

Separation of Ethanol from Ethanol/Water Mixtures by Pervaporation with Silicone Rubber Membranes: Effect of Silicone Rubbers

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Received 13 April 2010; accepted 19 June 2010

DOI 10.1002/app.32991

Published online 29 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, poly(dimethyl siloxane) (PDMS)/poly(vinylidene fluoride) (PVDF), poly(phenyl methyl siloxane) (PPMS)/PVDF, poly(ethoxy methyl siloxane) (PEOMS)/PVDF, and poly(trifluoropropyl methyl siloxane) (PTFMS)/PVDF composite membranes were prepared. The different functional compositions of these membranes were characterized by Fourier transform infrared spectroscopy. The surfaces and sections of these membranes were investigated by scanning electron microscopy. The hydrophobicity at the membrane surface was assessed with contact angle measurement. Swelling experiments were carried out to investigate the swelling behavior of these membranes. The composite membranes prepared in this study were used in the pervaporation separation of

ethanol/water mixtures, and their separation performances were compared. The results show that the separation performances of these membranes were strongly related to the silicone rubber components and composition, the total fluxes decreased in the following order: PDMS > PPMS > PEOMS > PTFMS. The separation factor followed the following order: PPMS > PEOMS > PDMS > PTFMS (5 wt % ethanol at 40°C). In addition, the effects of the feed temperature (40–70°C) and feed composition (5–20 wt %) on the separation efficiency were investigated experimentally. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3413–3421, 2011

Key words: membranes; selectivity; silicones

INTRODUCTION

In recent years, pervaporation (PV) has been studied as a promising effective and energy-saving membrane technique for separating azeotropic and close-boiling mixtures, isomers, and heat-sensitive compounds;^{1–4} the separation of ethanol/water mixtures with the PV technique has been given much attention. This process is expected to provide a continuous and economical method for concentrating

ethanol from fermentation broths. For the selective removal of ethanol from fermentation broths by the method of PV, it is very important to select suitable membrane materials that have excellent film-forming properties, high permeability, and high permselectivity.

Many organophilic polymeric materials have been reported to be good candidates for membranes for ethanol/water mixture separation,^{5–11} among which crosslinked poly(dimethyl siloxane) (PDMS) has been widely used for ethanol concentration from ethanol aqueous solutions. Such a separation property of the PDMS membrane is due to the high hydrophobicity of its surface and the high permeability of vapors through the membrane.¹² Other silanol-based silicones, such as poly(ethoxy methyl siloxane) (PEOMS),^{13,14} poly(phenyl methyl siloxane) (PPMS),^{13–16} poly(octyl methyl siloxane),^{17–20} and poly(trifluoropropyl methyl siloxane) (PTFMS),^{16,20} have also proven to be effective at separating ethanol. However, the relationship between the structure of these silicones and the PV performance was not studied sufficiently. For example, the permeation fluxes of PPMS, PEOMS, and PTFMS were not reported on the basis of the description in refs. 13–16. Vane et al.²¹ noted that the primary difference within this family arose from the groups attached to the silicone atoms, and they also studied the effect

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Contract grant sponsor: Major State Basic Research Program of China; contract grant number: 2009CB623404.

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 20736003 and 20906056.

Contract grant sponsor: National High Technology Research and Development Program of China; contract grant numbers: 2007AA06Z317 and 2008EG111021.

Contract grant sponsor: Foundation of Ministry of Education of China; contract grant number: 20070003130.

Contract grant sponsor: Foundation of the State Key Laboratory of Chemical Engineering; contract grant number: SKL-ChE-08A01.

Contract grant sponsor: Postdoctor Science Foundation of China; contract grant numbers: 20100470015 and 023201069.

Journal of Applied Polymer Science, Vol. 119, 3413–3421 (2011)
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TABLE I
Basic Properties of the Silicones

Silicone	Average molecular weight (g/mol)	Kinetic viscosity (mPa s)	Comment
PPMS	52,631	8,500	Ph/(Ph + CH ₃) = 11%
PEOMS	49,711	10,000	25% polymethyltriethoxy
PDMS	69,856	50,000	—
PTFMS	62,523	13,000	Si : F = 7 : 3 (molar ratio)

of silicone rubber components and compositions on the ethanol–water separation performance of mixed-matrix vinyl-based silicone rubber membranes. However, the PV performances of different silanol-based silicone rubber membranes were not investigated in the description of Vane et al.²¹

These silanol-based silicone rubber membranes have different selectivities for ethanol/water mixtures, primarily because they do not have any functional groups (ethoxy, phenyl, and trifluoropropyl) to create differential interactions between ethanol and water. Therefore, the study of the relationship between the structure of these silicones and the PV performance was necessary and may provide some useful information for ethanol permselective membrane structure design. In our previous research, we studied the separation of ethanol from ethanol/water mixtures using PDMS membranes with poly(vinylidene fluoride) (PVDF), polysulfone, poly(ether imide), and polyacrylonitrile supports; we observed that the PDMS/PVDF composite membrane showed the highest separation factor in these composite membranes;²² thus, a PVDF support was selected in this study. PDMS/PVDF, PPMS/PVDF, PEOMS/PVDF, and PTFMS/PVDF composite membranes were prepared and used in the PV separation of ethanol/water mixtures. Solubility parameter calculation and swelling experiments were performed to reveal the interaction between the membranes and permeating molecules. The separation performances of these membranes were investigated in terms of the flux and separation factors in detail.

EXPERIMENTAL

Materials

PPMS and PEOMS were purchased from Shanghai Resin Factory, China. PDMS was received from Beijing Chemical Reagents Corp., China. PTFMS was obtained from Hebei Guigu Chemical Reagents Corp., China. The basic properties and chemical structures of four kinds of polysiloxane are shown in Table I and Figure 1, respectively. *N*-Heptane, ethanol, tetraethoxysilane, and dibutyltin dilaurate (Beijing Jingyi Chemical Reagents Corp., China)

were used without further purification. PVDF (1015) was chosen for the preparation of the supports. Triethyl phosphate (TEP; reagent grade, Beijing Chemical Corp., China) was used as the solvent for PVDF membrane formation.

Membrane preparation

PVDF supporting membrane preparation

The PVDF support layer was prepared by the dissolution of PVDF in TEP solvent to form a 15 wt % solution. The PVDF/TEP solution was cast on the non-woven fiber and immersed in water to induce polymer precipitation. The residual solvents were fully exchanged with deionized water and dried at room temperature.

PDMS/PVDF, PPMS/PVDF, PEOMS/PVDF, and PTFMS/PVDF composite membrane preparation

PDMS and crosslinking reagents were dissolved in *n*-heptane with vigorous stirring, and then, a dibutyltin dilaurate catalyst was added to the solution. After it was degassed *in vacuo*, the solution was cast onto the PVDF membrane with a scraper. The membranes were first dried at room temperature for 24 h to evaporate the solvent and, then, were completely crosslinked in oven at 80°C for 5 h. Other silicone membranes were prepared following the same formulation. The thickness of the top skin layers was determined by means of scanning electron microscopy (SEM) spectroscopy.

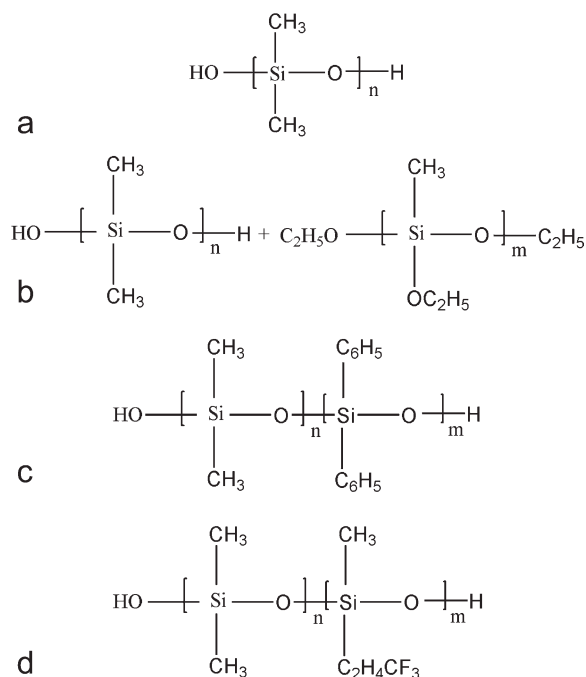


Figure 1 Chemical structures of (a) PDMS, (b) PEOMS, (c) PPMS, and (d) PTFMS.

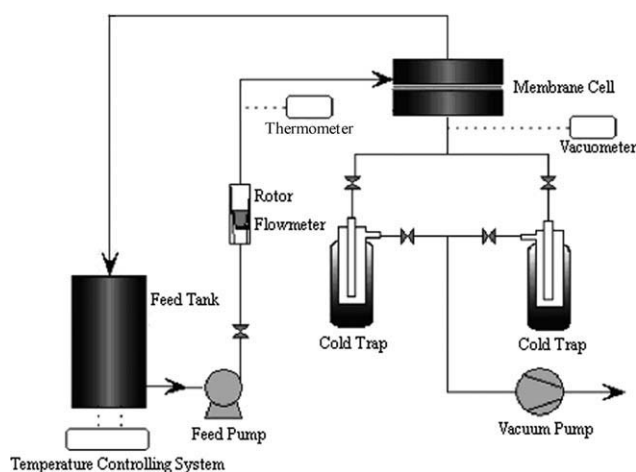


Figure 2 Scheme of the PV apparatus.

Membrane characterization

SEM

The morphology of the surface and cross section of the silicone composite membranes were observed by a scanning electron microscope (JSM-6301F, JEOL, Japan). The silicone membranes were immersed in liquid nitrogen and cracked. These samples were coated with a conductive layer of sputtered gold.

Fourier transform infrared (FTIR) spectra

The FTIR spectra of the silicone membranes were obtained from a Nicolet IR 560 spectrometer (USA) in the range $4000\text{--}500\text{ cm}^{-1}$.

Contact angle measurement

The contact angles were measured by an OCA-20 (Dataphysics, Germany) at a temperature of 25°C . Water was dropped separately on the sample surface at five different sites. The average often measured value for a sample was taken as its contact angle.

Swelling of the membranes

A piece of membrane sample was cut out and dried at 60°C in a vacuum drying oven for at least 24 h until the weight remained constant. Then, the piece of membrane was immersed into ethanol aqueous solution and soaked for 48 h. When the sample's weight remained constant, it was carefully taken out and rapidly wiped with tissue paper to remove the adherent solution, and then, the weight of the swollen membrane was quickly measured. All experiments were repeated at least three times, and the results were averaged. The swelling degree (SD) of the membrane was defined as follows:

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

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

PV experiments

PV experiments were conducted with an apparatus developed by our laboratory, as shown in Figure 2. The membrane was positioned in a stainless-steel permeation cell, and the effective surface area of the membrane in contact with the feed mixture in this cell was 22.4 cm^2 . The feed solution was continuously circulated from a feed tank to the upstream side of the membrane in the cell at the desired temperature by a pump, and the feed temperature was monitored by a digital vacuumeter. We carried out PV experiments by maintaining atmospheric pressure on one side (feed) and a pressure of about 100 Pa with a vacuum pump on the other side (permeate). After a steady state was obtained (ca. 1 h after startup), the permeation was collected in the cold traps and condensed by liquid nitrogen. The compositions of the feed solution and permeate were analyzed by gas chromatography (Shimadzu, GC-14C, Japan). The results for PV were reproducible, and the errors inherent in the PV measurements were less than 2%. The separation performances of the membranes were evaluated on the basis of the total flux and separation factors.

We determined the permeate total flux (J) by measuring the weight of the permeate collected in the cold trap and dividing it by the time and the membrane's surface area, as shown in eq. (2):

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

where W represents the mass of permeate, A is the effective membrane area, and t is the permeation time. Then, the selectivity of the membrane in a binary system was obtained as follows:

$$\alpha = \frac{y_a/y_b}{x_a/x_b} \quad (3)$$

where α is the separation factor; x and y represent the weight fractions of corresponding solute in the feed and permeate, respectively; and the subscripts a and b refer to the more permeable component (ethanol) and the less permeable one (water), respectively.

RESULTS AND DISCUSSION

SEM photographs of the composite membranes

The morphology of the PDMS/PVDF, PPMS/PVDF, PEOMS/PVDF, and PTFMS/PVDF composite membranes

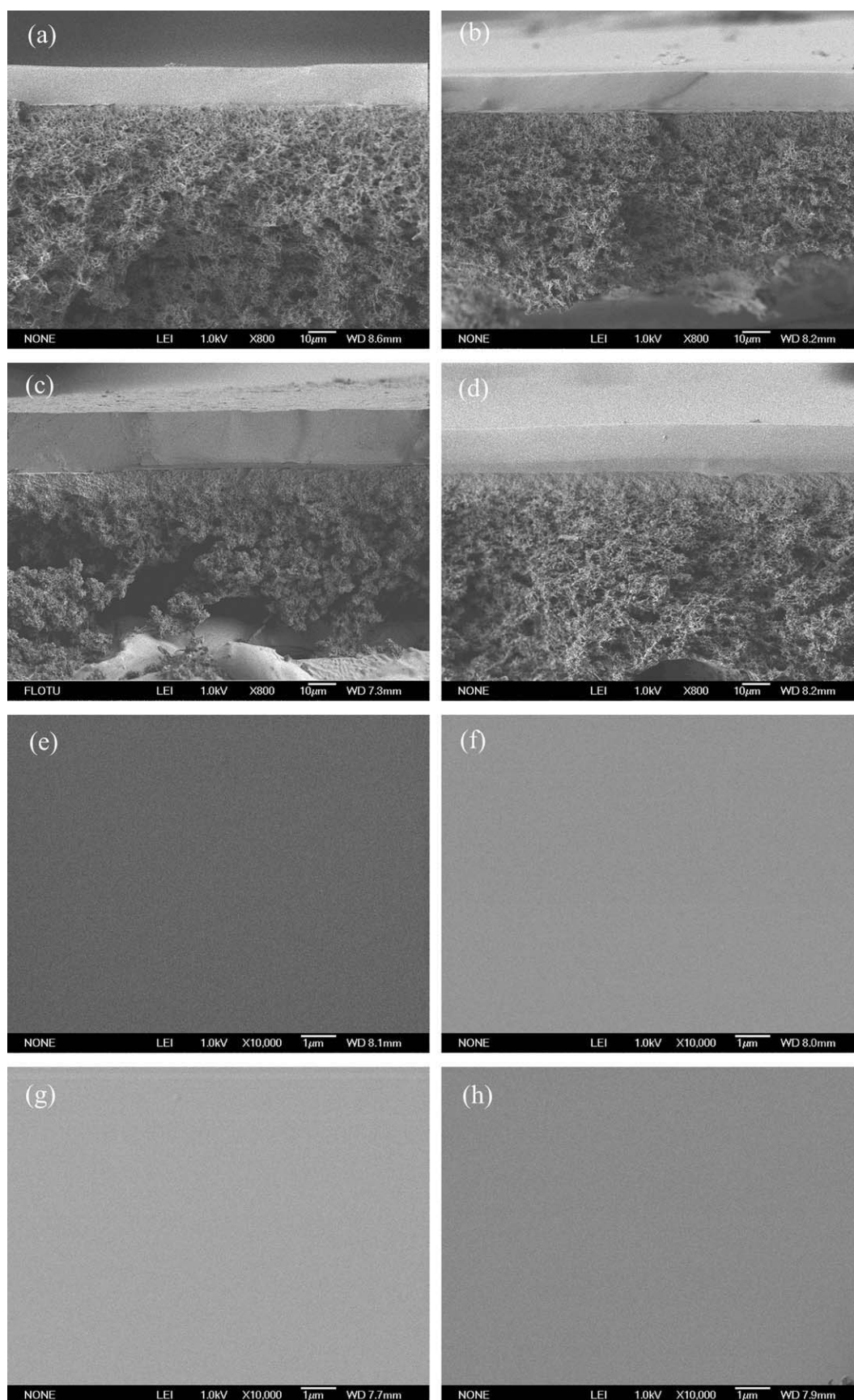


Figure 3 Cross sections of the composite membranes [(a) PDMS, (b) PEOMS, (c) PPMS, and (d) PTFMS] and the surface morphologies of the composite membranes [(e) PDMS, (f) PEOMS, (g) PPMS, and (h) PTFMS].

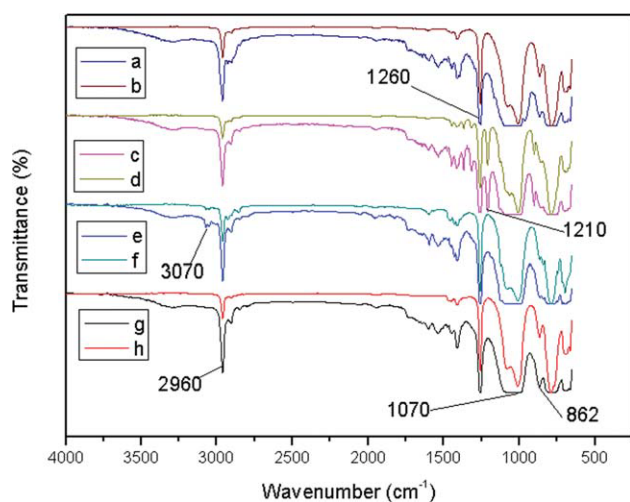


Figure 4 FTIR spectra of the composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

used in this study are shown in Figure 3. It was evident from the cross-sectional pictures that the top layers were all tightly and properly cast on the top of the PVDF substrate. Moreover, the thickness of the top layers were all almost 10 μm , as determined by SEM photographs. As shown by the surface photos of the membranes, the surfaces of the composite membranes were all dense, and there were no pinholes or cracks, which are important for ethanol/water separation.

FTIR spectra of the composite membranes

The FTIR spectra of the surface of the membranes are shown in Figure 4. The peak at 1260 cm^{-1} was assigned to the CH_3 absorbance signal (the symmetric deformation of two CH_3 's of $\text{Si}-\text{CH}_3$), and the peaks at 862, 1070, and 2960 cm^{-1} were assigned to the $\text{Si}-\text{OH}$ absorbance signals (stretching and angle bending vibrations, respectively).²³ The peak at 3070 cm^{-1} was characteristic of $\text{Ph}=\text{C}-\text{H}$,²⁴ and the peak at 1210 cm^{-1} was characteristic of CF_3 stretching.²⁵ Compared to that of the noncrosslinked membrane, the spectra of the crosslinked membranes showed that the absorbance signals of $\text{Si}-\text{OH}$ evidently weakened. These changes were evidence that the crosslinking reaction took place.

Contact angle measurement

According to surface chemistry theory, the contact angle between a solution and membrane can be used to judge the interaction between organics and the membrane. The bigger the contact angle is, the smaller the interaction is.¹⁵ As shown in Table II, the contact angles of four kinds of silicones ascended in the following order: PTFMS < PDMS < PEOMS <

TABLE II
Result of Contact Angle Measurement at 25°C

Membrane	Contact angle ($^\circ$)
PPMS	121.2
PEOMS	118.1
PDMS	116.0
PTFMS	113.1

PPMS, so the interaction between water and PPMS was the smallest; this indicated that the hydrophobicity of the PPMS membranes was the strongest.²⁶ Thus, the affinity of PPMS toward ethanol was enhanced; this may have been helpful to increase the selectivity of ethanol in the PPMS membrane. The hydrophobic nature of these membranes played an important role in their PV performance, which is discussed later.

Results of the swelling experiment

The swelling results of the PPMS, PDMS, PEOMS, and PTFMS membranes with different feed concentrations are given in Figure 5. The SD values of all of the membranes increased as the ethanol concentration increased. This indicated that ethanol was more easily dissolvable in the silicone membranes than in water; this was due to the stronger interaction between the ethanol and the membranes. Also, the order of SDs of the membranes was $\text{PPMS} > \text{PEOMS} > \text{PDMS} > \text{PTFMS}$; this indicated that the interaction between the ethanol and membranes followed the order $\text{PPMS} > \text{PEOMS} > \text{PDMS} > \text{PTFMS}$. We observed that the maximum SD of all of the membranes in the solution was no more than 4%; this should be suitable for practical application.

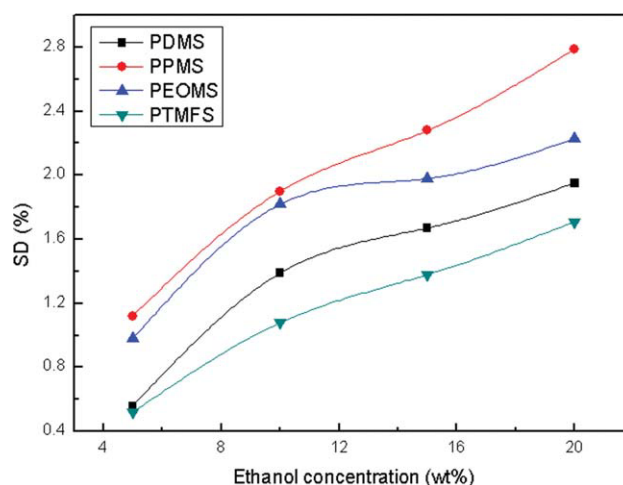


Figure 5 SD values of the membranes in ethanol/water mixtures at 40°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Solubility Parameters of the Membrane Materials, Ethanol, and Water

Solvent or membrane	δ_d	δ_p	δ_h	δ	$ \delta_A - \delta_M $	$ \delta_B - \delta_M $	$ \delta_A - \delta_M / \delta_B - \delta_M $
Ethanol	15.8	8.8	19.4	26.5	–	–	–
Water	15.5	16.0	42.4	47.9	–	–	–
PDMS	13.3	5.7	6.5	15.8	10.7	32	2.99
PPMS	14.1	5.6	6.5	16.5	10.0	31.4	3.14
PTFMS	12.8	5.4	6.3	15.3	11.2	32.5	2.90
PEOMS	13.5	5.8	6.8	16.2	10.3	31.7	3.08

δ , solubility parameter; δ_d , dispersion parameter; δ_p , polar parameter; δ_h , hydrogen bonding parameter.

It is well known that the SD of a membrane is dependent on the solubility of the components into the membrane on the basis of solution–diffusion theory. The solubility parameters (δ) of each silicone rubber, as determined by the group contribution method of Hansen,²⁷ are listed in Table III. According to solubility parameter theory, the higher the dissolution performance is between component A and membrane M, the lower the difference value ($|\delta_A - \delta_M|$) of their solubility parameter will be. Then, the higher the $|\delta_A - \delta_M| / |\delta_B - \delta_M|$ is, the larger the dissolution performance difference between membrane M and component A and component B will be, which is more favorable to the separation of A and B by membrane M.

For the membrane process, water and ethanol were chosen as components A and B. The calculation results reveal that the order of $|\delta_A - \delta_M|$ was PPMS > PEOMS > PDMS > PTFMS and the order of $|\delta_A - \delta_M| / |\delta_B - \delta_M|$ was also PPMS > PEOMS > PDMS > PTFMS. This indicated that the order of affinity to ethanol should have been PPMS > PEOMS > PDMS > PTFMS. The experimental results of membrane swelling were consistent with the analysis of the solubility parameters of silicones; this also proved the validity of the results of the swelling experiment.^{15,28}

Comparison of the membrane performances

For comparison purposes, the separation performances of the membranes in this study and in the litera-

ture are shown in Table IV. The separation factors of the PDMS and PTFMS membranes in this study were higher than those reported in the literature,^{13,16} and the separation factors of the PPMS and PEOMS membranes were slightly lower than those reported in the literature.¹³

In this study, the order of the permeation flux and separation factor were PDMS > PPMS > PEOMS > PTFMS and PPMS > PEOMS > PDMS > PTFMS, respectively. Because of the introduction of more hydrophobic phenyl groups and ethoxy groups, PPMS and PEOMS showed better SD and solubility selectivity values for ethanol than for PDMS; however, phenyl groups and ethoxy groups may have caused low chain mobility and resulted in the low diffusion of permeating molecules. Thus, PPMS and PEOMS showed higher separation factors and lower permeation fluxes than PDMS. As for PTFMS, the low SD may have caused a low free volume and low sorption selectivity, so PTFMS had a lower separation factor and permeation flux than PDMS.

Effect of the feed temperature

Figures 6 and 7 illustrate the effects of the feed temperature on the total flux and separation factor, respectively. The total fluxes increased and the separation factors decreased with increasing feed temperature from 40 to 70°C; this was consistent with a common rule.²⁹ The increment of total flux with temperature was due to the increase in the mobility of individual permeating molecules, caused by both

TABLE IV
Separation Performance of the Silicon Rubber Membranes for Ethanol/Water Mixtures

Membrane	Membrane thickness (μm)	Ethanol feed concentration (wt %)	PV temperature ($^{\circ}\text{C}$)	Total flux ($\text{g m}^{-2} \text{h}^{-1}$)	Separation factor	Reference
PDMS	120	4.4	50	–	5.3	13
PPMS	120	4.1	50	–	11.7	13
PEOMS	120	4.4	50	–	10.5	13
PDMS	20	16.5	40	–	8.0	16
PPMS	46	16.5	40	–	6.2	16
PTFMS	37	16.5	40	–	3.2	16
PDMS	10	5	40	500.7	8.3	This study
PPMS	10	5	40	450.1	9.4	This study
PEOMS	10	5	40	370.2	9.2	This study
PTFMS	10	5	40	345.3	7.9	This study

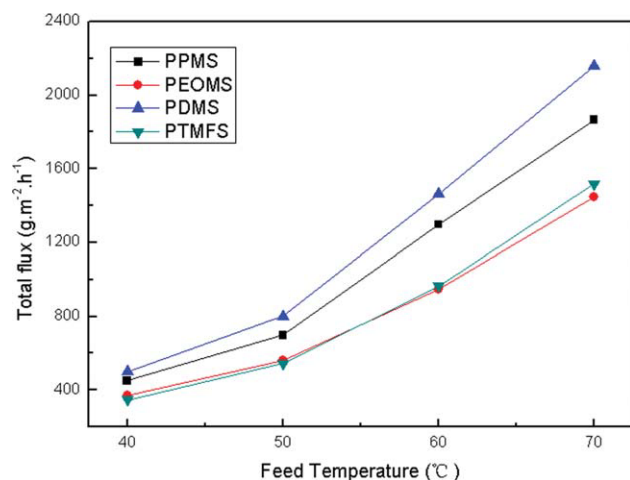


Figure 6 Effect of the feed temperature on the total flux of the composite membranes for 5 wt % ethanol/water solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

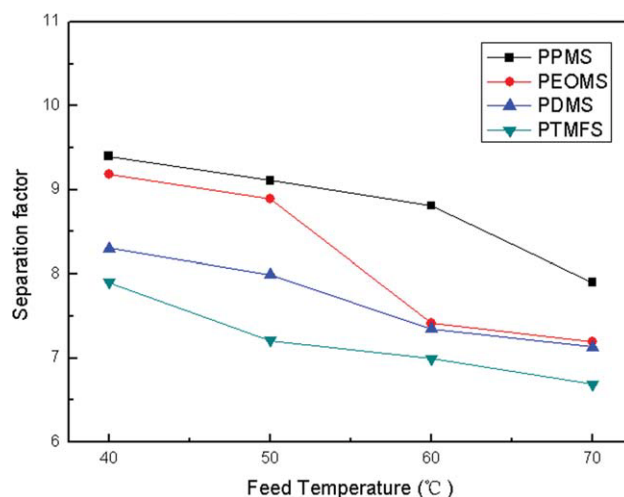


Figure 7 Effect of the feed temperature on the separation factor of the composite membranes for 5 wt % ethanol/water solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

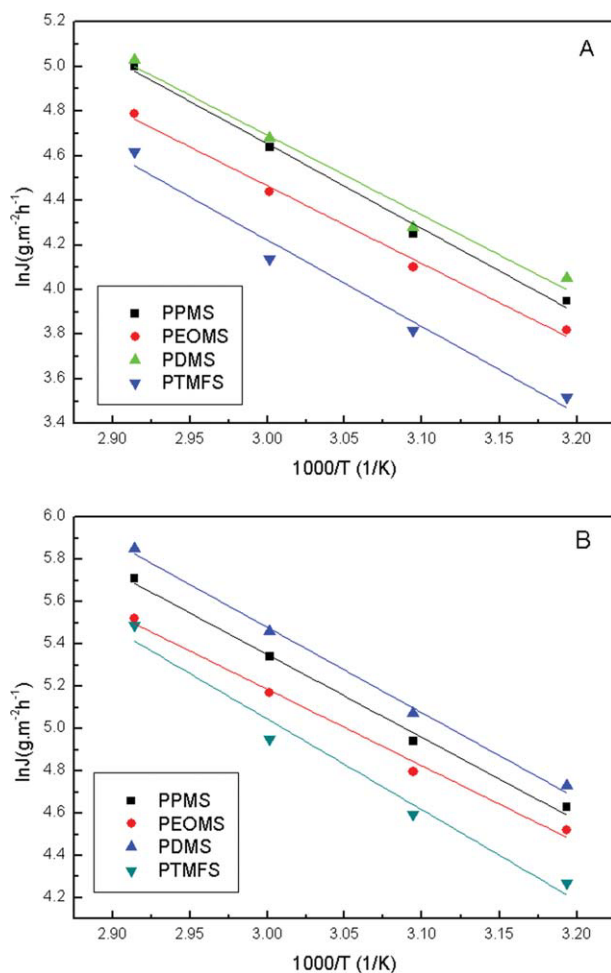


Figure 8 Arrhenius plot of the membranes for (A) ethanol and (B) water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the temperature and the enhanced mobility of the polymer segments.³⁰ On the other hand, the increase in SD of the membrane with temperature resulted in more water transport, which led to the decrease in selectivity to ethanol.³¹

To get a deeper view of the relationships between the temperature and permeation flux, an Arrhenius-type equation was applied as follows:

$$J_i = J_{0i} \exp\left(\frac{-E_{pi}}{RT}\right) \quad (4)$$

where J_i is the flux of component i , J_{0i} is the permeation rate constant, E_{pi} is the apparent activation energy of permeation for component i , T is the feed absolute temperature, and R is the molar gas constant. The J_{0i} and E_{pi} values for ethanol and water were determined from the slopes of the $\ln J$ versus $1/T$ plots (Fig. 8), and the results are summarized in Table V. Then, the permeate fluxes for individual components were predicted by the permeability correlations.

Effect of the feed composition

The effects of the ethanol content in the feed on the total fluxes and separation factors are depicted in Figures 9 and 10, respectively. As shown in Figure 9, the fluxes increased with increasing ethanol content in the feed. When the ethanol content in the feed increased, extensive swelling of the membrane occurred because of the strong affinity of ethanol to the membrane; this was attributed to the fact that ethanol permeated more easily than water at the same temperature. It is well known that remarkable swelling in polymer membranes leads to

TABLE V
Activation Energies and Permeability Correlations of Individual Components

Compound	Membrane	J_{oi} ($\text{g m}^{-2} \text{h}^{-1}$)	E_{pi} (kJ/mol)	Permeability correlation
Ethanol	PPMS	8.89×10^6	31.58	$\ln J_i = 16.0-3798/T$
	PEOMS	2.96×10^6	28.98	$\ln J_i = 14.9-3486/T$
	PDMS	4.88×10^6	29.76	$\ln J_i = 15.4-3579/T$
	PTFMS	7.65×10^6	32.22	$\ln J_i = 15.9-3876/T$
Water	PPMS	27.51×10^6	32.63	$\ln J_i = 17.1-3925/T$
	PEOMS	9.25×10^6	30.10	$\ln J_i = 16.0-3620/T$
	PDMS	4.40×10^6	33.60	$\ln J_i = 17.6-4040/T$
	PTFMS	61.84×10^6	35.73	$\ln J_i = 17.9-4297/T$

an open membrane structure and, consequently, an enhancement of the permeation in polymer membranes. Therefore, the total fluxes increased because of the enhanced activity of the polymer chains and bonds.

As shown in Figure 10, the separation factor decreased with increasing concentration of ethanol. That is, the ethanol permselectivity of the membranes decreased with increasing ethanol content. In general, the permselectivity of liquid mixtures through polymer membranes by PV depends on the differences in both the solubility of the permeants in polymer membranes (the sorption separation process) and the diffusivity of permeants in the polymer membranes (the diffusion separation process), namely, solution-diffusion theory.³² In the first step, the ethanol molecules have a higher affinity for the membranes than the water molecules. Then, in the second step, the diffusivity of these molecules in the diffusion separation process is significantly dependent on the molecular size and shape. In this case, increasing ethanol content led to a higher permeation rate and a lower separation factor.

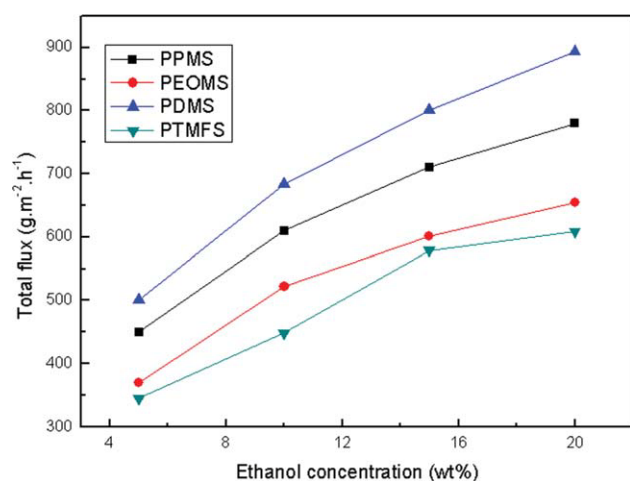


Figure 9 Effect of the feed concentration on the total flux of the composite membranes for 5 wt % ethanol/water solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In this article, four kinds of different silanol-based silicone/PVDF composite membranes were prepared, and the effects of silicone rubbers on the separation efficiency of ethanol from ethanol/water mixtures were investigated. The PV results indicate that the separation performances of these membranes were strongly related to the silicone rubber components and the composition; the order of the permeation flux and separation factor were PDMS > PPMS > PEOMS > PTFMS and PPMS > PEOMS > PDMS > PTFMS, respectively. Both the measurement of SD and the analysis of the solubility parameters of these membranes revealed that PPMS and PEOMS showed higher affinities to ethanol and PTFMS showed a lower affinity to ethanol than PDMS; consequently, PPMS and PEOMS had higher separation factors and PTFMS had a lower separation factor than PDMS. The introduction of phenyl groups, ethoxy groups, and trifluoropropyl may have caused low chain mobility and resulted in low diffusion of permeating molecules. Thus, PDMS had the highest permeation flux among these membranes.

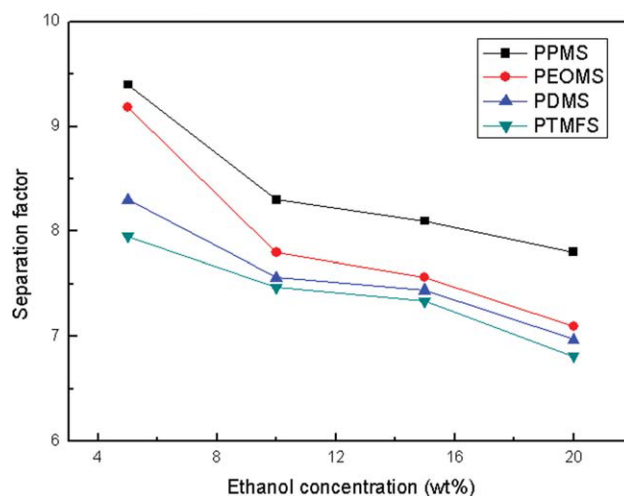


Figure 10 Effect of the feed concentration on the separation factor of the composite membranes for 5 wt % ethanol/water solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

References

1. Feng, X. S.; Huang, R. Y. M. *Ind Eng Chem Res* 1997, 36, 1048.
2. Jonquieres, A.; Clement, R.; Lochon, P.; Neel, J.; Dresch, M.; Chretien, B. *J Membr Sci* 2002, 206, 87.
3. Zhang, S.; Drioli, E. *Sep Sci Technol* 1995, 30, 1.
4. Chapman, P. D.; Oliveira, T.; Livingston, A. G.; Li, K. *J Membr Sci* 2008, 318, 5.
5. Okamoto, K.; Butsuen, A.; Tsuru, S. *Polym J* 1987, 19, 747.
6. Ishihara, K.; Matsui, K. *J Appl Polym Sci* 1987, 34, 437.
7. Zhan, X.; Li, J. D.; Huang, J. Q.; Chen, C. X. *Chin J Polym Sci* 2009, 27, 533.
8. Kashiwagi, T.; Okada, T.; Okita, K. *J Membr Sci* 1988, 36, 353.
9. Gonzalez-Velasco, J. R.; Lopez-Dehesa, C.; Gonzalez-Marcos, J. A. *J Appl Polym Sci* 2003, 90, 2255.
10. Chang, C. L.; Chang, M. S. *J Membr Sci* 2004, 238, 117.
11. Huang, Y. W.; Fu, J. W.; Pan, Y.; Huang, X. B. *Sep Purif Technol* 2009, 66, 504.
12. Nagase, Y.; Ando, T.; Yun, C. M. *React Funct Polym* 2007, 67, 1252.
13. Long, Y. C.; Chen, X.; Ping, Z. H. *Stud Surf Sci Catal* 1994, 84, 1083.
14. Chen, X.; Ping, Z. H.; Long, Y. C. *J Appl Polym Sci* 1998, 67, 629.
15. Luo, Y.; Tan, S. J.; Wang, H. F.; Wu, W. C. *Eng J* 2008, 137, 496.
16. Takegami, S.; Yamadaa, H.; Tsujii, S. *J Membr Sci* 1992, 75, 93.
17. Kanani, D. M.; Nikhade, B. P.; Balakrishnan, P.; Singh, G.; Pangarkar, V. G. *Ind Eng Chem Res* 2003, 42, 6924.
18. Olsson, J.; Tragardh, G.; Lipnizki, F. *Sep Sci Technol* 2002, 37, 1199.
19. She, M.; Hwang, S. T. *J Membr Sci* 2006, 271, 16.
20. Trifunovic, O.; Tragardh, G. *Sep Purif Technol* 2006, 50, 51.
21. Vane, L. M.; Namboodiri, V. V.; Bowen, T. C. *J Membr Sci* 2008, 308, 230.
22. Zhan, X. *Preparation and Pervaporation Performance of Ethanol Permselective Silicone Membranes*; Tsinghua University: Beijing, 2009; Chapter 2.
23. Chen, J.; Li, J. D.; Lin, Y. Z.; Chen, C. X. *J Appl Polym Sci* 2009, 112, 2425.
24. Li, L.; Xiao, Z. Y.; Tan, S. J.; Pu, L.; Zhang, Z. B. *J Membr Sci* 2004, 243, 177.
25. Yu, Q. J.; Ma, X. H.; Hao, T. T.; Yuan, D. Z. *Acta Polym Sin* 2008, 9, 874.
26. Kulkarni, S. A.; Ogale, S. B.; Vijayamohan, K. P. *J Colloid Interface Sci* 2008, 318, 372.
27. Barton, A. F. M. *Handbook of Solubility Parameters and other Cohesion Parameters*, 2nd ed.; CRC: Boca Raton, FL, 1991.
28. Praptowidodo, V. S. *Chem Eng Sci* 2005, 739, 207.
29. Inui, K.; Tsukamoto, K.; Miyata, T.; Uragami, T. *J Membr Sci* 1998, 138, 67.
30. Jiratananon, R.; Chanachai, A.; Huang, R. Y. M.; Uttapap, D. *J Membr Sci* 2002, 195, 143.
31. Lin, L.; Wang, G.; Qu, H.; Yang, J.; Wang, Y.; Shi, D.; Kong, Y. *J Membr Sci* 2006, 280, 651.
32. Miyata, T.; Iwamoto, T.; Uragami, T. *J Appl Polym Sci* 1994, 51, 2007.