteristics of membranes

2.3.1. FT-IR analysis

The thin PPMS or PDMS skin layers were peeled from the composite membrane and analyzed directly by FT-IR method. All IR spectra were obtained using a NEXUS 870 FT-IR spectrometer (NICOLET Company, USA) in transmission mode (resolution 4 cm^{-1} and averaging over 2000 scans).

2.3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to study the morphology of the surface and cross-section of the PPMS and PDMS composite membranes and to measure the skin layer thicknesses. The composite membranes were fractured in liquid nitrogen [11]. The fractured section was coated with a conductive layer of sputtered gold. The cross-section of the composite membrane was investigated using a XL30 SEM (AMERICAN FEI, USA).

2.3.3. Contact angle measurement

Contact angles were measured by CAM200 (KSV Instruments Ltd, Finland.) at the temperature of 25 °C. The 5 wt.% methanol/water, ethanol/water and acetone/water were dropped on the sample surface at ten different sites separately. The average often measured values for a sample was taken as its contact angle [12].

2.4. Swelling measurement

The measured membranes were immersed in 5 wt.% ethanol/water, methanol/water and acetone/water dilute solution separately for 24 h at 40 °C. After they were taken out of the solution, excess solvent on the membranes was removed quickly by tissue paper. Then the swelled membranes were weighted by digital analytical balance. The degree of swelling of the membrane was defined by the following equation:

$$SD = \frac{(W_s - W_d)}{W_d} \times 100\% \quad (1)$$

Where W_d and W_s denote the weight of dry and swelled membranes, respectively, and SD denotes the degree of swelling.

2.5. Pervaporation experiments

Feed solutions for the experiments were binary aqueous solutions containing methanol, ethanol, and acetone, respectively.

Pervaporation experiments were carried out using a continuous set-up reported by Li [13]. The circular flat membrane was clamped on a porous sintered metal support in a sealed stainless steel test cell. The effective membrane area was about 224 cm^2 . The liquid flow rate was measured by means of a rotameter. The cell temperature was controlled by a thermostat with a temperature fluctuation of ± 0.5 °C. A vacuum pump was used to maintain the downstream pressure at 667–1334 Pa. After a steady state was obtained, the permeating vapor was collected by two stages of cold traps. The first cold trap was provided with a refrigerant stream of -10 to -5 °C, while the freezing medium in the second trap was liquid nitrogen.

The experimental conditions were chosen in the following two series. One series of experiments was performed under constant feed temperature of 40 °C and variable feed organics concentration in the range of 2 wt.% to 40 wt.%, to investigate the effect of the feed concentration on the mass transfer through both membranes. The other series of experiments was conducted under variable feed temperatures in the range of 20–45 °C and fixed feed organic concentration of 5 wt.%, to evaluate the effect of the temperature on the mass transfer through both membranes. Furthermore, the effect of the physicochemical properties of different compounds on mass transfer coefficients through both membranes could also be elucidated by experimental measurements with the same methods for various diffusing compounds under constant feed temperature and feed concentration.

The permeation flux (J) at steady state was determined from the weight (M_p) of the collected permeant by using the following equation:

$$J = \frac{M_p}{At} \quad (2)$$

Where M_p denotes the weight of the collected permeant, t the experimental time interval for the pervaporation, and A the effective membrane surface area.

A densimeter (DMA500, Anton Paar, Austria) was used to measure the liquid densities (the accuracy of 0.000001 g ml⁻¹) and determine the organic concentrations (the accuracy of 0.001 wt.%) by means of the respective standard curve of density versus concentration. The permselectivity of the membrane was calculated via the separation factor (α) defined as:

$$\alpha = \frac{Y_i/Y_w}{X_i/X_w} \quad (3)$$

Where X and Y are the weight fractions of species in the feed and permeate, respectively. Subscript “ i ” denotes organic compound and “ w ” water.

3. Results and discussion

3.1. Physicochemical properties of PPMS and PDMS membrane

3.1.1. FT-IR analysis

It is observed from Fig. 1 that the peaks at 3060 and 700 cm⁻¹ in PPMS are characteristic of the Ph=C–H, which is absent in PDMS. Moreover, the peaks at 1260 and 1070 cm⁻¹, which are the characteristic of the –CH₃ in Si–CH₃ and the Si–O in –Si–O–Si– straight chain respectively, both appear in PPMS and PDMS membranes Fig. 2.

3.1.2. SEM pictures

The morphology of the composite PPMS-CA and PDMS-CA membranes used in this study are presented in Fig. 3. It is evident from the cross-sectional pictures that both the PPMS and PDMS top layers are tightly and properly cast on the top of the CA substrate. The thickness of both membranes, which is controlled by the volume of PPMS and PDMS solutions, are

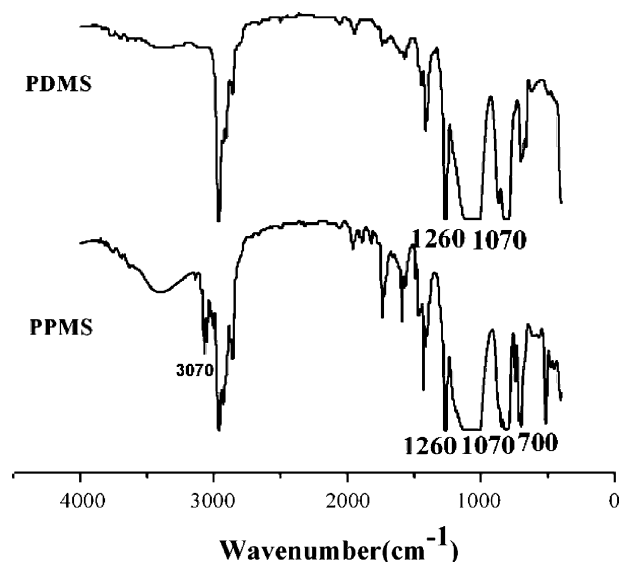


Fig. 2. FT-IR spectra of PPMS and PDMS membranes.

about 1–2 μm. It can also be found that less intrusion of PPMS or PDMS into the micropores of the substrate occurs as a result of the fabrication method used in this study.

From the surface photos of PPMS and PDMS membranes, it can be seen that the minute ravines have distributed symmetrically on the surface of the two membranes, so it can be concluded that the active layer of both composite membranes have symmetrical thickness.

3.1.3. Contact angle measurement

According to surface chemistry theory, the contact angle between solution and membrane can be used to judge the interaction between organic and membrane. The bigger is the contact angle, the smaller is the interaction. As observed from Table 1, the contact angles between solution and PPMS are bigger than those between solution and PDMS, so the interaction between water and PPMS is smaller, which indicates that the hydrophobicity of the PPMS membranes is stronger. Thus the affinity of PPMS towards organics can be enhanced, which can be helpful to increase the solution selectivity of organics in the PPMS membranes.

Besides, the contact angles on both PPMS and PDMS have ascended by the following order: methanol/water mixture < ethanol/water mixture < acetone/water mixture, which also has proved that the both membranes have the higher affinity to acetone than two other organics.

Table 1
Result of contact angle measurement at 25 °C

Mixtures	Contact angle (°)	
	PPMS	PDMS
5 wt.% Ethanol/water	98.1	96.3
5 wt.% Methanol/water	97.6	95.5
5 wt.% Acetone/water	102.9	101.8

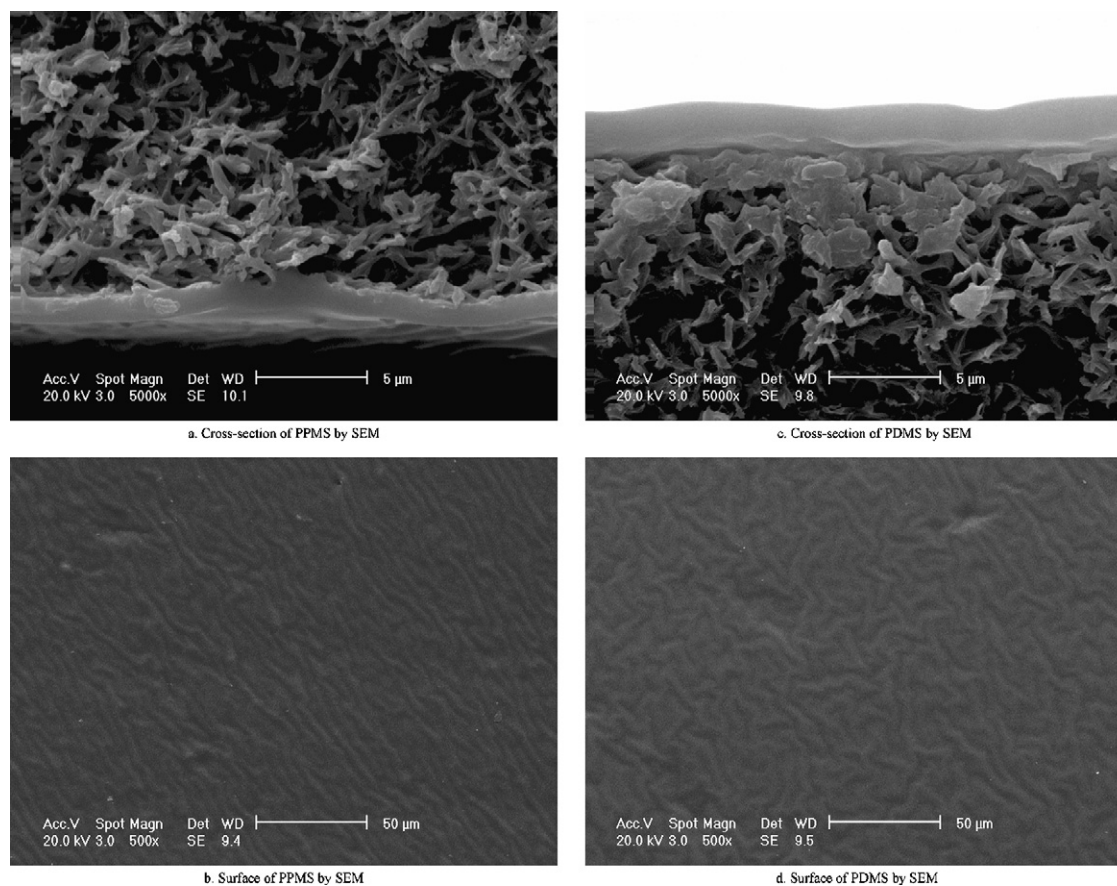


Fig. 3. Cross-section and surface of composite PDMS and PPMS membranes by SEM.

3.2. Swelling of PPMS and PDMS membranes in organics/water mixtures

The results of swelling measurements of PPMS and PDMS membranes in 5 wt.% organic/water binary mixtures 25 °C are presented in Fig. 4. Swelling Degree of PPMS in three organic/water mixtures is higher than that of PDMS. Besides, it can be found that degree of swelling values of both membranes in acetone/water mixtures is the highest in three mixtures.

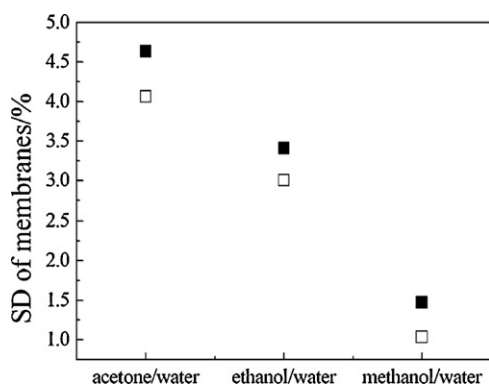


Fig. 4. Swelling degree of PPMS and PDMS membranes in 5 wt.% acetone/water, ethanol/water and methanol/water mixtures at 40 °C (■) PPMS (□) PDMS.

It is well known that swelling degree of membranes is dependent of the solubility of the components into the membranes based on the solution-diffusion theory. It is evident in Table 2 that solubility parameter difference between acetone and PDMS membrane is much lower than those between ethanol or methanol and PDMS membranes. Besides, due to the introduction of Phenyl groups, the solubility parameter of PPMS is bigger than that of PDMS, which makes the solubility parameter difference between organics and PPMS smaller than those between organics and PDMS. Thus the above data from the solubility parameters have proved the validity of experimental results of membrane swelling [15,16].

Table 2
Solubility parameter and molecular volume of ethanol, acetone, and methanol [14]

	Solubility parameter (MPa) ^{1/2}	Calculated molecular volume (cm ³ /mol)
PDMS	14.9	–
PPMS	>14.9	–
Water	47.9	18.156
Ethanol	26.2	53.200
Methanol	29.7	27.283
Acetone	19.7	26.737

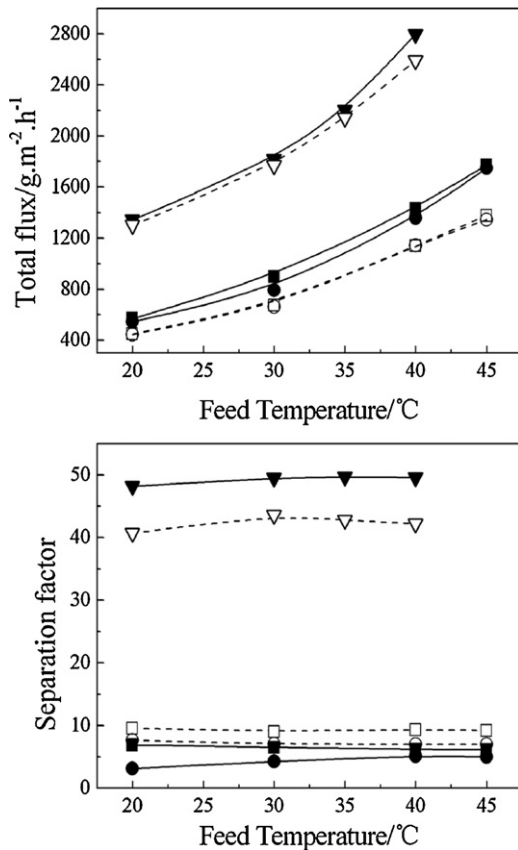


Fig. 5. Effects of temperature on separation performance of PPMS and PDMS membranes for 5 wt.% organic/water solutions. (solid line)—PPMS, (dashed line)—PDMS; (●, ○) methanol/water; (■, □) ethanol/water; (▼, ▽) acetone/water.

3.3. Effect of feed temperature

Fig. 5 presents the effect of feed temperature on pervaporation performance of 5 wt.% ethanol/water, methanol/water and acetone/water mixtures through PPMS and PDMS membranes. As can be seen, the total permeation fluxes for all three mixtures increase separately with the increasing temperature. It can be explained based on the fact that during PV process, permeating molecules diffuse through free volumes of the membrane. Thermal motions of polymer chains in amorphous regions randomly produce free volumes. As feed temperature increases, frequency and amplitude of polymer jumping chains increases, which leads to more free volume of the membrane. Meanwhile the mobility of permeating molecules is enhanced. As a result, when feed temperature gets up, diffusion rate of individual permeating molecule ascends, which results in high permeation fluxes [13,17].

As can be seen from Fig. 5, the total permeation flux of organic/water mixture increases according to the following order: methanol/water mixture < ethanol/water mixture < acetone/water mixture and the same conclusion can be found for the separation factor. The order is in accordance with that of the swelling degree of both membranes in three organic/water mixtures. It indicates that increasing swelling

degree of the membranes is in favor of the PV performance of the organics [3,18].

In Fig. 5, as feed temperature increases, the separation factors of the organics change little. It may be explained that the effect of increasing temperature on the solubility and diffusion of both organics and water is close.

It can also be observed from Fig. 5, acetone have the highest separation factor due to its highest solubility selectivity and smaller molecular size while the ethanol/water mixture and methanol/water mixture have similar separation factor. This may be attributed to the mutual balance of solubility and diffusion of two organics. Both membranes are more swollen in the ethanol/water mixture, which indicates that both membranes have preferable solubility selectivity for ethanol versus methanol. However methanol molecule has smaller size compared with ethanol, which can be seen in Table 2. The difference of molecular size has made the diffusion rate of methanol higher than that of ethanol. Based on the solution-diffusion resistance model, the separation factor of ethanol/water and methanol/water is close.

3.4. Effect of feed concentration

Fig. 6 demonstrates the effect of feed concentration on pervaporation performance of ethanol/water, methanol/water and

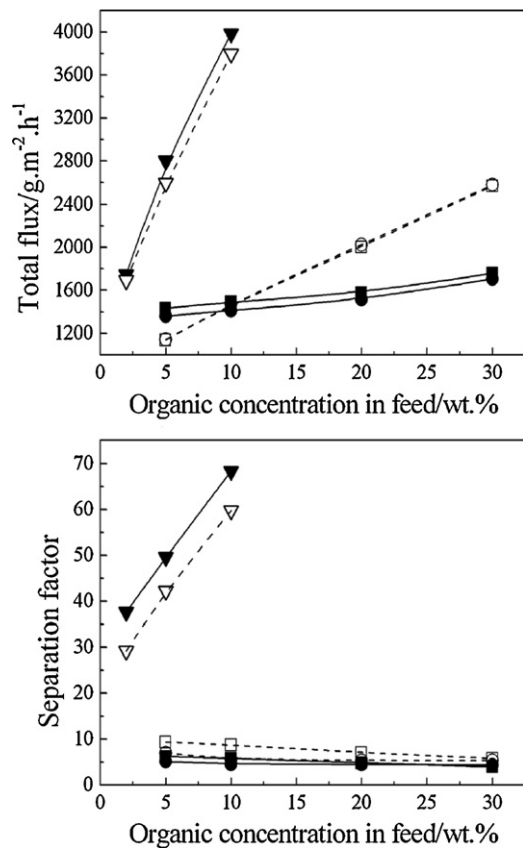


Fig. 6. Effect of feed concentration on the separation performance of PPMS membrane and PDMS membrane for organic/water mixtures at 40°C . (Solid line)—PPMS, (dashed line)—PDMS; (●, ○) methanol/water; (■, □) ethanol/water; (▼, ▽) acetone/water.

Table 3
Separation performance of 5 wt.% organic aqueous solution at 40 °C

	Membranes	Ethanol/water mixture	Methanol/water mixture	Acetone/water mixture
Total flux ($\text{g m}^{-2} \text{h}^{-1}$)	PPMS	1432.6	1360.6	2799.1
	PDMS	1139.6	1142.6	2592.6
Separation factor	PPMS	6.2	5.1	49.6
	PDMS	9.3	7.0	42.2

acetone/water mixtures through PPMS and PDMS membranes with the same feed temperature at 40 °C. It can be seen that as organic concentration increases, the total fluxes increase separately. This is owing to the increasing impetus of mass transfer as feed concentration ascends.

As can be observed in Fig. 6, separation factors of ethanol and methanol keep almost the same as the feed concentration increases. It indicates that the increase extent of swelling degree of both membranes in above both mixtures is still limited with changing concentration while diffusion selectivity is the dominant factor for the separation process [19]. However, separation factor of acetone/water mixture ascends sharply with increasing feed concentration, which is far higher than those of ethanol/water and methanol/water. This has illuminated that for acetone/water mixture, the separation factor is most dependent of solubility selectivity in the membranes. When the feed concentration of acetone/water mixture increases, the swelling degree of the membranes ascends greatly and the solubility selectivity of acetone versus water is enhanced.

3.5. Comparison of pervaporation performance of PPMS and PDMS membranes

For the comparison of pervaporation performance of PPMS and PDMS membranes, Figs. 5 and 6 and Table 3 have presented the separation behavior of methanol/water, ethanol/water and acetone/water mixtures through both membranes. It is observed that PPMS has better pervaporation performance than PDMS for acetone/water mixture. Total flux of acetone/water mixture by PPMS at 5 wt.% feed concentration and 40 °C was $2799 \text{ g m}^{-2} \text{ h}^{-1}$, and the separation factor at the same condition reaches 49.6. Due to the introduction of more hydrophobic phenyl groups, PPMS membranes have shown better swelling degrees and solubility selectivity for acetone than PDMS. Besides, for phenyl groups are more rigid than methyl groups, the advantage of diffusion rate of water molecule through PPMS has been diminished, which can lead to the enhancement of diffusion selectivity of acetone versus water. Thus separation performance of acetone/water through PPMS membranes has been improved greatly. As for ethanol/water and methanol/water, the flux of organics is enhanced owing to the increase of hydrophobicity of PPMS, but the selectivity changes little and even descends because the strong hydrogen-bonding interaction between ethanol/methanol and water makes the solubility of water increase accordingly during the transport process [20].

Besides, as the feed concentration increases, PDMS membranes have higher flux for the ethanol/water and methanol/water mixtures than PPMS. This may be explained by the effect of plasticity of polymer chains on the separation process. PDMS membrane has more soft chains than PPMS due to the absence of rigid phenyl groups compared with PPMS. When the feed concentration increases, the plasticity of PDMS membranes is enhanced greatly due to the swelling process. So organics and water molecules absorbed into the surface of PDMS membranes can pass it more easily than PPMS membranes.

4. Conclusions

In this study, PPMS-CA and PDMS-CA membranes were prepared and used for the concentration of volatile organic compounds such as methanol, ethanol and acetone from aqueous solutions by pervaporation. The effects of experimental conditions such as feed concentration and operating temperature on separation process were discussed thoroughly.

The contact angles between organics solution and PPMS are bigger than those between solution and PDMS, which indicates that the hydrophobicity of the PPMS membranes is stronger. Swelling Degree of PPMS in three organic/water mixtures is also higher than that of PDMS.

The total permeation flux of organic/water mixture increased according to the following order: methanol/water mixture < ethanol/water mixture < acetone/water mixture and the same conclusion can be found for the separation factor. The total permeation fluxes for all three mixtures increase separately with the increasing temperature while separation factors change little. Total fluxes increase separately with changing feed concentration. Separation factors of ethanol and methanol are nearly independent of feed concentration, but that of acetone/water mixture ascends sharply.

PPMS membranes have better pervaporation performance than PDMS for acetone/water mixture. Total flux of acetone/water mixture by PPMS at 5 wt.% feed concentration and 40 °C is $2799 \text{ g m}^{-2} \text{ h}^{-1}$, and the separation factor at the same condition reaches 49.6. It can be attributed to the introduction of more hydrophobic and rigid phenyl groups.

Acknowledgements

The present work was supported financially by National 985 Project of PR China (No. 985XK-015) and Scientific Research Foundation of Graduate School of Nanjing University (No. 2005CL10).

References

- [1] A. Baudot, M. Marin, Pervaporation of aroma compounds: comparison of membrane performances with vapour–liquid equilibria and engineering aspects of process improvement, food and bioproducts processing, *Trans. Inst. Chem. Eng. C* 75 (1997) 117–142.
- [2] F.B. Peng, F.S. Pan, D. Li, Z.Y. Jiang, Pervaporation properties of PDMS membranes for removal of benzene from aqueous solution: Experimental and modeling, *Chem. Eng. J.* 114 (2005) 123–129.
- [3] J.D. Jou, W. Yoshida, Y. Cohen, A novel ceramic-supported polymer membrane for pervaporation of dilute volatile organic compounds, *J. Membr. Sci.* 162 (1999) 269–284.
- [4] L. Li, Z.Y. Xiao, Z.B. Zhang, S.J. Tan, Pervaporation of acetic acid/water mixtures through carbon molecular sieve-filled PDMS membranes, *Chem. Eng. J.* 97 (2004) 83–86.
- [5] M. Peng, L.M. Vane, S.X. Liu, Recent advances in VOCs removal from water by pervaporation, *J. Hazard. Mater.* B98 (2003) 69–90.
- [6] B.K. Dutta, S.K. Sikdar, Separation of azeotropic organic liquid mixtures by pervaporation, *AIChE J.* 37 (4) (1991) 581.
- [7] H.J.C. TeHennepe, D. Bargeman, M.H.V. Mulder, C.A. Smolders, Zeolite filled silicone rubber membranes. Part-I, membrane permeation and pervaporation results, *J. Membr. Sci.* 35 (1987) 39.
- [8] S. Ray, S.K. Ray, Separation of organic mixtures by pervaporation using crosslinked and filled rubber membranes, *J. Membr. Sci.* 285 (2006) 108–119.
- [9] S. Ray, S.K. Ray, Separation of organic mixtures by pervaporation using cross-linked rubber membranes, *J. Membr. Sci.* 270 (2006) 132–145.
- [10] Z.P. Fang, H.F. Feng, H. Wu, Z.Y. Jiang, Study on preparation, osmotic pervaporation and separation performances of modified PDMS membranes, *J. Tianjin Polytech. Univ.* 245 (2005) 28–32 (in Chinese).
- [11] X.Z. Tian, B.K. Zhu, Y.Y. Xu, P (VDF-co-HFP) membrane for recovery of aroma compounds from aqueous solutions by pervaporation I. Ethyl acetate/water system, *J. Membr. Sci.* 248 (2005) 109–117.
- [12] C.L. Li, K.R. Lee, Dehydration of ethanol/water mixtures by pervaporation using soluble polyimide membranes, *Polym. Int.* 55 (2006) 505–512.
- [13] L. Li, Z.Y. Xiao, S.J. Tan, L. Pu, Z.B. Zhang, Composite PDMS membrane with high flux for the separation of organics from water by pervaporation, *J. Membr. Sci.* 243 (2004) 177–187.
- [14] S. Mandal, V.G. Pangarkar, Separation of methanol–benzene and methanol–toluene mixtures by pervaporation: effects of thermodynamics and structural phenomenon, *J. Membr. Sci.* 201 (2002) 175–190.
- [15] V.S. Praptowidodo, Influence of swelling on water transport through PVA-based membrane, *J. Mol. Struct.* 739 (2005) 207–212.
- [16] Kuo, *Silicone Release Coatings for the Pressure Sensitive Industry—Overview and Trends*, D.C. Corporation, A.C.M., 2003, pp. 1–4.
- [17] P. Sampraniboon, R. Jiratananon, D. Uttapap, X. Feng, R.Y.M. Huang, Separation of aroma compounds from aqueous solutions by pervaporation using polyoctylmethylsiloxane (PDMS) membranes, *J. Membr. Sci.* 174 (2000) 55–65.
- [18] A. Sungpet, A. Pimsert, R. Jiratananon, J.D. Way, Facilitated transport of unsaturated hydrocarbons through crosslinked-poly(sulfonated styrene), *Chem. Eng. J.* 87 (2002) 321–328.
- [19] T. Mohammadi, A. Aroujalian, A. Bakhshi, Pervaporation of dilute alcoholic mixtures using PDMS membrane, *Chem. Eng. Sci.* 60 (2005) 1875–1880.
- [20] J.P. Hu, L.M. Xiong, X.H. Tang, W. Zhou, Advance in the modification of epoxy resin, *Appl. Eng. Plast.* 33 (2005) 73–76 (in Chinese).