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Pervaporation performance of trifluoroethoxy substituting polyphosphazene membrane for different organic compounds aqueous solutions

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ABSTRACT

A series of phosphazene heteropolymers (NP $(OC_6H_4C_3H_5)_x(OC_6H_5)_y(OCH_2CF_3)_z)_n)$ with different percentages of 2,2,2-trifluoroethoxy groups were synthesized and found to have a high affinity for VOCs through pervaporation experiments and sorption studies. The pervaporation performance of as-prepared membranes for removal of tetrahydrofuran, acetone and ethanol from water was characterized, in order to study the effect of 2,2,2-trifluoroethoxy pendant group on pervaporation performance. The membranes had better selectivity for THF/water and acetone/water (maximum 30.2 and 24.1, respectively) compared with a polydimethylsiloxane membrane. As the content of 2,2,2-trifluoroethoxy group increased, both selectivity and flux was increased for ethanol/water. However, selectivity for THF/water and acetone/water was decreased. The swelling and sorption experiments of polymers, solubility parameter and diffusivity analysis provide insight into the process.

Keywords: Pervaporation performance; Polyphosphazene; Membrane; 2,2,2-Trifluoroethoxy

1. Introduction

The need to remove and recover volatile organic compounds (VOCs) from contaminated media, such as air or water, has steadily grown in importance because of the potential of these compounds to adversely affect human health and the environment. Pervaporation (PV) is very attractive in that VOCs can be selectively removed from the feed. Although the PV separation of many industrial solvents such as alcohols, ketones and esters has been widely studied, few applications have come to an industrial scale. The reason is probably the lack of high performance specific materials and membranes. The separation of each organic solute from aqueous solution requires a specific type of membrane due to the varying nature of the organic solvents employed. Generally, membranes showing high VOC permeabilities and low water permeabilities are required. Polydimethylsiloxane (PDMS) is the most important and promising polymer membrane for VOC-permselective presently [1–10], which has the highest permeability for gas or vapors [11] and a high separation performance for organic chemicals in water [12,13] among all the commercially available polymers. However, PDMS membrane has two intrinsic disadvantages. Its mechanical strength is poor and it is not easy to tailor its chemical structure to further improve the performance of membrane for specific VOCs.

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Polyorganophosphazene (POP) is also an important type of inorganic-organic hybrid polymer that has some similar properties with PDMS, such as inorganic polymer backbone and very low glass transition temperature (T_g) [14]. The low T_g of POP renders the material highly permeable to solvents. Most importantly, compared with PDMS, chemical and physical properties of POPs can be easily tailored by incorporation of various pendant groups [14–16]. Therefore, a POP with high affinity and selectivity toward VOC and good hydrophobicity can be designed and prepared. However, PV performance of POP membranes for VOC/water was studied to a lesser degree. A few studies that were limited to the separation of alcohol/water have been reported. Stewart et al [17,18] synthesized a POP with three pendant groups: 2-(2-methoxyethoxy) ethoxy, 4-methoxyphenoxy, and 2-allylphenoxy. The polymer was prepared into a membrane with 3 μm thickness supported by ceramic membrane. In the separation of 10 wt% aqueous 2-propanol solution by the membrane, the flux is less than 0.1 kg m^{-2} h^{-1} and separation factor is about 7. In the separation of 10 wt% aqueous methanol solution by the membrane, the flux is approximately 0.2 kg m^{-2} h^{-1} and separation factor is nearly 3.8. Roizard et al [19] synthesized a siloxane-phosphazene copolymer membrane. The membrane was used to separate butanol-water solutions. PV flux is less than 0.1 kg m^{-2} h^{-1} and separation factor is 36.

Fluorinated groups generally possess high affinity to VOCs and hydrophobic properties. Allcock et al. have reported the use of fluorinated groups to increase the hydrophobicity of polyphosphazene [20]. Incorporation of fluorinated groups can increase polymer mobility and ensure high diffusivity. Thereby, they are ideal candidate groups for the separation of VOCs/water. In previous work [21], the organophilic PV behavior of poly [bis(2,2,2-trifluoroethoxy)phosphazene, PTFEP] membrane was studied; however, PTFEP membrane did not display acceptable permselectivity toward VOC. Additionally, Sun et al. [22–23] studied the sorption and diffusion behavior of organic vapors in PTFEP. It should be noted that the PTFEP is not cross-linked. Complete substitution with 2,2,2-trifluoroethoxy (TFE) group results in high affinity of polymer to solvent (e.g. ethanol) and significant swelling, which reduces selectivity.

In this work, we have prepared a series of cross-linkable polyphosphazenes with varying amounts of TFE groups, referred to as 2CF polymers. Additionally, we have investigated the PV performance of 2CF membranes for ethanol/water, acetone/water and THF/water mixtures. The effect of TFE content and different VOCs on PV performance was discussed in detail based on the swelling and sorption results, solubility parameters and diffusion data analysis.

2. Experiment

2.1. Materials

Ethanol, acetone, toluene, petroleum ether, tetrabutylammonium bromide and phenol were purchased from Shanghai Chemical Reagents Corp. Sodium hydride (60% dispersion in mineral oil) was purchased from Rohm-Haas Corp. 2,2,2-Trifluoroethanol and 2-allylphenol was purchased from Aldrich Corp. All of them were used without further purification. Tetrahydrofuran (THF, Shanghai Chemical Reagents Corp) was treated with sodium and was then distilled before used. Benzoyl peroxide (Shanghai Chemical Reagents Corp) was purified by several times of precipitation from THF solution to methanol. Nylon microporous membrane (diameter 100 mm, pore size 0.22 μm, thickness 140 μm) was kindly provided by Shanghai Yadong Heji Resin Company.

2.2. Synthesis of 2CFs

Poly (dichlorophosphazene) (PDCP) was synthesized by one step method as described by Carriedo and coworkers [24]. The general preparation process of (NP $(OC_6H_4C_3H_5)_x(OC_6H_5)_y(OCH_2CF_3)_z)_n$, 2CF) polymers was carried out following the reported method. The ratio of the three substituted groups was tailored by the amount of substituents used. In a typical process, a solution of PDCP (3.85 g, 0.033 mol) was made with THF (50 ml) in a three-neck flask. In a separate flask, a solution of 2-allylphenoxide was made from the addition of sodium hydride (0.13 g, 3.2 mmol) to a solution of 2-allylphenol (0.43 g, 3.2 mmol) in 50 ml of THF. The 2-allylphenoxide solution was stirred at room temperature until NaH was completely consumed, approximately 10 min, after which it was added to the PDCP solution. In the third flask, NaH (0.60 g, 0.015 mol) was added to a solution of phenol (1.41 g, 0.014 mol) and 100 ml of THF and the resulting solution was stirred at 40°C for 20 min to ensure complete consumption of the NaH. This solution was then added to the PDCP solution and stirred at 40°C for 12 h. A fourth separate solution was prepared using trifluoroethanol (2.10 g, 0.021 mol) and NaH (0.88 g, 0.022 mol) in 100 ml of THF. This solution was added to the PDCP solution. The final mixture was heated to 40°C for 24 h. Isolation of the polymer was accomplished through precipitation from THF into water and petroleum ether several times. The solid polymer was finally dried in vacuum. Products were isolated in 43%, 55% and 56% yield, respectively, for 2CF-1, 2CF-2 and 2CF-3. ^{1}H NMR ($CDCl_3$) characterization data: δ (ppm) 7.0 (brs), 5.7(brs), 4.8 (brs), 4.1 (brs), 3.2 (brs). ^{31}P NMR ($CDCl_3$) characterization data: δ (ppm) −7.0 (brs), −11.4 (brs),

−12.7 (brs), −16.4 (brs) and −19.0 (brs) ppm. FTIR data: C=C (allyl) 1,641 cm^{-1}; P=N 1,285, 1,255 cm^{-1}; P–O–Ar 1,199, 930 cm^{-1}; CH=CH$_2$ 995, 904 cm^{-1}. P–O–C 1,419, 1,048, 962 cm^{-1}; C–F 1,172 cm^{-1}. Elemental analysis data: C: 2CF-1: 60.9%; H: 5.7%; N: 7.2%; O: 15.7%; Cl: <0.1% (Calculated: C: 61.1%; H: 5.5%; N: 7.0%; O: 16.0%; Cl: 0%). 2CF-2: C 54.5%, H 4.1%, O 16.3%, N 6.8%; Cl: <0.1% (Calculated: C: 54.2%; H: 4.1%; N: 7.0%; O: 16.0%; Cl: 0%). 2CF-3: C 42.2%, H 3.3%, O 16.1%, N 7.0%; Cl: 0.1% (Calculated: C: 42.5%; H: 3.3%; N: 7.8%; O: 15.8%; Cl: 0%).

2.3. Membrane preparation

2CF membranes were prepared as follows: casting solutions were made from toluene with 5 wt.% POPs and 6% benzoyl peroxide (w.r.t. POP) by stirring at 25°C for 5 h and then filtered by cellulose filter paper to remove any particles. Afterwards, the solution was cast on a nylon microporous support membrane. Prior to use, the nylon support was soaked by water and then placed on a glass plate. Excess water on the nylon support surface was wiped off with a filter paper. Afterwards, a glass ring (50 mm diameter, 3 mm thickness) was placed on the nylon support to hold the 2CF solutions. The solutions were covered by glass cover. The toluene solvent was allowed to evaporate completely at ambient temperature leaving defect free thin dense films as discrete layers on the nylon support. Cross-linking was accomplished by heating at 110°C for 1 h.

2.4. Analytical equipments and techniques

^{1}H NMR spectra were obtained from a Varian Mercury Plus-400 NMR spectrometer. Infrared spectra were recorded on a Perkin–Elmer 936 spectrometer. DSC analyses were performed on a PYRIS 1 DSC under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. Molecular weights were determined in DMF solution by a Series 200 with a calibration curve for polystyrene standards. Elemental analysis was conducted on a Perkin Elmer 2400 elemental analyzer.

2.5. Swelling and sorption measurements

Swelling and sorption measurements were used for the determination of swelling degree and sorption data. It was performed through immersion of pre-weighed samples of cross-linked polymer in water, VOC and 5 wt% aqueous VOC solutions, respectively, at 40°C for 5 d in order to ensure equilibrium swelling. The VOCs used in this work were ethanol, acetone and THF. The degree of swelling (DS) and sorption (S %) was calculated by

$$\mathrm{DS} = \frac{W_\mathrm{s} - W_\mathrm{d}}{W_\mathrm{d}}, \tag{1}$$

$$S\% = \frac{W_\mathrm{s} - W_\mathrm{d}}{W_\mathrm{d}} \times 100\%, \tag{2}$$

where W_d and W_i are the weights of the dry and swollen polymer samples, respectively. The uptake liquids were collected in cold trap immersed in liquid nitrogen. The uptake liquid composition was determined by ^{1}H NMR, according to literature precedent [25]. The molar ratio of each component in a mixture was calculated from the ratio of the integrated areas of each corresponding peak. The molar ratios were converted to mass percentages. The weight fractions of VOCs and water of the liquid adsorbed in membrane are represented by z_voc and z_w. The values were obtained by three times repeated experiments. The sorption selectivity (α_s), sorption of VOC (S_voc) and water (S_w) were calculated by following methods:

$$\alpha_S = \frac{z_\mathrm{voc}/z_\mathrm{w}}{x_\mathrm{voc}/x_\mathrm{w}}, \tag{3}$$

$$S_\mathrm{voc} = S \times z_\mathrm{voc}, \tag{4}$$

$$S_\mathrm{w} = S \times z_\mathrm{w}, \tag{5}$$

x_voc and x_w are the weight compositions of VOCs and water in feed solution, respectively. The weight compositions of VOCs in membrane (z'_voc) can be calculated by

$$z'_\mathrm{VOC} = \frac{z_\mathrm{VOC} \times \mathrm{DS}}{1 + \mathrm{DS}}. \tag{6}$$

2.5 PV experiments

PV experiments were carried out using the set-up shown schematically in Figure 1. The effective area of membrane was 23.8 cm^2. Permeate was collected in cold traps that were immersed in liquid nitrogen. To achieve a steady-state condition at a given temperature, the experiment was run for 2 h prior to collection of the permeate. The feed solutions studied were aqueous ethanol, acetone and THF solutions. The feed concentration were predetermined from 2% to 8% (wt %). The concentrations in the feed and the permeates were determined by ^{1}H NMR. PV experiments were carried out respectively at temperature of 30, 40 and 50°C. Downstream pressure was kept at 10 mmHg. Membrane performance is characterized by permeability and selectivity, in terms of permeation flux and

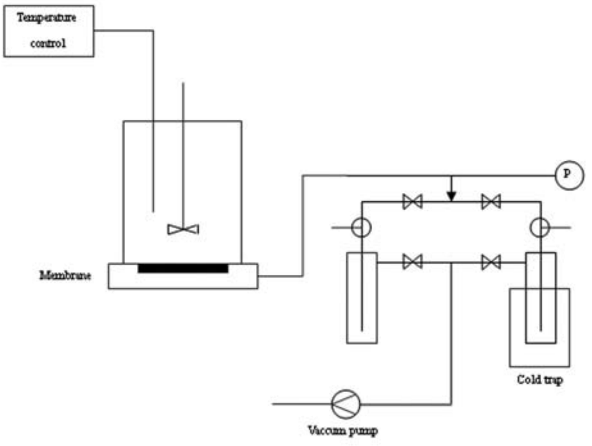

Fig. 1. Schematic diagram of the pervapoation experimental setup.

separation factors, respectively. Permeation flux is defined by the following equation:

$$J = \frac{Q}{At}, \tag{7}$$

where J, Q, A, t are permeation flux (g m^{-2} h^{-1}), total amount of permeate (g), membrane area (m^2), operating time (h), respectively. The membrane selectivity for this binary system is expressed in terms of the separation factor, α, defined as the concentration ratio in the permeate divided by the concentration ratio in the feed:

$$\alpha = \frac{y_{VOC}/y_W}{x_{VOC}/x_W}, \tag{8}$$

y_W, y_{VOC} are weight fractions of water and VOC in the permeate side, and x_W, x_{VOC} are the weight fractions of water and VOC in the feed side.

The diffusion coefficients of VOC and water in membrane were calculated by

$$J_{VOC}^{diff} = \frac{z'_{VOC}(1+(1/r))}{\ln\left[1/\left(1-z'_{VOC}(1+(1/r))\right)\right]} J_{VOC}, \tag{9}$$

$$J_W^{diff} = \frac{z'_W(1+r)}{\ln\left[1/\left(1-z'_W(1+r)\right)\right]} J_W, \tag{10}$$

where r is the ratio of the observed mass flux between VOC and Water, J_{voc} and J_w are, respectively, the flux of VOCs and water. The diffusion coefficient ($\bar{D}$) was then calculated according to Fick's law.

$$J_i^{diff} = \bar{D}\rho \frac{d_{w_i}}{d_x} \approx \bar{D}\rho \frac{z'_i}{l}, \tag{11}$$

where ρ is the density of membrane and l is the thickness of membrane.

The calculation of $\bar{D}$ was described in literature [26]. The diffusion selectivity (α_D) can be calculated by:

$$\alpha_D = \alpha/\alpha_S. \tag{12}$$

3. Results and discussions

3.1. Polymer properties and membrane preparation

Table 1 summarizes the relative ratios of pendant groups on the 2CFs, molecular weight and glass transition temperatures (T_g) of 2CFs. The percentages of TFE group on the backbone are 32%, 45% and 68%, respectively, which were calculated by intensity ratio of peaks of the pendant groups in ^{1}H NMR spectra. The polymers are sequentially called 2CF-1, 2CF-2 and 2CF-3. The introduction of TFE group gives rise to lowered glass transition temperature and increased chain flexibility. The molecular weights of three 2CFs are between 1.3×10^5 to 1.7×10^5 g mol^{-1} and in addition, the 2CFs possess good film forming properties. The cross-linking of all membranes was completed by thermal curing at 110°C for 1 h. The membrane thicknesses were approximately 25 μm. PDMS membranes were prepared by the method described in reports [9,10] (using a weight ratio of PDMS to cross-linker of 10:1).

3.2. Swelling and sorption studies

Polymer swelling bears a direct relationship with permeation flux and selectivity. The sorption of VOC

Table 1
Names, structure, molecular weight and T_g of 2CFs

2CFs	Percentage of 2-allylphenoxy (%)	Percentage of phenoxy (%)	Percentage of TFE (%)	M_n (g/mol)	T_g (°C)
2CF-1	12	56	32	132,000	−24.0
2CF-2	10	45	45	143,000	−34.3
2CF-3	10	22	68	173,000	−45.1

Table 2
Swell behavior of 2CFs in water, ethanol, acetone and THF and their aqueous solutions

Solvent	Swelling degrees of materials			
	2CF-1	2CF-2	2CF-3	PDMS
Water	0.66	0.73	0.84	0.007
Ethanol	1.43	1.65	2.37	0.056
Acetone	2.15	2.91	3.48	0.108
THF	5.81	5.91	5.87	1.47
Water–ethanol (5 wt.%)	0.80	0.98	1.14	–
Water–acetone (5 wt.%)	1.09	1.72	2.57	–
Water–THF (5 wt.%)	1.24	2.76	4.22	–

solutions increases along with increase of the swelling degree (see Eq (1) and (2)). On the other hand, the chain mobility and free volume of polymer [27,28], which influence the diffusion coefficient of solvent, also increase with increasing swelling degree. However, this in turn, will sacrifice selectivity of membranes if VOC has strong interaction with water. The affinity of a membrane to water could be enhanced with increasing the amount of VOC absorbed into membrane. That is to say, the partial flux of water could increase in spite of the decrease in water content in the feed mixture, and thus reducing selectivity. This special interaction between permeate molecules is called ''coupling effect'' [29]. Therefore, polymer swelling generally results in increased permeation flux and decreased selectivity.

In our experiments, swelling was carried on for enough time (5 d) to assure swelling equilibrium was achieved. Therefore, only the affinity between polymers and permeating molecules, the thermodynamic factor, determines the ultimate swelling degree and sorption data. Moreover, the effect of cross-linking degree on swelling degree in our case is negligible because 2CFs have a similar content of allyl group and cross-linking time and the experimental temperature was the same.

Table 2 shows swelling degrees of all 2CFs immersed in water, VOCs and their aqueous solutions at 40°C. The lowest swelling degrees were recorded for water, e.g. ≤ 1 regardless of the polymer tested. These values were significantly higher than PDMS. This observation could be ascribed to the polarity of the polyphosphazene backbone and the P–O bond. The comparison of the three 2CFs lead to the conclusion that the higher content of TFE group, the higher the swelling degrees in water (from 2CF-1 to 2CF-3 the swelling degree increases from 0.66 to 0.84).

In the cases of ethanol and acetone sorption, the increased content of TFE group leads to increased sorption, due to the higher affinity. PDMS membranes exhibited much lower acetone and ethanol sorption values as compared with the 2CF membranes. In the case of THF sorption, because 2CFs are soluble in THF, all membranes significantly swell (the swelling degrees are, respectively, 5.81, 5.91 and 5.87), and thus the differences of swelling degree and sorption value are not obvious. The THF sorption value of PDMS is much higher than the acetone and ethanol values. However, it is still lower as compared with the 2CF membranes.

Table 3
Sorption data of aqueous VOCsolutions in 2CF membranes

Water-VOC (95:5)	Sorption results	2CF membranes		
		2CF-1	2CF-2	2CF-3
EtOH	z_{voc}	0.11	0.22	0.26
	z_{w}	0.89	0.78	0.74
	S_{voc} (%)	8.8	21	30
	S_{w} (%)	71	76	84
	z'_{voc}	0.049	0.11	0.14
Acetone	z_{voc}	0.48	0.51	0.50
	z_{w}	0.52	0.49	0.50
	S_{voc} (%)	52	88	128
	S_{w} (%)	57	85	128
	z'_{voc}	0.25	0.32	0.36
THF	z_{voc}	0.54	0.59	0.52
	z_{w}	0.46	0.41	0.48
	S_{voc} (%)	67	163	219
	S_{w} (%)	57	113	202
	z'_{voc}	0.30	0.43	0.42

Swelling experiments in aqueous solutions of VOCs also shows direct relation with the content of TFE group. From 2CF-1 to 2CF-3, the swelling degrees in aqueous THF, acetone and ethanol solution, respectively, increase from 1.24 to 4.22, 1.09 to 2.57, and 0.80 to 1.14. The sorption behavior of VOCs is analyzed based on z_{voc} and S_{voc} (see Table 3). As TFE content increases, all S_{voc} increase, indicating that TFE moiety renders good affinity to the three VOCs. The z_{voc} and S_{voc} of THF are highest among the three VOCs, indicating that the 2CF membranes have highest affinity and selectivity to THF. The result that z_{voc} for acetone and THF decreases from 2CF-2 to 2CF-3 and the S_{w} increases from 2CF-1 to 2CF-3 is correlated to coupling effect. The S_{w} for ethanol/water mixture is much higher than S_{voc}, which might be responsible for the lowest selectivity for ethanol.

3.3. Hansen solubility parameter

The affinity between 2CFs and VOCs was investigated in more detail by the use of Hansen solubility parameters for the 2CF membranes and VOCs. The

Table 4
Hansen solubility parameters of different solvents

Solvents	δ_d	δ_p	δ_h	δ_t
Ethanol	15.8	8.8	19.4	26.5
Acetone	15.5	10.4	7	20.1
THF	16.8	5.7	8.0	19.4
Water	15.6	16.0	42.3	47.8

total Hansen parameter, δ_t, consists of three parts: δ_d, the dispersion component; δ_P, the polar component; and δ_h, the hydrogen-bonding component. The Hansen solubility parameters of the VOCs and water are listed in Table 4 [30]. The order of hydrogen bond strength is water>ethanol>THF>acetone, and water>acetone> ethanol>THF for polarity. The Hansen solubility parameters of each 2CF membrane (Table 5) were calculated from the Hansen solubility parameters and the volume ratios of the pendant groups, based on the atomic group contribution method [17,30]. The differences in the parameters of polymer and acetone, ethanol and THF, namely Δ_{ethanol}, Δ_{acetone}, and Δ_{THF}, respectively, were calculated using following equations:

$$\Delta_{\text{ethanol}} = \Big[\left(\delta_{\text{polymer,d}} - \delta_{\text{ethanol,d}}\right)^2 + \left(\delta_{\text{polymer,p}} - \delta_{\text{ethanol,p}}\right)^2 + \left(\delta_{\text{polymer,h}} - \delta_{\text{ethanol,h}}\right)^2\Big]^{1/2}, \tag{13}$$

$$\Delta_{\text{acetone}} = \Big[\left(\delta_{\text{polymer,d}} - \delta_{\text{acetone,d}}\right)^2 + \left(\delta_{\text{polymer,p}} - \delta_{\text{acetone,p}}\right)^2 + \left(\delta_{\text{polymer,h}} - \delta_{\text{acetone,h}}\right)^2\Big]^{1/2}, \tag{14}$$

$$\Delta_{\text{THF}} = \Big[\left(\delta_{\text{polymer,d}} - \delta_{\text{THF,d}}\right)^2 + \left(\delta_{\text{polymer,p}} - \delta_{\text{THF,p}}\right)^2 + \left(\delta_{\text{polymer,h}} - \delta_{\text{THF,h}}\right)^2\Big]^{1/2}, \tag{15}$$

where δ_{polymer} and δ_{solvent} are the total solubility parameter of polymer and solvent, A smaller Δ means the stronger affinity between 2CF membranes and solvent.

Table 5
Solubility parameters of 2CFs, PDMS and the differences in solubility parameter between polymer material and solvents

	Calculation results for different materials			
Parameters	2CF-1	2CF-2	2CF-3	PDMS
δ_d	20.3	20.3	20.2	15.9
δ_p	6.1	6.3	6.8	0.4
δ_h	6.0	6.0	6.4	4.7
δ_t	22.0	22.1	22.2	16.5
Δ_{water}	37.9	37.9	37.3	40.7
Δ_{ethanol}	14.4	14.4	13.9	16.9
Δ_{acetone}	6.5	6.4	6.0	10.3
Δ_{THF}	4.1	4.1	4.0	5.5

The calculation results reveal that the Hansen solubility parameters of 2CFs are higher than that of PDMS. For 2CFs, the Δ_{water} are much higher than Δ_{acetone}, Δ_{ethanol} and Δ_{THF}, in addition, $\Delta_{\text{THF}} < \Delta_{\text{acetone}} < \Delta_{\text{ethanol}}$, which are consistent with the results that 2CF membranes have high sorption for the VOCs, especially for THF. Δ_{acetone} and Δ_{ethanol} of PDMS are much higher than that of 2CFs, indicating much lower affinity of PDMS for ethanol and acetone. Δ_{THF} of PDMS is low (5.5) and slightly higher than that of 2CFs. Therefore, VOC sorption in PDMS is lower than that in 2CFs. Moreover, it can be found that Δ_{water}, Δ_{ethanol}, Δ_{acetone} and Δ_{THF} slightly decrease with the increase in TFE content. It was described [31,32] that only a little difference in solubility parameter can correlate to a large difference in solubility property between materials. Therefore, the increase of swelling degree in water and VOC with increasing the TFE content is reasonable.

3.4. PV performance

3.4.1. Effect of TFE content on PV for different VOCs

Table 6 presents the separation performance for 2CF-1, 2CF-2 and 2CF-3 membranes. For the three aqueous VOCs solutions (5 wt.%), 2CF membranes show an increase of VOCs, water and total flux with increasing TFE content. It was due to the increase in diffusion coefficient and sorption of both VOCs and water (see Tables 3 and 6), which can be explained by the effect of swelling on polymer free volume and the coupling effect, respectively. Additionally, from 2CF-1 to 2CF-3, the flux for aqueous ethanol, acetone and THF solutions display increases of 128, 311, and 435 g m^{-2} h^{-1}. The highest increase of permeation flux for THF/water corresponds to the highest sorption and diffusion data for THF solution, which is attributed to extremely high affinity of polymer to THF.

Although it results in the increase in α_s, the increase in TFE content leads to the reduction of α value, which is presumably due to the decrease in α_D value. The reduction in α_D value was as a result of that D_w increase more compared with D_{voc}, with the increase of polarity and free volume of polymer. The higher sorption selectivity for THF and acetone is responsible for the higher

Table 6
PV performance of 2CF membranes for 5 wt.% aqueous VOCsolutions

Water-VOC (95:5)	PV results	Polymer membranes			
		PDMS	2CF-1	2CF-2	2CF-3
EtOH	J (g m^{-2} h^{-1})	195	145	210	273
	J_{voc} (g m^{-2} h^{-1})	59	29	55	79
	J_{w} (g m^{-2} h^{-1})	136	126	155	194
	D_{voc} (10^{-8} cm^2/s)		1.54	2.68	2.87
	D_{w} (10^{-8} cm^2/s)		1.91	1.98	2.36
	α_{S}		2.35	5.36	6.68
	α_{D}		2	1.25	1.18
	α	8.0	4.7	6.7	7.9
Acetone	J (g m^{-2} h^{-1})	423	201	362	512
	J_{voc} (g m^{-2} h^{-1})	206	112	187	249
	J_{w} (g m^{-2} h^{-1})	217	89	175	263
	D_{voc} (10^{-8} cm^2/s)		2.34	2.60	2.64
	D_{w} (10^{-8} cm^2/s)		1.47	2.42	2.95
	α_{S}		17.5	19.8	19
	α_{D}		1.38	1.03	0.95
	α	18.0	24.1	20.4	18
THF	J (g m^{-2} h^{-1})	595	217	410	653
	J_{voc} (g m^{-2} h^{-1})	327	132	236	338
	J_{w} (g m^{-2} h^{-1})	268	85	274	315
	D_{voc} (10^{-8} cm^2/s)		2.22	2.54	2.72
	D_{w} (10^{-8} cm^2/s)		1.45	2.24	2.77
	α_{S}		22.3	27.3	20.6
	α_{D}		1.35	0.94	0.99
	α	23.4	30.2	25.8	20.4

total selectivity. The effect of TFE content on sorption selectivity for ethanol is greater as compared to acetone and THF. In aqueous ethanol solution, the swelling degrees for the 2CFs membranes were low (<1) and the differences between the membranes was also low (from 0.80 to 1.14) with increasing TFE content, the coupling effect was presumed to be low, which increased sorption selectivity.

3.4.2. Comparison of PV performance

The PV performance of PDMS for ethanol/water, THF/water and acetone/water are presented (see Table 6), in order to compare with the 2CF membranes. It can be seen that for ethanol/water, 2CF-1 and 2CF-2 membranes show lower separation factors (respectively 4.7 and 6.1) but 2CF-3 membrane shows comparable separation factor (7.9) with PDMS (about 8.0). Further, 2CF membranes except 2CF-1 show slightly higher flux than PDMS.

For acetone/water and THF/water, the selectivity for acetone of PDMS and 2CF-1 are 18 and 24.1, respectively. The selectivity for THF of PDMS and 2CF-1 are 23.4 and 30.2, respectively. Thus, the 2CF-1 membrane shows higher separation performance for THF/water and acetone/water than PDMS. The higher separation factor for acetone can be explained as higher affinity of 2CF membranes to acetone and their lower swelling degree. The separation factor of PDMS for THF is relatively low, although PDMS membrane has high sorption of THF but greatly low sorption of water (0.7%). The lower selectivity could be due to the fact that water can permeate through PDMS membrane which has high chain mobility, as reflected in a lower T_g as compared to the 2CF polymers. Additionally, only the 2CF-3 membrane shows higher flux than PDMS for water-acetone and water-THF mixtures.

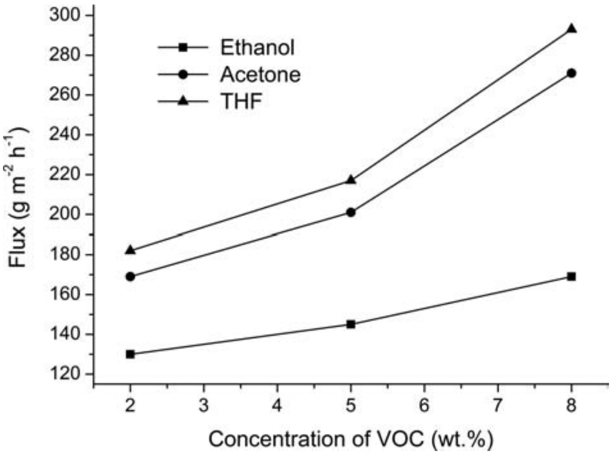

Fig. 2. The effect of VOC concentration on the permeation flux of 2CF-1 membranes for aqueous VOCs solutions at 40°C.

3.4.3. Concentration and temperature effect on PV

PV performance of POPs membrane was assessed using varying temperatures and compositions of VOCs in the feed. Fig. 2 shows the typical results of the total flux of 2CF-1 membrane with 2, 5 and 8 wt.% aqueous VOC solutions. The permeation flux increases with increasing VOC concentration. The increase in VOC concentration leads to an increase in VOC sorption into the membrane, and as a result, the membrane becomes more swollen. Swelling of polymers further improves the mobility of segments of the rubbery 2CF polymer. Thus, the permeation flux of both VOC and water slightly increase. Separation factors at 2, 5 and 8 wt.% VOCs concentration are plotted in Fig. 3. Separation factor of the 2CF-1 membrane decreases with the increase in feed VOC fractions. Above phenomenon is consistent with the intrinsic trade-off relationship between permeation flux and selectivity that is typically observed in polymeric membranes.

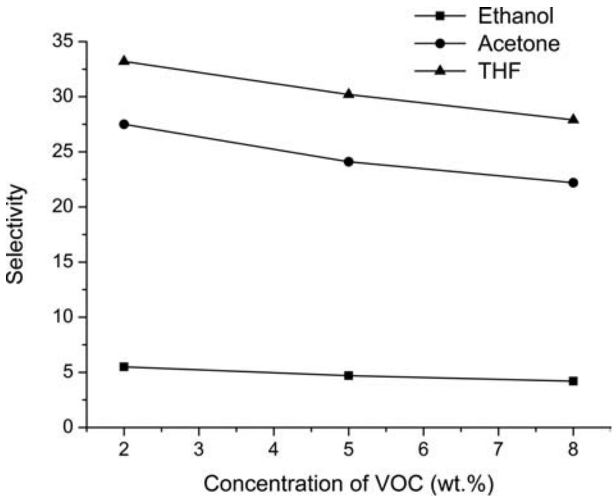

Fig. 3. The effect of VOC concentration on the selectivity of 2CF-1 membranes for aqueous VOCs solutions at 40°C.

Fig. 4 presents the effect of temperature on PV flux of 5 wt.% aqueous VOC solutions through a 2CF-1 membrane. The increase in the feed temperature from 30 to 50°C results in an increase in the total fluxes. Additionally, it can be seen that for ethanol/water, the total flux seems to exhibit a simple linear correlation with temperature. However, for acetone/water and THF/water, the total flux increase appears more exponential with increasing temperature. Fig. 5 reveals the effect of temperature on separation factors for the 2CF-1 membrane. The separation factor for THF/water and acetone/water increases and for ethanol/water it is unchanged with increasing temperature. A similar trend of selectivity with temperature was reported by Li et al. [9] and Molina et al. [1]. Both found that the separation factor for ethanol increased as temperature increased. The effect of temperature was influenced by many factors: such as different VOCs, polymers and support membranes. In order to clarify this, further studies based on the change of partition and diffusion coefficients with temperature are on-going.

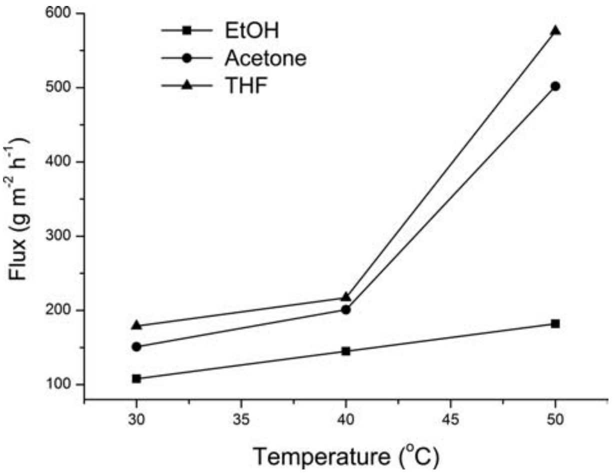

Fig. 4. The effect of temperature on the permeation flux of 2CF-1 membranes for 5 wt.% aqueous VOCs solutions.

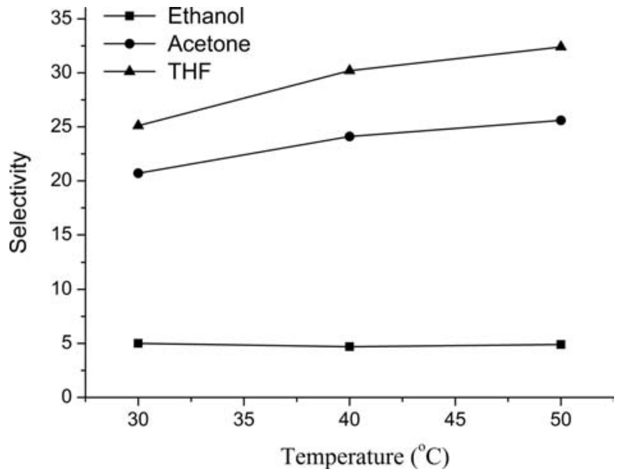

Fig. 5. The effect of temperature on the selectivity of 2CF-1 membranes for 5 wt.% aqueous VOCs solutions.

3.4.4. The effect of cross-linking on PV results

Table 7 presents the effect of cross-linking on PV performance. After cross-linking, the permeation flux for all the VOCs decrease, but the permselectivity increases. This result accords with trade-off relationship and can be explained by the fact that cross-linking can reduce the swelling of polymer and sorption of VOCs. The decrease in VOCs sorption will lead to the reduction of interaction of swelled polymer with water, and thus negating much of the coupling effect on permselectivity.

4. Conclusion

Three 2CFs membranes with different percentages of TFE group on the backbone were prepared for the investigation of sorption and PV performance for different aqueous VOC solutions. The 2CF membranes displayed better selectivity toward THF and acetone and comparable selectivity toward ethanol as compared to PDMS, which is presumably due to the high sorption selectivity of 2CF membranes.

With increases in TFE content, the membranes displayed higher sorption and sorption selectivity toward the VOCs which is due to the introduction of TFE

Table 7
PV results of uncross-linked and cross-linked 2CF-1 membrane for different aqueous VOCs solutions

	Water-ethanol (95:5)		Water-acetone (95:5)		Water-THF (95:5)	
Membranes	Flux (g m^{-2} h^{-1})	Selectivity	Flux (g m^{-2} h^{-1})	Selectivity	Flux (g m^{-2} h^{-1})	Selectivity
Uncross-linked 2CF-1	330	3.8	406	19.7	508	22.5
Cross-linked 2CF-1	145	4.7	217	24.1	201	30.2

group, which was described by solubility parameter analysis. The increase in TFE content leads to the increase of permeation flux but the decrease of selectivity for acetone/water and THF/water, which is due to the reduction of diffusion selectivity. However, for ethanol/water, increases in both permeate flux and selectivity were observed with an increase of TFE content. Differing swelling and PV behaviors for the various VOC solutions is attributed to the varying coupling effect between VOCs and water. Ultimately, performance depends on the interaction between VOCs and water.

Reference

[1] J.M. Molina, G. Vatai and E.B. Molnar, Comparison of pervaporation of different alcohols from water on CMG-OM-010 and SULZER membranes, Desalination, 149 (2002) 89.

[2] S. Mishima and T. Nakagawa, The behavior of solute organic compounds and water in poly(dimethylsiloxane), J. Appl. Polym. Sci., 78 (2000) 1304–1311.

[3] C.L. Chang and P.Y. Chang, Performance enhancement of silicone/PVDF composite membranes for pervaporation by reducing cross-linking density of the active silicone layer, Desalination, 192 (2006) 241–245.

[4] R. Muzzalupo, G.A. Ranier, G. Golemme and E. Drioli, Self-diffusion measurements of organic molecules in PDMS and water in sodium alginate membranes, J. Appl. Polym. Sci., 74 (1999) 1119–1128.

[5] C. Dotremont, S. Goethaert, and C. Vandecasteele, Pervaporation behaviour of chlorinated hydrocarbons through organophilic membranes, Desalination, 91 (1993) 177–186.

[6] S.J. Lue, S.F. Wang, L.D. Wang, W.W. Chen, K.M. Du and S.Y. Wu, Diffusion of multicomponent vapors in a poly(dimethyl siloxane) membrane, Desalination, 233 (2008) 277–285.

[7] H.J. Kim, S.S. Nah and B.R. Min, A new technique for preparation of PDMS pervaporation membrane for VOC removal, Adv. Environ. Res., 6 (2002) 255–264.

[8] M. Bennett, B.J. Brisdon, R. England and R.W. Field, Performance of PDMS and organofunctionalised PDMS membranes for the pervaporative recovery of organics from aqueous streams, J. Membr. Sci., 137 (1997) 63–88.

[9] L. Li, Z.Y. Xiao, S.J. Tan, L. Pa and 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.

[10] F.J. Xiangli, Y.W. Chen, W.Q. Jin and N.P. Xu, Polydimethylsiloxane (PDMS)/ceramic composite membrane with high flux for pervaporation of ethanol-water mixtures, Ind. Eng. Chem. Res., 46 (2007) 2224–2230.

[11] S.A. Stern, Y. Mi, H. Yammamoto and A.K.St. Clair, Structure/permeability relationships of polyimide membranes. Applications to the separation of gas mixtures, J. Polym. Sci: Part B: Polym. Phys., 27 (1989) 1887–1909.

[12] T. Miyata, Y. Nakanishi and T. Uragami, Ethanol permselectivity of poly(dimethylsiloxane) membranes controlled by simple surface modifications using polymer additives, Macromolecules, 30 (1997) 5563–5565.

[13] J. Miyata, O.H. Higuchi and T. Uragami, Preparation of polydimethylsiloxane/polystyrene interpenetrating polymer network membranes and permeation of aqueous ethanol solutions through the membranes by pervaporation, J. Appl. Polym. Sci., 61 (1996) 1315–1324.

[14] M. Gleria1 and R.D. Jaeger, Polyphosphazenes: A Review, Top. Curr. Chem., 250 (2005) 165–251.

[15] P. Potin and R. De Jaeger, Polyphosphazenes: synthesis, structures, properties, applications, Eur. Polym. J., 27 (1991) 341–348.

[16] H. R. Allcock, Chemistry and applications of polyphosphazenes. Hoboken:Wiley; 2003.

[17] C.J. Orme, F.F. Stewart, M.K. Harrup, J.D. McCoy and D.H. Weinkauf, Pervaporation of water–dye, alcohol–dye, and water–alcohol mixtures using a polyphosphazene membrane, J. Membr. Sci., 197 (2002) 89–101.

[18] F.F. Stewart, M.K. Harrup, T.A. Luther, C.J. Orme and R.P. Lash, Formation of pervaporation membranes from polyphosphazenes having hydrophilic and hydrophobic pendant groups: Synthesis and characterization, J. Appl. Polym. Sci., 80 (2001) 422–431.

[19] D. Roizard, R. Clement, P. Lochon, J. Kerres and G. Eigenberger, Synthesis, characterization and transport properties of a new siloxane-phosphazene copolymer. Extraction of n-butanol from water by pervaporation. J. Membr. Sci., 113 (1996) 151–160.

[20] H.R Allcock, L.B. Steely and A. Singh, Hydrophobic and superhydrophobic surfaces from polyphosphazenes, Polym, Inter., 55 (2006) 621–625.

[21] F. Suzuki, K. Onozato and H. Yaegashi, Pervaporation of organic solvents by poly[bis(2,2,2-trifluoroethoxy)phosphazene] membrane, J. Appl. Polym. Sci., 34 (1987) 2197–2204.

[22] Y.M. Sun, C.H. Wu and A. Lin, Permeation and sorption properties of benzene, cyclohexane, and n-hexane vapors in poly[-bis(2,2,2-trifluoroethoxy)phosphazene] (PTFEP) membranes, Polymer, 47 (2006) 602–610.

[23] Y.M. Sun, C.L. Lin, Y.K. Chen and C.H. Wu, Sorption and diffusion of organic vapors in poly[bis(trifluoroethoxy)phosphazene] and poly[bis(phenoxy)phosphazene] membranes, J Membr. Sci., 134 (1997) 117–126.

[24] G.A. Carriedo, G. Alonso, F.J. Gomez-Elipe, P.J.I. Fidalgo, G. lvarez and J.L.A. Presa-Soto, A simplified and convenient laboratory-scale preparation of 14N or 15N high molecular weight poly(dichlorophosphazene) directly from PCl_5, Chem. Eur. J., 9 (2003) 3833–3836.

[25] S.C. Huang, I.J. Ball and R.B. Kaner, Polyaniline membranes for pervaporation of carboxylic acids and water, Macromolecules, 31 (1998) 5456–5464.

[26] H.D. Kamaruddin and W.J. Koros, Some observations about the application of Fick's first law for membrane separation of multicomponent mixtures, J Membr Sci., 135 (1997) 147–159.

[27] L. Bueso, M. Osorio-Galindo, I. Alcaina-Miranda and A. Ribes-Greus, Swelling behavior of pervaporation membranes in ethanol-water mixtures, J. Appl. Polym. Sci., 75 (2000) 1424–1433.

[28] R. Muzzalup, G.A. Ranieri, G. Golemme and E. Drioli, Self-diffusion measurements of organic molecules in PDMS and

water in sodium alginate membranes, J. Appl. Polym. Sci., 74 (2009) 1119–1128.

[29] M. Khayet, C. Cojocaru and G. Zakrzewska-Trznadel, Studies on pervaporation separation of acetone, acetonitrile and ethanol from aqueous solutions. Sep. Purif. Technol., 63 (2008) 303–310.

[30] D.W. Van krevelen, In Properties of Polymers: Their Estimation and Correlation with Chemical Structure; Elsevier Science B.V, Amsterdam. Part VII, 1997, pp. 761–845.

[31] J.H. Kim, S.B. Lee and S.Y. Kim, Incorporation effects of fluorinated side groups into polyimide membranes on their physical and gas permeation properties, J. Appl. Polym. Sci., 77 (2000) 2756–2767.

[32] C. Bas, R. Mercier, J. Sanchez-Marcano, S. Neyertz, N.D. Alberola and E. Pinel, Copolyimides containing alicyclic and fluorinated groups: Solubility and gas separation properties, J. Polym. Sci.: Part B: Polym. Phys., 43 (2005) 2413–2426.