

Sorption and Diffusion of Volatile Organic Compounds in Fluoroalkyl Methacrylate-Grafted PDMS Membrane

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Received 5 November 1998; accepted 1 July 1999

ABSTRACT: Pervaporation is known as an excellent method for the purification of contaminated water, the extraction of aroma compounds, etc., and has been widely studied. The prediction of permeation is important for treatment, extraction, and quantitative analysis. To predict permeation, a solution–diffusion mechanism is proposed. The octanol–water partition coefficient (Pow) has been generally used in expressing hydrophobicity. The hydrophobicity, Pow , is closely related to the solubility of organic compounds. Also, the molecular volume is closely related to the diffusion of organic compounds. In this study, we improved polydimethylsiloxane (PDMS) membranes by plasma grafting of fluoroalkyl methacrylates (FALMA) to enhance the affinity of PDMS to volatile organic compounds (VOCs). Furthermore, we investigated the pervaporation through the plasma-grafted PDMS membrane and the PDMS membrane and the solution–diffusion mechanism of various VOCs. The permselectivity of tetrachloroethylene (PCE) and toluene determined by the sorption and the diffusion characteristics permeating in the membrane was high. Because the molecular volume of the VOCs is greater than that of water and the permeates quickly penetrate in rubbery membranes like PDMS, permselectivity was not affected by the diffusivity. Solubility significantly affected the permselectivity during pervaporation through a hydrophobic rubbery membrane. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 773–783, 2000

Key words: volatile organic compounds; fluoroalkyl methacrylate-grafted PDMS membrane; permselectivity; sorption, diffusion

INTRODUCTION

Volatile organic compounds (VOCs) have been considered toxic in the human body. Recently, a problem was found in that ground water and soil have been contaminated with VOCs. Ways of purifying the ground water and waste water, which are contaminated by chlorinated hydrocarbons, aeration, adsorption, and steam stripping, etc., have been studied.^{1,2}

Recently, pervaporation has gained widespread acceptance by the chemical industries as an effective process method for the separation and recovery of liquid mixtures.^{3–6} The pervaporation membrane–separation technique is a fractionation process which uses a dense polymeric membrane as a separation barrier between the liquid feed and the permeate vapor. The pervaporation–separation process is potentially useful when distillation is difficult to use, such as with fractionation of azeotropic mixtures, close boiling components, thermal decomposition, and isomeric mixtures, because of its energy-saving features.^{7–12} Therefore, pervaporation is of growing interest for industrial applications. Pervapora-

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Journal of Applied Polymer Science, Vol. 75, 773–783 (2000)

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CCC 0021-8995/00/060773-11

Table I Physicochemical Properties of VOCs

Compound	Abbreviation	Formula	Molecular Weight	Solubility in Water at 20°C (wt %)
Trichloroethylene	TCE	CHCl=CCl ₂	131.39	0.11
Tetrachloroethylene	PCE ^a	CCl ₂ =CCl ₂	165.83	0.015
Benzene		C ₆ H ₆	78.11	0.181
Toluene		C ₆ H ₅ CH ₃	92.13	0.047
Ethyl butanoate	EBU	CH ₃ (CH ₂) ₂ COOCH ₂ CH ₃	116.16	0.68
Ethyl benzoate	EBZ	C ₆ H ₅ COOCH ₂ CH ₃	150.2	0.08

^a The another name of tetrachloroethylene is perchloroethylene.

tion has been known as the superior method when applied to the purification of contaminated water and the extraction of aroma compounds, etc., and has been widely studied.^{3–13} The pervaporation membrane–separation technique can be applied to other various uses.

The quantitative analysis method for VOCs is an area of study. For the pervaporation membranes, the application of quantitative analysis is appropriate when the relationship between the feed concentration and the permeate concentration is observed to be linear. In that case, the feed concentration is able to be introduced from the permeate concentration.

The prediction of permeation is important for treatment, extraction, and quantitative analysis. To account for the permeation through a nonporous membrane, a solution–diffusion mechanism is important factor. For predicting permeation, a solution–diffusion mechanism is proposed and has been studied.^{14–19}

The need for hydrophobicity data in the studies of organic compounds can be traced back at least to the turn of the century. The hydrophobicity is used to indicate the physical property of the molecule which governs its partitioning into the nonaqueous portion of an immiscible or partially immiscible solvent pair.²⁰

According to Nernst,²⁰ the partition coefficient can be simply described as

$$P = C_o/C_w \text{ or } \log P = \log C_o - \log C_w \quad (1)$$

where C_o and C_w represent the molar concentrations of the partitioned compound in the organic and aqueous phases, respectively. The octanol–water partition coefficient (P_{ow}) has been generally used in expressing hydrophobicity. The hydrophobicity, P_{ow} , is closely related to the solubility of organic compounds.²¹ Also, the molecular

volume is closely related to the diffusivity of organic compounds. The molecular volume is important for the diffusivity of the permeability.

Polydimethylsiloxane (PDMS) is well known as an excellent polymer membrane material based on its high permeability to gases and liquids.²² It is desirable to enhance the selectivity of PDMS for VOCs, which has been studied.^{23–28} Also, fluorinated polymers have been studied as organic compounds due to their hydrophobicity based on their low surface energy.^{29–31}

In this study, we improved the PDMS membranes by the plasma-grafting of fluoroalkyl methacrylates (FALMA) to enhance the affinity of PDMS to VOCs. Furthermore, we investigated the pervaporation through the plasma-grafted PDMS membrane and the PDMS membrane and the solution–diffusion mechanism for various VOCs.

EXPERIMENTAL

Materials

Commercial PDMS membranes (Fuji Systems Corp., Tokyo, Japan), 50- μ m thick, were used throughout this work. 1H,1H,9H-hexadecafluorononyl methacrylate (HDFNMA); Daikin Fine Chemical Laboratory Corp., Tokyo, Japan) was used as received to avoid homopolymerization. Trichloroethylene (TCE), tetrachloroethylene (perchloroethylene, PCE), benzene, toluene, ethyl butanoate (EBU), ethyl benzene (EBZ), and acetone (special grade, Wako Pure Chemical Industries, Ltd., Tokyo, Japan) were used as received. The physicochemical properties of VOCs used in this study are shown in Table I.

Graft Polymerization of HDFNMA by Plasma

The plasma graft polymerization was performed as reported by Ihm and Ihm³² and Hiritsu,³³ and

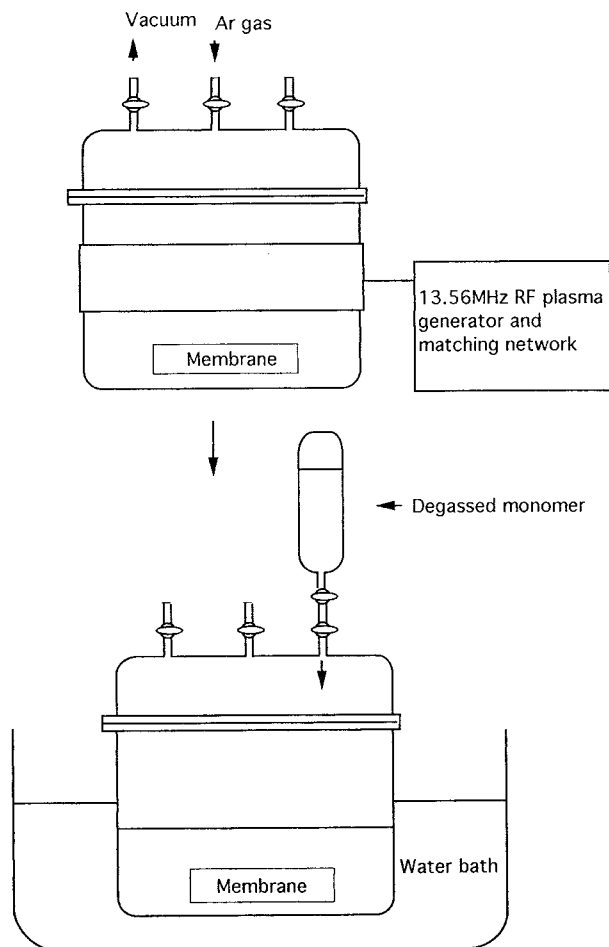


Figure 1 Apparatus for the graft polymerization by plasma.

a schematic diagram of the apparatus is shown in Figure 1. The PDMS membranes used in this study stuck to glass. To treat one surface, PDMS membranes of 7×7 cm were placed in a flask without any spaces between the surface and the glass of bottom so not to introduce air. The PDMS membranes in a flask were under a vacuum overnight. Ar gas was then introduced into the flask. Next, the flask was evacuated. The introduction of Ar gas and evacuation was repeated several times. The membrane was treated by 13.56 MHz plasma and at 10 W for 180 s. The membranes were then contacted with HDFNMA in the liquid phase at 60°C for 1 h. After the polymerization stopped, the membranes were rinsed in acetone overnight to remove the homopolymers and any nonreacted monomers, then dried for 48 h in an evacuated vessel.

In this study, seven sheets of membranes were subjected to treatment. The degree of grafting was calculated as

$$\text{Degree of grafting (\%)} = (W_1 - W_0)/W_0 \times 100 \quad (2)$$

where W_0 and W_1 denote the weight of the PDMS membrane and the grafted PDMS membrane, respectively. The coefficient of standard deviation (V_s) for their degree of grafting was 0.32. Among them, the V_s of three samples was 0.10. Therefore, the three samples were used in the subsequent investigation. The average of the degree of grafting for the three samples was 7.0 wt %.

Characterization of the Grafted PDMS Membrane

X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IPS-9000SX (JEOL, Ltd.) with $\text{MgK}\alpha$ exciting radiation (1253.6 eV). The X-ray gun was operated at 10 eV with a sample chamber vacuum of less than 5×10^{-9} Torr. The XPS spectra were recorded at two electron emission angles (ϑ) of 30° and 90° .

Pervaporation Experiment

The pervaporation experiments were performed in a previous study^{23–25} using the continuous-feed type at 25°C . The feed solution was circulated through the cell and the feed tank. The grafted surface of the membrane was kept in touch with the feed solution in the cell. The effective membrane area in the cell was 19.6 cm^2 . The pressure at the permeation side was kept below 10 Torr by vacuum pumps. Upon reaching steady-state flow conditions, the permeate was collected in traps cooled by liquid nitrogen (-196°C) at timed intervals, isolated from the vacuum system, and weighed. The permeation rate, flux (J), was obtained using eq. (3):

$$J = Q/At \quad (3)$$

where Q is the amount that permeated during the experimental time interval, t , and A is the effective surface area.

The VOC and water flux were calculated from the total flux and the permeate composition. The concentration of VOC in the feed and permeate solution was determined by gas chromatography using an FID detector. The VOC concentration in the permeate was high, which is far beyond its solubility limit in water. The phase separation took place in the permeate. Isopropanol was added to the permeate solution. The permeate solution was homogenized and analyzed to deter-

mine the VOC concentration. The separation factor, α_{pv} , was calculated as

$$\alpha_{pv} = \{Y(1 - X)\} / \{(1 - Y)X\} \quad (4)$$

where X and Y denote the concentrations of VOC in the feed and permeate solutions, respectively.

Sorption Measurement

The dried and weighed membrane was immersed in the VOC solution or VOC liquid and sealed at 25°C until equilibrium was reached. The membrane was then taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of sorption or VOC liquid of the VOC solution into the membranes was measured as

$$\text{Degree of sorption (\%)} = (W_1 - W_0) / W_0 \times 100 \quad (5)$$

where W_0 and W_1 denote the weights of the dried membrane and the swollen membrane, respectively.

The concentration of the VOC solution soaked into the membrane was determined using the apparatus shown in Figure 2. The membrane, upon reaching equilibrium, was taken out of the vessel, quickly wiped with filter paper, and placed in the cold trap (A). The trap was connected to the apparatus and quickly cooled by liquid nitrogen. After the apparatus was sufficiently evacuated, valve (B) was closed and the VOC solution soaked in the membrane was vaporized by heating with a drier and collected in the cold trap (C).

The concentration of the VOC solution in the feed and the soaked membrane was determined by gas chromatography, the same as was the pervaporation experiment. The solubility coefficient (K) and the separation factor during sorption, α_s , were calculated as

$$K = Y' / X \quad (6)$$

$$\alpha_s = \{Y'(1 - X)\} / \{(1 - Y')X\} \quad (7)$$

where X and Y' denote the concentrations of VOC in the feed solution and the swollen membranes, respectively.

RESULTS AND DISCUSSION

Characterization of the Grafted PDMS Membrane

The surface morphologies of the grafted membranes were analyzed using XPS spectra. The

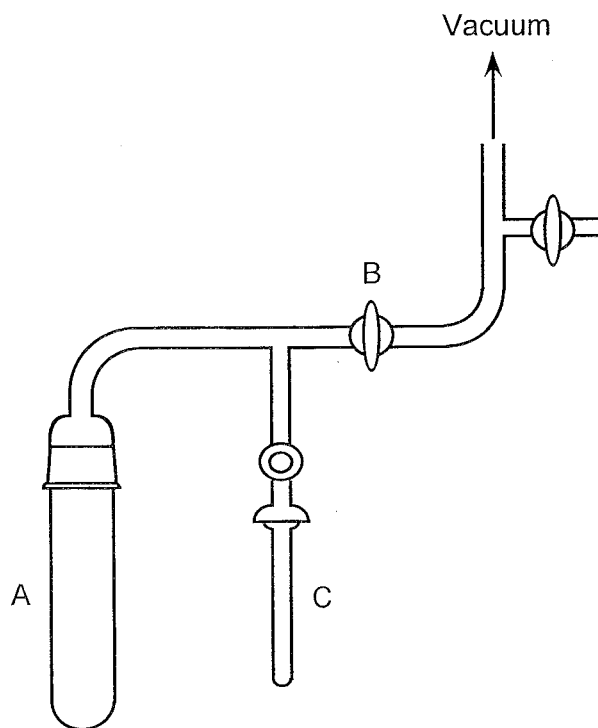


Figure 2 Apparatus for the composition measurement in the membrane: (A) cold trap for membrane; (B) valve; (C) cold trap for collecting samples.

ratio of fluorine, oxygen, carbon, and silicon atoms were analyzed and calculated for ~ 9 nm beneath the surface of the grafted membrane at 30° and 90° photoelectron emission angles and are characterized in Table II. In these spectra, the composition of atoms are determined up to 4.5 and 9 nm deep from the surface at the photoelectron emission angles of 30° and 90°, respectively.³⁴

The F/Si ratio on the reverse side of the grafted membranes was lower than on the grafted surface. The O/Si and C/Si ratios on the reverse side of the grafted membranes were almost the same as on the grafted surface. The degree of grafting for the whole membrane was 7.0 wt %. The thickness of the grafted PDMS membrane was almost the same as that of untreated PDMS membrane. After the irradiation, the degassed HDFNMA was introduced into the reactor and the PDMS membranes were soaked in HDFNMA and grafted. The graft polymerization started with the surface of membrane and was proceeded into the PDMS membrane. Hence, the degree of grafting on the inside and reverse side of the PDMS membranes was lower than on the surface.

Table II Fluorine-to-Silicon, Oxygen-to-Silicon, and Carbon-to-Silicon Atomic Ratios for Surface of PDMS and Grafted PDMS Membranes by XPS Analysis

Plasma Graft Condition			Atomic Ratio		
Power (W)	Exposure Time (S)	Electron Emission Angle (°)	F/Si	O/Si	C/Si
Surface of Grated PDMS Membrane					
10	180	30	0.110	1.80	3.34
		90	0.101	2.15	4.82
Reverse side of Grated PDMS Membrane					
		30	0.0288	1.29	1.83
		90	0.0268	1.36	1.80
Under air after plasma exposure: not grafted					
10	180	90	—	1.60	1.21
PDMS					
		90	—	1.42	1.85

^a F/Si: fluorine atomic ratio (%) / silicon atomic ratio (%); O/Si: oxygen atomic ratio (%) / silicon atomic ratio (%); C/Si: carbon atomic ratio (%) / silicon atomic ratio (%). —: not detected.

Pervaporation of Grafted PDMS Membrane Aqueous VOC Solution

The pervaporation properties of various VOC aqueous solutions were determined in this study. The total flux as a function of the VOC concentration in the feed solution is shown in Figure 3 for the PDMS membrane and the grafted PDMS membrane. Except for benzene, when the feed VOC concentration increased, the total flux was almost constant in the PDMS membrane. For benzene, the total flux increased with the feed concentration in the PDMS membrane. For the HDFNMA-grafted membranes, the total flux was almost constant when the feed VOC concentration increased.

The water flux and VOC flux as a function of the VOC concentration in the feed solution are shown in Figure 4 for the PDMS membrane and the grafted PDMS membrane. Except for benzene, when the feed VOC concentration increased, the water flux was almost constant in the PDMS membrane. For benzene, the water flux increased with the feed concentration in the PDMS membrane. This results in the total flux being increased with the feed benzene concentration in the PDMS membrane.

To account for the permeation of the mixture, the penetrates and the membrane interact with each other and one component affects the transport of the other component.¹⁹ The diffusion of

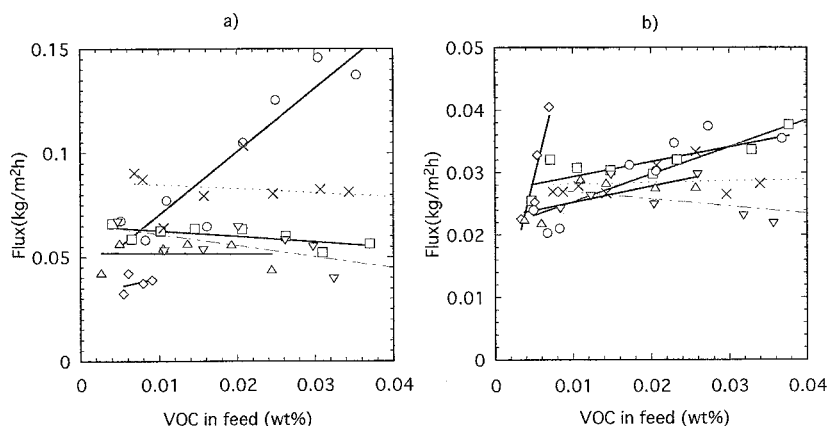


Figure 3 Effect of feed concentration on total flux for VOC–water mixtures during pervaporation through (a) PDMS membrane and (b) grafted PDMS membrane: (□) TCE; (◇) PCE; (○) benzene; (△) toluene; (×) EBU; (▽) EBZ.

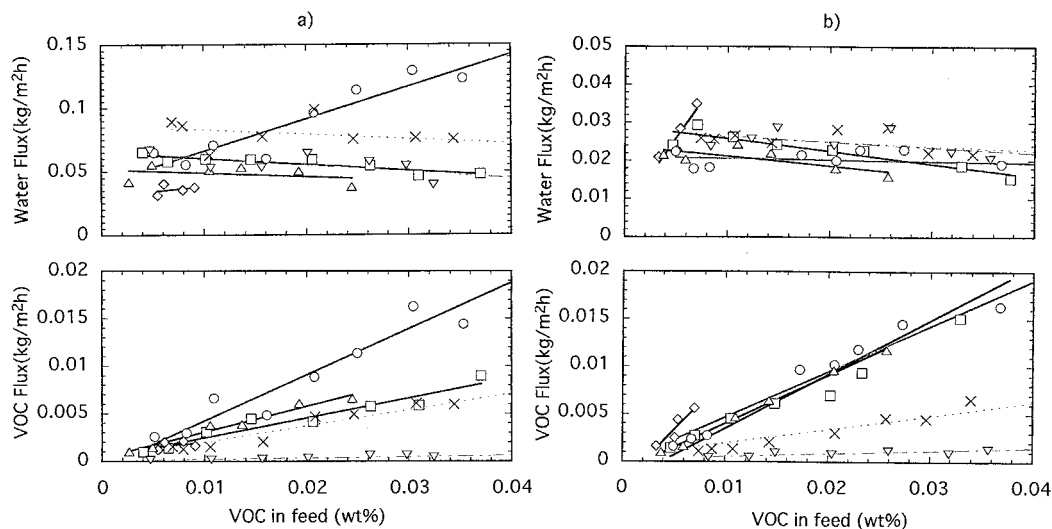


Figure 4 Effect of feed concentration on water and VOC flux for VOC–water mixtures during pervaporation through (a) PDMS membrane and (b) grafted PDMS membrane: (□) TCE; (◇) PCE; (○) benzene; (△) toluene; (×) EBU; (▽) EBZ.

molecules are promoted or inhibited by another component. Huang et al.^{35,36} proposed a permeation ratio (ϑ) which represents the ratio of the actual flux to the ideal flux, that is, the interaction of one component with the other component or the membrane. ϑ is described as

$$\vartheta = J/J_0 \quad (8)$$

where J and J_0 represent the actual flux and the ideal flux, respectively. When $\vartheta > 1$, the transport of the component is promoted. When $\vartheta < 1$, the transport of the component is inhibited. In pervaporation, the membrane can be swollen by the penetration of components and the diffusion is promoted. In this case, the water flux was affected by the benzene and increased with the feed benzene concentration. While the feed benzene solution used in this study was a dilute aqueous solution, it may be considered that the swelling effect by benzene affected the permeation of the water.

In the HDFNMA-grafted membranes, the water flux was almost constant with increasing feed concentration of the VOCs. The promotion of the water transport was not observed. In our previous studies,^{24,25} for the membranes grafted with fluoroalkyl methacrylate, the diffusion of water was prevented and the water flux decreased with increasing feed concentration. In this study, the diffusion of water in the benzene solution was not promoted in the HDFNMA-grafted PDMS mem-

branes, while the diffusion of water in the benzene solution was promoted in the PDMS membranes. Grafted HDFNMA inhibited increase of the water flux. The VOCs flux was increased with the feed concentration in both the PDMS membrane and the grafted PDMS membrane.

The relationships between the feed concentration and the permeate concentration are shown in Figure 5 for the PDMS membrane and the grafted PDMS membrane. The VOC flux increased with the feed concentration in both the PDMS membrane and the grafted PDMS membrane. In the grafted PDMS membrane, the best separation performance was due to introducing the hydrophobic polymer, poly(HDFNMA). The permselectivity for PCE and toluene was high in both the PDMS membrane and the grafted PDMS membrane. The permselectivity for EBU and EBZ was low in both the PDMS membrane and the grafted PDMS membrane.

TCE and Benzene-mixed Aqueous Solution

The pervaporation properties of TCE and benzene-mixed aqueous solutions were studied. The flux as a function of the TCE concentration in the feed solution is shown in Figure 6 for the PDMS membrane and the grafted PDMS membrane. The feed benzene concentration was fixed at 0.015 wt %. For the PDMS membrane, when the feed TCE concentration increased, the water flux and the benzene flux were almost constant. The TCE flux increased with the feed concentration. Hence,

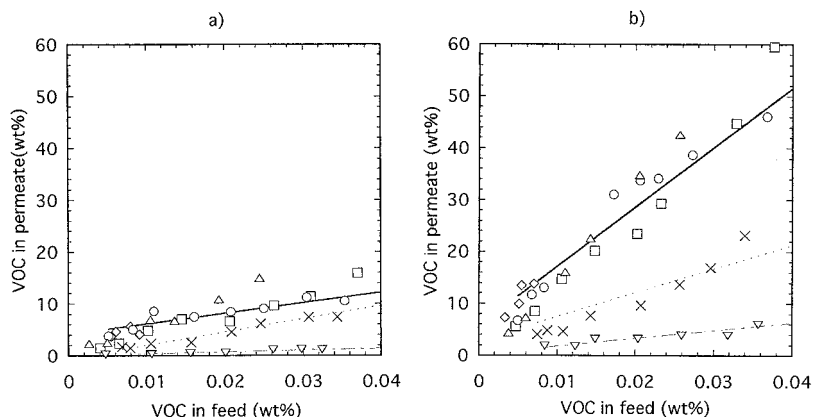


Figure 5 Relationship between VOC concentration in feed and permeation during pervaporation through (a) PDMS membrane and (b) grafted PDMS membrane: (□) TCE; (◇) PCE; (○) benzene; (△) toluene; (×) EBU; (▽) EBZ.

the total flux increased with the feed concentration. The relationship between the TCE flux and feed TCE concentration of this TCE–benzene–water mixture was almost the same as the relationship between the TCE flux and the feed TCE concentration of the TCE–water mixture. Benzene did not affect the permeation of TCE in the PDMS membrane.

For the grafted membrane, the pervaporation property of TCE and benzene-mixed aqueous solutions was different from the PDMS membrane. The water flux decreased with increasing feed TCE concentration over TCE = 0.02 wt %. The TCE flux increased with the feed concentration,

and the increase was kept down at a high feed concentration, in the grafted PDMS membrane. The benzene flux decreased with increasing feed concentration. The total flux decreased with increasing feed TCE concentration over TCE = 0.02 wt %. For the pervaporation property in the grafted PDMS membrane, the TCE quantity sorbed into the membrane was very high due to introducing the hydrophobic polymer, HDFNMA, so that the diffusion of water and benzene was prevented; in turn, the flux decreased. Compared with the pervaporation for the TCE–water mixture, the TCE flux for the TCE–benzene–water mixture was low. The TCE flux was prevented by

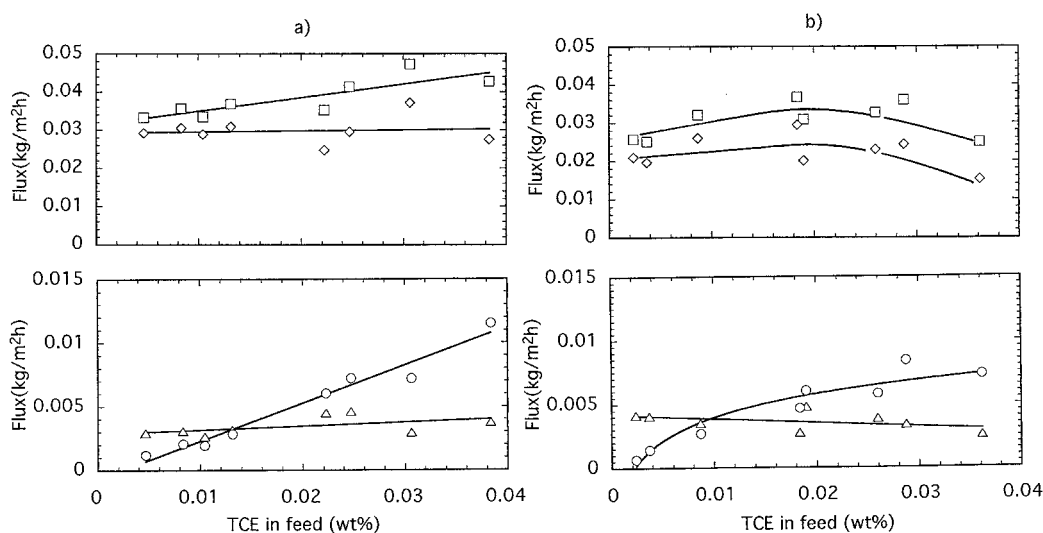


Figure 6 Effect of feed TCE concentration on flux for TCE–benzene–water mixture during pervaporation through (a) PDMS membrane and (b) grafted PDMS membrane at 0.015 wt % feed benzene concentration: (□) total; (◇) water; (○) TCE; (△) benzene.

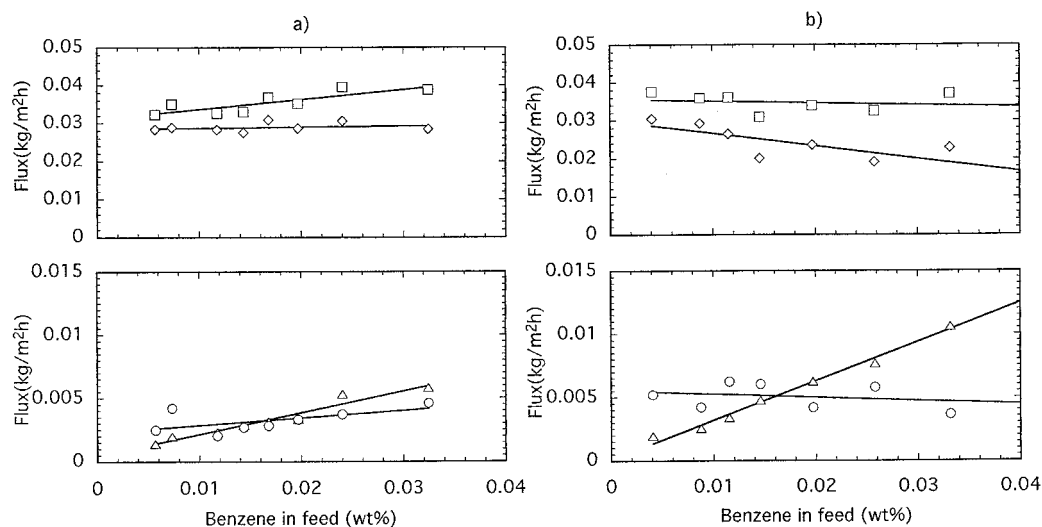


Figure 7 Effect of feed benzene concentration on flux for TCE–benzene–water mixture during pervaporation through (a) PDMS membrane and (b) grafted PDMS membrane at 0.015 wt % feed TCE concentration: (□) total; (◇) water; (○) TCE; (△) benzene.

benzene during pervaporation of the TCE–benzene–water mixture. During pervaporation for TCE–benzene–water mixture through the grafted PDMS membrane, the compounds which permeate interfere with each other.

Next, the feed TCE concentration was fixed at 0.015 wt % and the feed benzene concentration was varied. The flux as a function of the benzene concentration in the feed solution is shown in Figure 7 for the PDMS membrane and the grafted PDMS membrane. For the PDMS membrane, the water flux and the TCE flux were almost constant when the feed TCE concentration increased. The benzene flux increased with the feed concentration. The total flux was almost constant when the feed TCE concentration increased. While the water flux increased with the feed benzene concentration during pervaporation of the benzene–water mixtures, the phenomenon was not observed for benzene–TCE–water mixture through the PDMS membrane. TCE molecules prevented increase of the water flux.

For the grafted PDMS membrane, the water flux decreased with increasing feed concentration. The TCE flux was almost constant when the feed TCE concentration increased. The benzene flux increased with the feed concentration. The total flux was almost constant when the feed TCE concentration increased. For the pervaporation of the benzene–water mixture through the grafted PDMS membrane, promotion of the water permeation was prevented. In addition to that, TCE

molecules inhibited increase of the water flux during pervaporation of the benzene–TCE–water mixture through the PDMS membrane. It is considered that during pervaporation of the benzene–TCE–water mixture through the grafted PDMS membrane both the grafted HDFNMA and TCE molecules prevented the permeation of the water molecules.

Sorption of Grafted PDMS Membrane

The sorption isotherms for the VOCs are presented in Figure 8 for both the PDMS membrane and the grafted PDMS membrane. The relationship between the feed concentration and the concentration in PDMS membranes was observed to be linear. For the grafted PDMS membranes, the concentration of the VOC solution soaked into the membrane was significantly increased with increasing feed concentration. The sorption selectivity for VOCs was higher in the grafted PDMS membrane than in the PDMS membrane. In consideration of the characterization, the grafting started with the surface of membrane and then proceeded into the PDMS membrane. It is considered that introducing hydrophobic HDFNMA to the PDMS membrane enhances the sorption selectivity. The grafted PDMS membrane that had the high VOC concentrations in the sorbed solution showed an excellent separation performance.

The solubility for PCE and toluene was high in both the PDMS membrane and the grafted PDMS

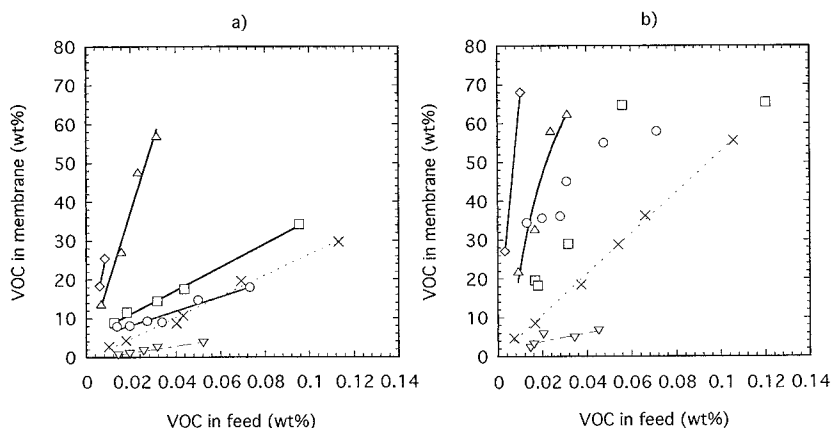


Figure 8 Sorption of VOC on PDMS membrane as a function of the feed concentration at equilibrium for (a) PDMS membrane and (b) grafted PDMS membrane: (\square) TCE; (\diamond) PCE; (\circ) benzene; (Δ) toluene; (\times) EBU; (∇) EBZ.

membrane. The solubility for EBU and EBZ was low in both the PDMS membrane and the grafted PDMS membrane.

The need for hydrophobicity data in studies of organic compounds can be traced back at least to the turn of the century. The hydrophobicity is used to indicate the physical property of the molecule which governs its partitioning into the non-aqueous portion of an immiscible or partially immiscible solvent pair. Pow , the partition coefficient between water and *n*-octanol, expressed the hydrophobicity of the compounds.

Lamer et al.²¹ considered the relationship between the $\log Pow$ of aroma compounds and their solubility for the PDMS membrane. The hydrophobicity, Pow , is closely related to the solubility of organic compounds.²¹ The solubility coefficient (K) represents the solubility of organic compounds for a membrane. The decimal logarithms of the solubility coefficient (K) as a function of the $\log Pow$ are shown in Figure 9 for the PDMS membrane and the grafted PDMS membrane. The solubility ($\log K$) for PCE and toluene, which have a high $\log Pow$, were high in both the PDMS membrane and the grafted PDMS membrane. The solubility ($\log K$) for EBU, which has a low $\log Pow$, was low in both the PDMS membrane and the grafted PDMS membrane.

The solubility ($\log K$) for EBZ was low in both the PDMS membrane and the grafted PDMS membrane, while EBZ has a high $\log Pow$. Then, the ability for VOCs to penetrate the membrane was investigated. The degree of sorption for the pure VOC liquid in the membranes is shown in Table III. The degree of sorption for TCE, PCE,

benzene, toluene, and EBU are above 80 wt % (above 1 mol/PDMS 100 mg). The solubility for compounds in a membrane is affected by its dispersion and polarization. Polarization can be considered using the Pow value. The ability of dispersion is determined by the diffusivity. The degree of sorption for EBZ was low, 23.1 wt % (0.154 mol/PDMS 100 mg). The molecular volume of EBZ is much greater than that of the other VOCs;

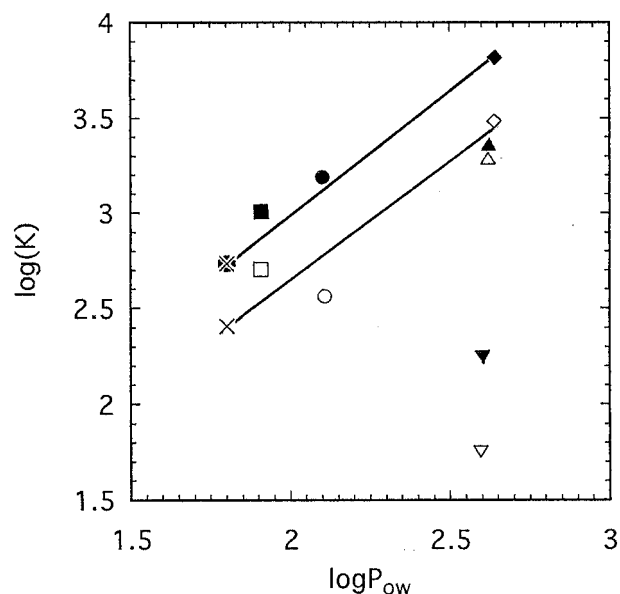


Figure 9 Relationship between the hydrophobicity of VOC and the sorption in grafted PDMS membrane: (\square) TCE; (\diamond) PCE; (\circ) benzene; (Δ) toluene; (\times) EBU; (∇) EBZ. (Open) For PDMS membrane; (closed) for grafted PDMS membrane.

Table III Sorption and Diffusion Data of Various VOCs for PDMS and Grafted PDMS Membrane

Compound	log <i>Pow</i>	log <i>K</i>		Degree of Sorption in PDMS Membrane (mol/PDMS 100 g)	Molecular Volume (cm ³ /mol)	Separation Factor (α_D)	
		PDMS Membrane	Grafted PDMS Membrane			PDMS Membrane	Grafted PDMS Membrane
TCE	1.91	2.71	3.25	2.04	90.0	0.705	0.918
PCE	2.638	3.48	4.20	1.60	102	0.121	0.133
Benzene	2.103	2.55	3.42	1.05	88.9	0.999	0.809
Toluene	2.626	3.28	3.63	1.45	106	0.214	0.611
EBU	1.805	2.40	2.89	1.34	132	0.934	0.962
EBZ	2.602	1.76	2.27	0.154	144	0.511	0.935

therefore, the diffusivity of EBZ is low. Hence, the degree of sorption for EBZ was low and the solubility for EBZ was low in the membrane.

Diffusion of the Grafted Membrane

Pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane. The relationship between the separation factor during permeation (α_{pv}), the separation factor during sorption (α_s), and the apparent separation factor during diffusion (α_D) is given by eq. (9):

$$\alpha_{pv} = \alpha_s \alpha_D \quad (9)$$

α_D is described by eq. (10) using eqs. (4), (7), and (9):

$$\alpha_D = \{Y(1 - Y')\} / \{(1 - Y)Y'\} \quad (10)$$

where Y and Y' denote the concentration of VOCs in the permeate solution and in the swollen membranes for the same feed solution, respectively.

α_D was calculated by eq. (10) using the sorption isotherms in Figure 8 and the pervaporation in Figure 5. α_D , as a function of the VOC concentration in the feed solution, is shown Table III for both the PDMS membrane and the grafted PDMS membrane. The diffusivity for benzene and EBU was high in both the PDMS membrane and the grafted PDMS membrane. The diffusivity for PCE was low in both the PDMS membrane and the grafted PDMS membrane. The molecular volumes and α_D of the VOCs are shown in Table III. The molecular volumes of benzene and EBU are much smaller than those of the other VOCs in that their diffusivities are high. PCE has four Cls

with a much larger molecular volume; therefore, the diffusivity is very low.

Permselectivity is determined by the sorption and the diffusion characteristics of the permeating components in the membrane. The permselectivity of PCE and toluene were high. Because the molecular volume of the VOCs is greater than that of water and the permeate quickly penetrates in a rubbery membrane like PDMS, permselectivity was not affected by the diffusivity. Solubility significantly affects the permselectivity during pervaporation through the hydrophobic rubbery membrane.

CONCLUSIONS

The pervaporation properties of various VOC aqueous solutions were studied in this investigation. The pervaporation performance of a membrane is determined by both the sorption and the diffusion characteristics of the permeating components in the membrane. The sorption and diffusion for the VOC-water mixture during pervaporation through the PDMS membrane and the HDFNMA-grafted PDMS membrane were studied.

In the grafted PDMS membrane, the best separation performance was due to introducing the hydrophobic polymer, poly(HDFNMA). During pervaporation, the components which permeate and membrane interface with each other. The phenomenon was significantly observed in pervaporation for the ternary mixture through the grafted PDMS membrane.

The solubility (log K) for PCE and toluene, which have a high log Pow , were high in both the PDMS membrane and the grafted PDMS membrane. The solubility (log K) for EBU which has a low log Pow was low in both the PDMS mem-

brane and the grafted PDMS membrane. The solubility ($\log K$) for EBZ was low in both the PDMS membrane and the grafted PDMS membrane, while EBZ has a high $\log Pow$. The solubility for compounds in a membrane is affected by its dispersion and polarization. Polarization can be considered using the Pow value. The ability of dispersion is determined by the diffusivity. The degree of sorption for EBZ was low compared to the other VOCs. The molecular volume of EBZ is much greater than that of the other VOCs; therefore, the diffusivity of EBZ is low. Hence, the degree of sorption for EBZ was low and the solubility for EBZ was low in the membrane. PCE has four Cls with a much larger molecular volume; therefore, the diffusivity is very low.

Permeability is determined by the sorption and the diffusion characteristics of the permeating components in the membrane. The permeability of PCE and toluene was high in this study. Because the molecular volume of the VOCs is greater than that of water and the permeate quickly penetrates in a rubbery membrane like PDMS, permeability was not affected by the diffusivity. Solubility significantly affects the permeability during pervaporation through the hydrophobic rubbery membrane.

The authors are grateful to the Fuji Systems Corp. for providing the PDMS membranes.

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