

Pervaporation of 1,2-Dimethoxyethane from Aqueous Solutions by Crosslinked Oligosilylstyrene–Poly(dimethylsiloxane) Composite Membranes

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ABSTRACT: Crosslinked oligosilylstyrene–poly(dimethylsiloxane) composite membranes were used to separate 1,2-dimethoxyethane (1,2-DME) from dilute aqueous solutions through a pervaporation process. The composite membranes were prepared through the casting of solutions of H-terminated oligosilylstyrene and vinyl-terminated poly(dimethylsiloxane) onto the surfaces of polysulfone ultrafiltration membranes. A crosslinked poly(dimethylsiloxane) gel was generated through the reaction of H-terminated oligosilylstyrene and vinyl-terminated poly(dimethylsiloxane), with a platinum complex used as a catalyst. The pervaporation characteristics of the composite membranes were

investigated with respect to the feed composition of 1,2-DME, the feed temperature, the downstream pressure, and the top-layer thickness of the composite membranes. The composite membranes exhibited preferential selectivity to 1,2-DME. Depending on the operation conditions, the separation factor and permeation rate of 1,2-DME were 55–184 and 0.31–3.3 g/m² h, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2284–2294, 2004

Key words: composites; membranes; waste-water treatment; polydimethylsiloxane; oligosilylstyrene; 1,2-dimethoxyethane

INTRODUCTION

Two kinds of polymer membranes are widely used in the pervaporation process.^{1–5} One is the selective removal of water from water–organic mixtures. Normally, the membranes exhibit a hydrophilic property. Another type of membrane with hydrophobic characteristics, such as a poly(dimethylsiloxane) (PDMS) membrane, preferentially allow organics to permeate through it.⁶ The reason that a PDMS membrane with organics is perselective is that the PDMS chains contain Si–O bonds with free rotation characteristics and rather small, nonpolar CH₃ side groups.⁷ Much research has conducted on the removal of aromatic and chlorinated hydrocarbons from organic–water mixtures with PDMS-related membranes.^{8–16} PDMS membranes have also been used to remove chemicals with good miscible properties with water.^{17–19} How-

ever, during the pervaporation process, the selectivity of PDMS membranes without modification is low because of the swelling of the PDMS membranes by organics. Meanwhile, the mechanical properties are rather poor.²⁰ These disadvantages can be improved through the addition of hydrophobic zeolites to PDMS membranes or through the fabrication of PDMS membranes with the structure of a graft, blend, block, crosslinking, or interpenetrating polymer network.^{21–25}

One technique has been developed to modify PDMS membranes with H-terminated oligosilylstyrene (oligo-SiH₃).²⁶ Oligo-SiH₃ is an oligomer with the characteristics of siloxane chain and styrene structure units. Modified PDMS membranes with oligo-SiH₃ are more hydrophobic and have higher tensile strength and thermostability than unmodified PDMS membranes. Basically, oligo-SiH₃ is a crosslinking agent that can be used to generate the crosslinked oligosilylstyrene–PDMS network when it is reacted with vinyl-terminated poly(dimethylsiloxane) (vinyl-PDMS) in the presence of a platinum catalyst.²⁷ Therefore, it can be expected that both the mechanical properties and separation performance of the crosslinked oligosilylstyrene–PDMS membranes can be improved greatly. In a previous article,²⁶ the pervaporation performance of crosslinked oligosilylstyrene–PDMS com-

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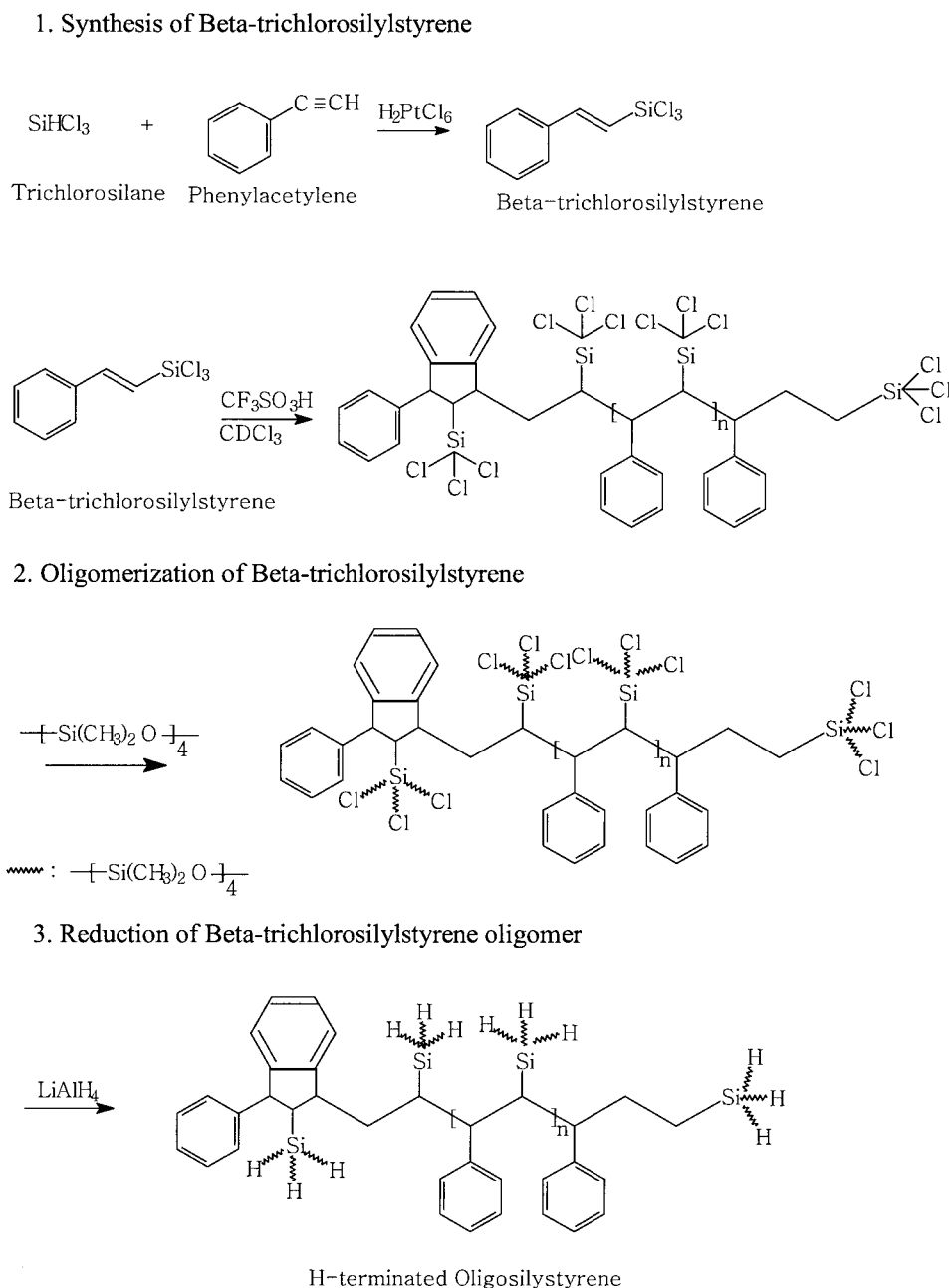


Figure 1 Schematic illustration of the synthetic route for oligo-SiH₃.

posite membranes was investigated through the removal of a series of hydrophobic compounds, such as aromatic and chlorinated compounds, from aqueous solutions. The composite membranes exhibited preferential selectivity to those compounds. Both a high permeation rate and a reasonable separation factor were observed. It should be interesting to evaluate the pervaporation process for this kind of membrane through the removal of chemicals with hydrophilic properties from aqueous solutions. In this study, the pervaporation of 1,2-dimethoxyethane (1,2-DME) from dilute aqueous solutions was evaluated with

crosslinked oligosilylstyrene-PDMS membranes. 1,2-DME shows good miscibility with water and has been extensively applied as a solvent in organic syntheses,²⁸⁻³¹ as a monomer and additive in polymerizations,^{32,33} and as a cosolvent in batteries.^{34,35}

EXPERIMENTAL

Materials

Phenylacetylene (98%; Aldrich, Milwaukee, WI) was purified by distillation. Vinyl-PDMS (Hülser-Petrach,

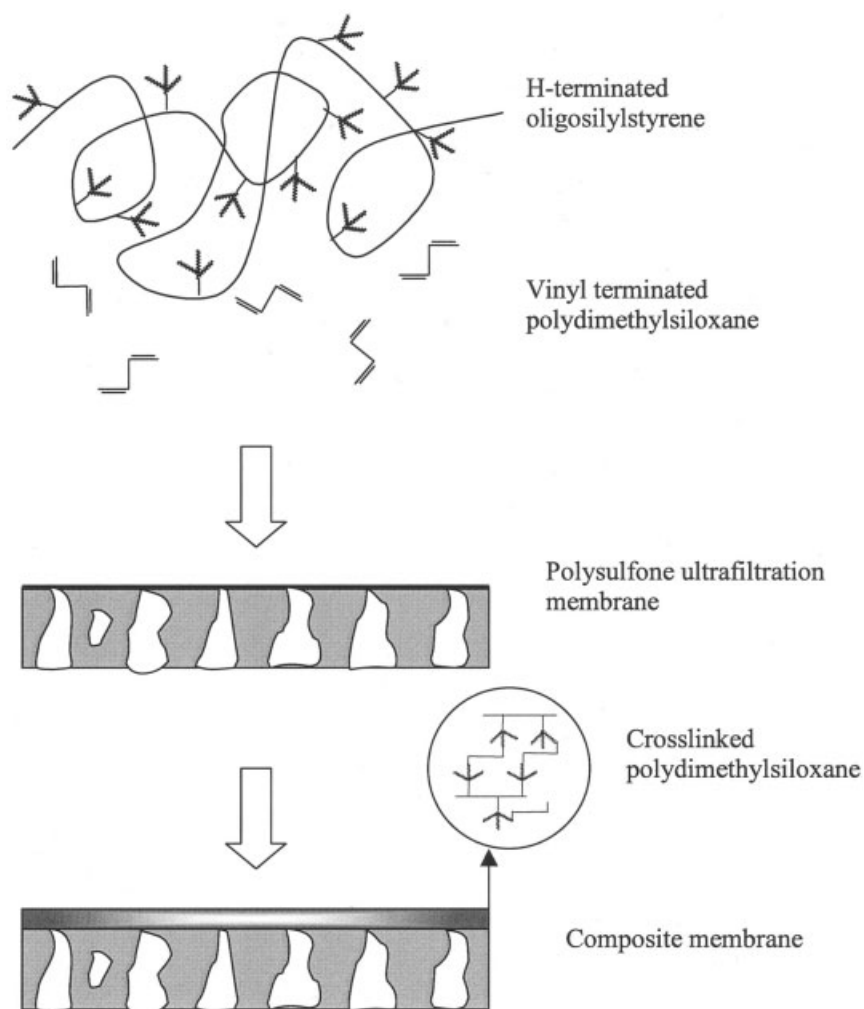


Figure 2 Schematic representation of the composite membranes from oligo-SiH₃ and vinyl-PDMS.

Sussex, NJ) with a viscosity of 500 cs, platinum divinyltetramethyldisiloxane complex (3% in toluene; Gelest, Tullytown, PA), hexane (99%; Fisher, Pittsburgh, PA), 1,2-DME (99%; Fisher), LiAlH₄ (powder; 95%; Aldrich), trichlorosilane (99%; Aldrich), trifluoromethanesulfuric acid (CF₃SO₃H; 99%; Aldrich), and octamethylcyclotetrasiloxane {[—Si(CH₃)₂O—]₄; 99%; Aldrich} were used without further purification. Deionized water was used in all the experiments. A polysulfone (PSF) ultrafiltration membrane (U.S. Filter, Warrendale, PA) with nonwoven polypropylene fibers and a dextran molecular weight cutoff of 100,000 was used as the support membrane. For purification, the PSF membrane, about 175 μm thick, was dipped in isopropyl alcohol overnight and then was exposed in a hood for complete drying.

Synthesis of oligo-SiH₃

The synthesis method of oligo-SiH₃ has been described in previous articles,^{26,27} and a schematic illus-

tration is shown in Figure 1. The synthetic procedure can be described as follows. Trichlorosilane (370 g) was added to phenylacetylene (636 g). To this solution, H₂PtCl₆ (0.8 mL, 0.3% in isopropyl alcohol) was added at 0°C, and the solution was allowed to stir for 6 days at room temperature. β-Trichlorosilylstyrene (TCSS) was obtained after the distillation of excess trichlorosilane. The oligomerization of TCSS was carried out through the mixing of TCSS (43.3 g) with CDCl₃ (3.0 mL), and then CF₃SO₃H (1.2 mL) was added at -15°C. Then, [—Si(CH₃)₂O—]₄ (3 equiv/SiCl₃) was added to the reaction system at 0°C. Finally, the reduction of the trichlorosilylstyrene oligomer was processed through the addition of the trichlorosilylstyrene oligomer (124.1 g) to 150 mL of ether; 3.9 g of LiAlH₄ was added to 80 mL of ether under an atmosphere of N₂. The solution of the trichlorosilylstyrene oligomer was added dropwise to the LiAlH₄ suspension with stirring. The supernatant was carefully decanted from the reaction solids. After a period of drying, oligo-SiH₃ as a clear oil was obtained through

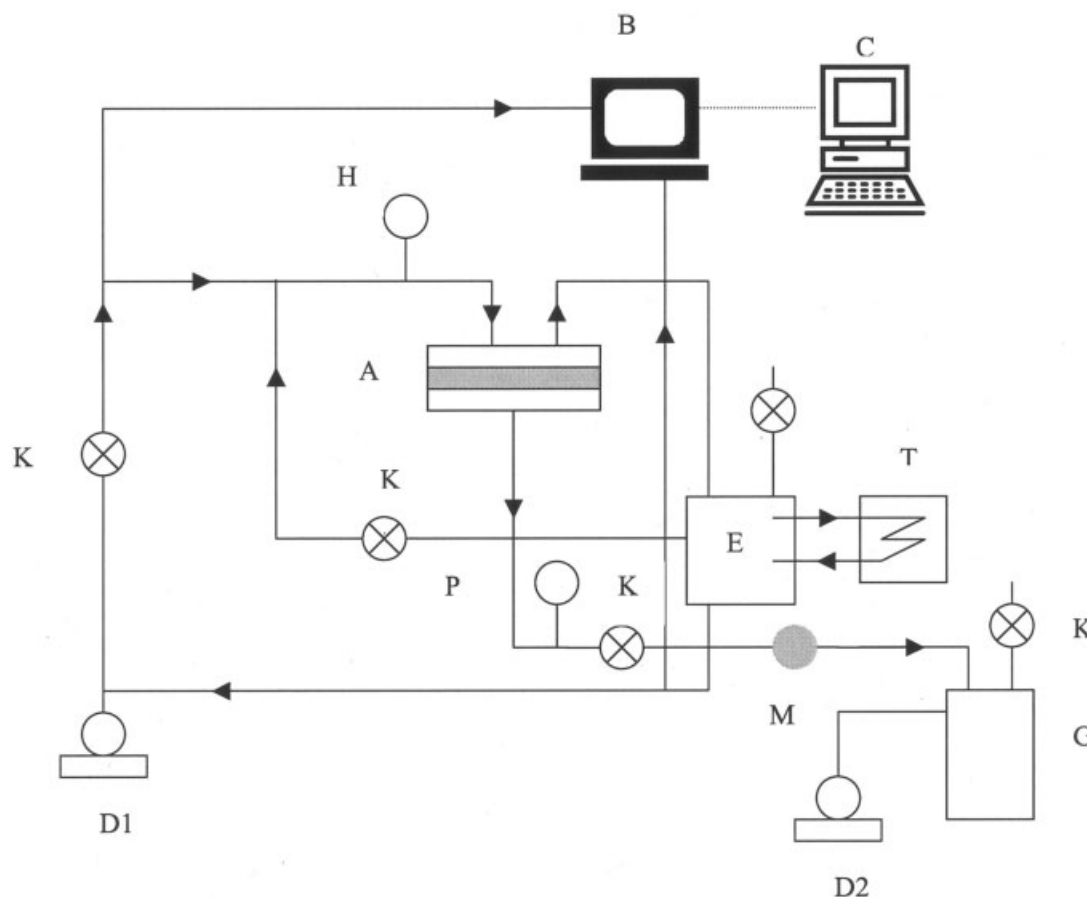


Figure 3 Schematic illustration of the pervaporation apparatus used to remove 1,2-DME from aqueous solutions: (A) pervaporation cell, (B) gas chromatograph, (C) computer, (D1) recirculating pump, (D2) vacuum pump, (E) feed tank, (F) thermostat, (G) cold trap, (H) temperature transducer, (K) control valve, (M) mass flow meter, (P) pressure transducer, and (T) thermocouple.

the evaporation of the solvents of the organic phase at temperatures of up to 100°C for 2–3 h *in vacuo*; 94.6 g (84.0% yield) was produced.

Preparation of the composite membranes

A vinyl-PDMS solution (16.7 wt %) containing 0.2 mL of platinum divinyltetramethyldisiloxane complex was prepared through the dissolution of 1.0 g of vinyl-PDMS with 500 cs in 5 mL of hexane at room temperature via stirring. An oligo-SiH₃ solution (16.7 wt %) was prepared through the dissolution of 0.2 g of oligo-SiH₃ in 1 mL of hexane at room temperature via stirring. Two polymer solutions were mixed with a magnetic stirrer to generate a homogeneous solution for 0.5 h at room temperature. The mixture was poured onto the surface of a PSF membrane clamped onto a cell with a diameter of 90 mm, and the solvent was allowed to evaporate at room temperature overnight. The composite membrane was further cured in an oven at 100°C for an additional 8 h. By adjusting

the amount of the casting solution and the concentration of the polymer in the casting solution, we controlled the thickness of the top layer of the composite membrane. A micrometer with an error range of ± 5 μm was used to measure the thickness of the top layer. Figure 2 show a schematic of the composite membrane from vinyl-PDMS and oligo-SiH₃.

Pervaporation

Pervaporation was performed with the equipment presented in Figure 3. The feed solution was recirculated between the feed tank and pervaporation cell with a recirculating pump (flow rate ~ 1 L/min). A composite membrane with an effective area of 31.2 cm² was clamped onto the radial cell. The feed temperature, downstream pressure, and feed flow rate were controlled with a thermocouple, pressure transducer, and mass flow meter, respectively, as indicated in Figure 3. The permeation rate (P) was calculated from the amount of the first solute (Q_1) or the second

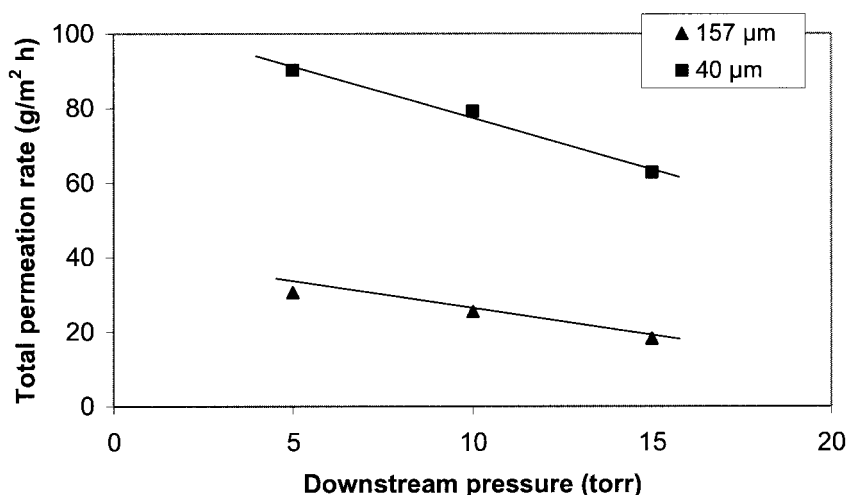


Figure 4 Effect of the downstream pressure on the total permeation rate [feed temperature = 30°C, feed composition = 120 ppm 1,2-DME in water, thickness of top layer = (■) 40 or (▲) 157 μm].

solvent (Q_2) through the effective membrane (F) at time t as follows:

$$P = Q_1 \text{ (or } Q_2) / (Ft) \quad (1)$$

The concentrations of the feed and permeate were determined with an HP 5890 gas chromatograph (Palo Alto, CA) equipped with a flame ionization detector and a Poropak P column heated at 150°C. The separation factor of the pervaporation process (α) was determined as follows:

$$\alpha = (Y_A / Y_B) / (X_A / X_B) \quad (2)$$

where X_A and X_B are the molar fractions of 1,2-DME and water in the feed and Y_A and Y_B are the molar

fractions of 1,2-DME and water in the permeate. All the operating parameters of the pervaporation process were monitored and recorded with a computer. P and α were calculated with Genesis software (Hamilton, Ontario, Canada). The error ranges of P and α with 95% confidence were 3 and 10%, respectively.

RESULTS AND DISCUSSION

Effect of the downstream pressure

Figures 4 and 5 show the effect of the downstream pressure on the total permeation rate and separation factor for membranes with top layers of 40 and 157 μm at a fixed feed composition of 1,2-DME (120 ppm) and at a feed temperature of 30°C. The feed

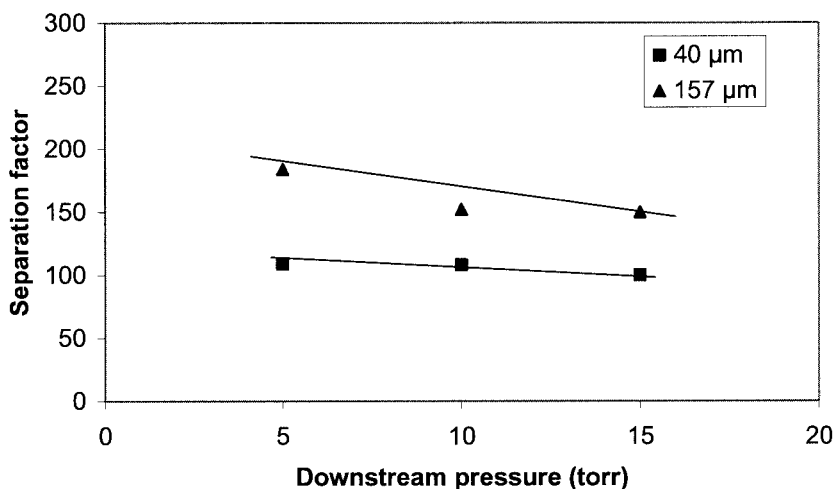


Figure 5 Effect of the downstream pressure on the separation factor [feed temperature = 30°C, feed composition = 120 ppm 1,2-DME in water, thickness of top layer = (■) 40 or (▲) 157 μm].

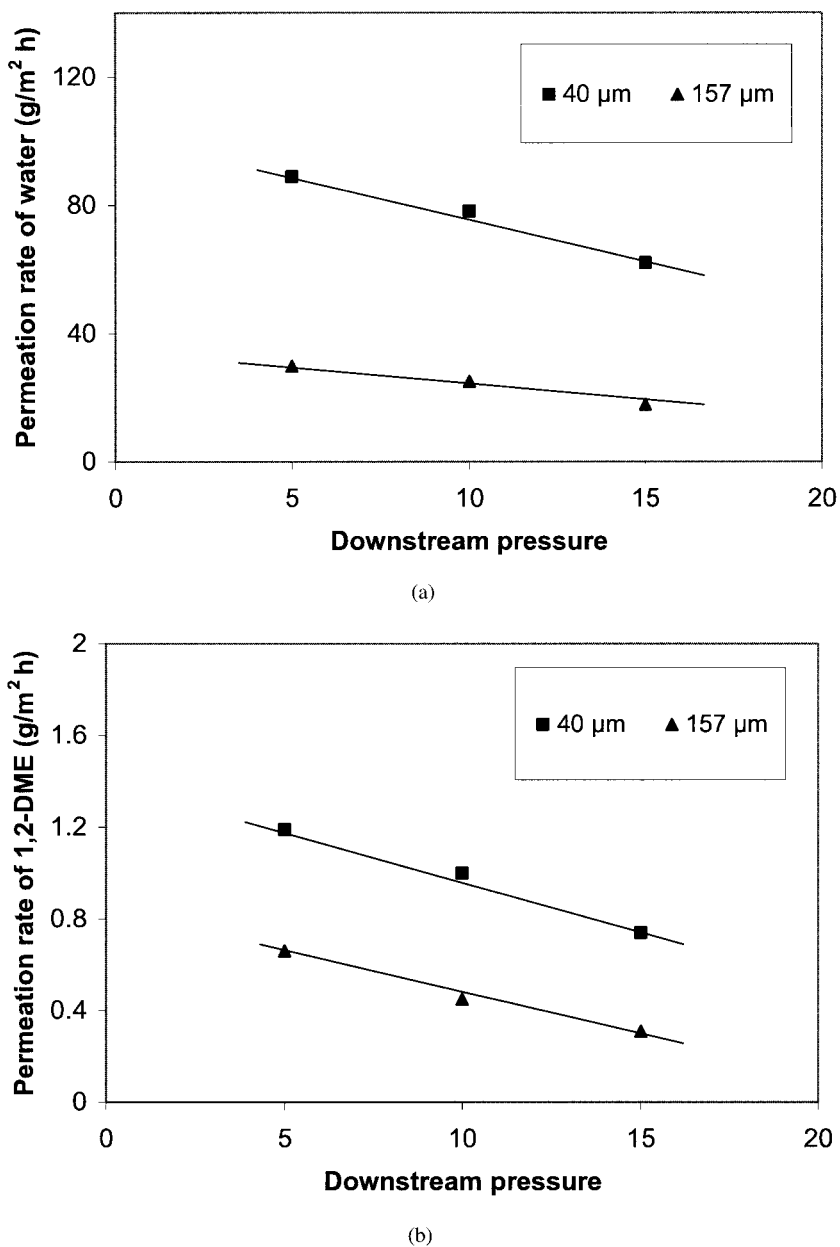


Figure 6 Effect of the downstream pressure on the permeation rates of (a) water and (b) 1,2-DME [feed temperature = 30°C, feed composition = 120 ppm 1,2-DME in water, thickness of top layer = (■) 40 or (▲) 157 μm].

temperature (30°C) and the feed composition (120 ppm 1,2-DME in water) were chosen to simulate normal pervaporation conditions (ca. room temperature and a low level of organics in the feed solution). As expected, Figure 4 shows that the total permeation rate decreased as the downstream pressure increased for both membranes because the driving force of permeation was reversed proportionally to the downstream pressure. The permeation rate of the thin membrane (40 μm) was almost three times greater than that of the thick membrane (157 μm). The permeation rate of the membrane

with a thin top layer was higher than that of the membrane with a thick top layer because the total resistance of the membranes was reduced as the thickness decreased. However, the separation factor of the composite membrane with a thin top layer was lower than that of the composite membrane with a thick top layer, as shown in Figure 5. The reduction of the membrane resistance made it possible to transfer more water through the membrane so that the separation factor decreased with the decreasing membrane thickness. Figure 6 presents the relationship between the permeation rate of wa-

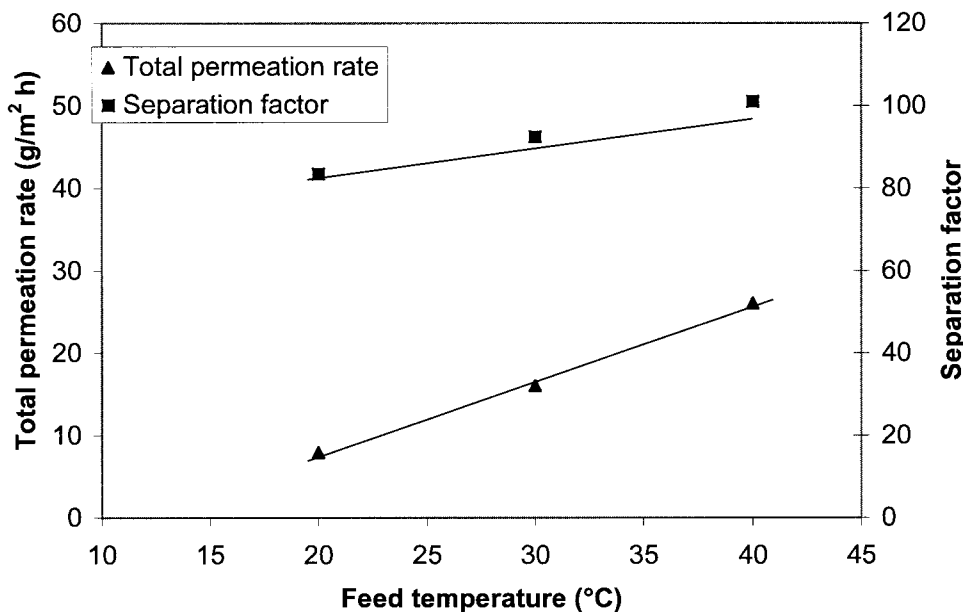


Figure 7 Effect of the feed temperature on the total permeation rate and separation factor (feed composition = 700 ppm 1,2-DME in water, downstream pressure = 5 mmHg, thickness of top layer = 157 μm).

ter (or 1,2-DME) and the downstream pressure. The permeation rates of both water and 1,2-DME decreased with increasing downstream pressure, and the thick membrane had a low permeation rate in comparison with the thin membrane.

Effect of the feed temperature

We used the feed composition (700 ppm 1,2-DEM in water) to study the effect of the temperature on pervaporation to avoid an error in measurement because

of the low permeation rate of 1,2-DME at low temperatures. The effect of the feed temperature on the total permeation rate and separation factor is shown in Figure 7. All the experiments were performed at a 1,2-DME concentration of 700 ppm and at a downstream pressure of 5 mmHg. Both the total permeation rate and separation factor increased with as the feed temperature increased. Because the frequency and amplitude of the polymer chain motion become larger and a PDMS membrane expands at a high temperature, the diffusion rates of permeability molecules can

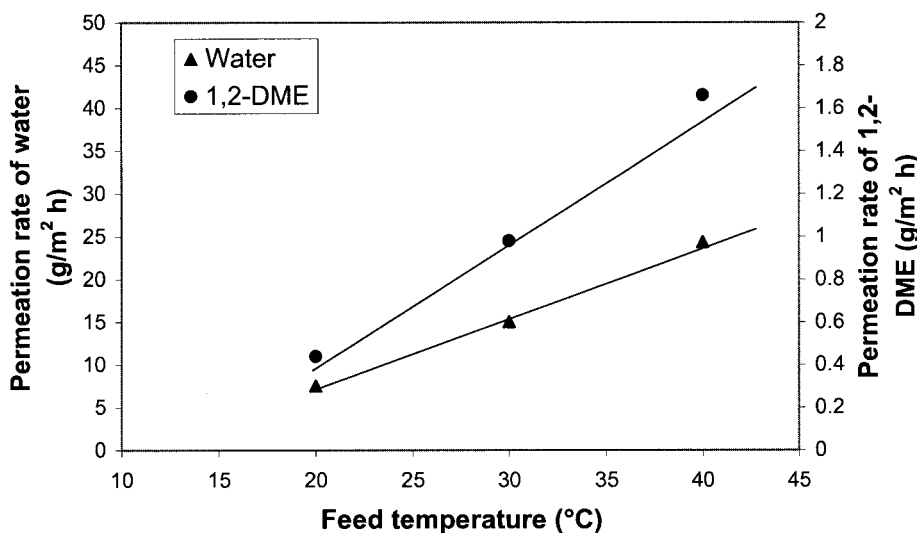


Figure 8 Effect of the feed temperature on the permeation rates of 1,2-DME and water (feed composition = 700 ppm 1,2-DME in water, downstream pressure = 5 mmHg, thickness of top layer = 157 μm).

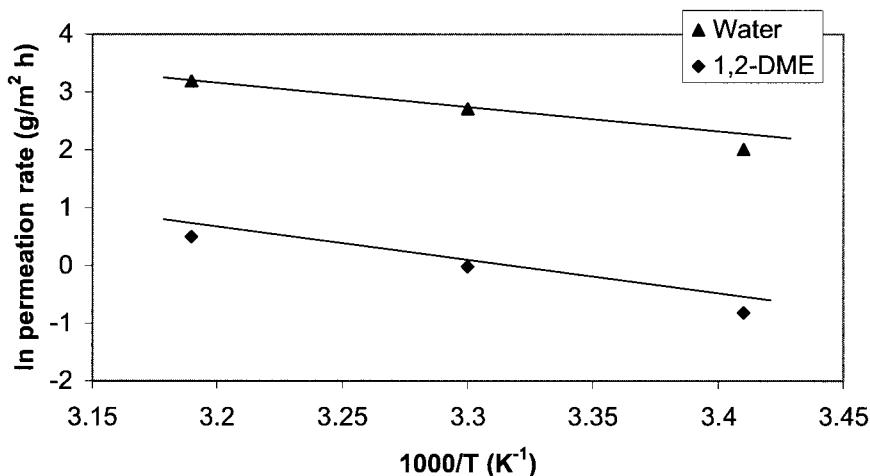


Figure 9 Arrhenius plots of the flux of water and 1,2-DME versus the inverse feed temperature (feed composition = 700 ppm 1,2-DME in water, downstream pressure = 5 mmHg, thickness of top layer = 157 μm).

be increased.³⁶ The increase in the separation factor was attributed to the fact that the increase in the permeation rate of 1,2-DME was faster than that of water as the feed temperature increased. Figure 8 shows that the dependence of the permeation rates of water and 1,2-DME on the feed temperature. The permeation rates of both water and 1,2-DME linearly increased as the feed temperature increased. Figure 9 shows the apparent activation energies of water (10.7 kcal/mol) and 1,2-DME (11.9 kcal/mol), which were obtained through the plotting of the inverse temperature as the logarithmical permeation rate based on the Arrhenius equation.³⁷ The linear regression coefficients are 0.99 for both lines in Figure 9. In comparison

with 1,2-DME, water with a lower activation energy demonstrated a higher permeation rate, as shown in Figure 8.

Effect of the feed composition

Figures 10 and 11 show the effect of the feed composition on the total permeation rate and separation factor at a downstream pressure of 5 mmHg and at a feed temperature of 30°C, respectively. The composite membranes preferentially permeated 1,2-DME at a feed composition of 120–737 ppm because the separation factor was higher than 50. Both the total permeation rate and the separation factor decreased as the

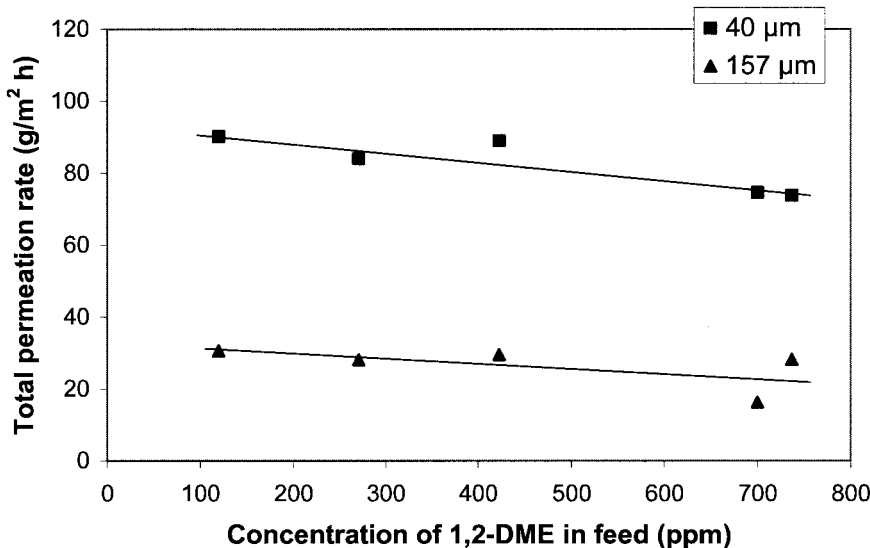


Figure 10 Effect of the feed composition on the total permeation rate [feed temperature = 30°C, downstream pressure = 5 mmHg, thickness of top layer = (■) 40 or (▲) 157 μm].

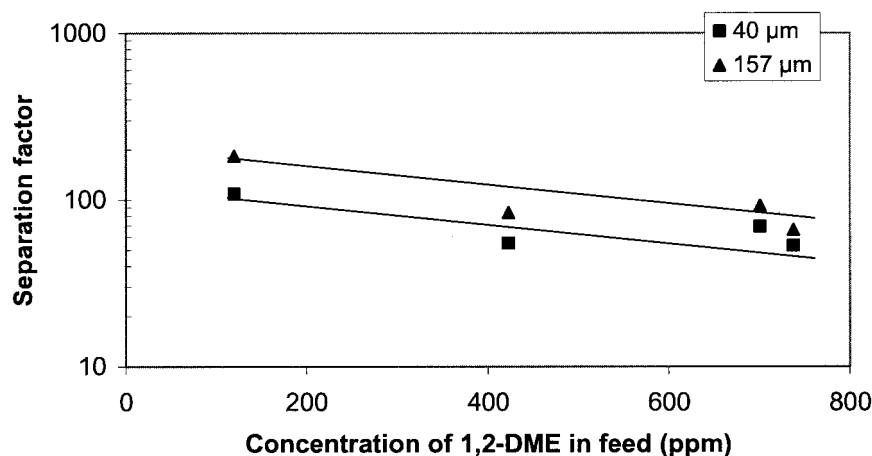


Figure 11 Effect of the feed composition on the separation factor [feed temperature = 30°C, downstream pressure = 5 mmHg, thickness of top layer = (■) 40 or (▲) 157 μm].

feed concentration increased. More 1,2-DME could be transferred through a membrane as the amount of 1,2-DME increased in the feed, as shown in Figure 12, because the driving force for permeating 1,2-DME increased. Although the permeation rate of 1,2-DME increased, the total permeation rate still decreased because most of the permeate was water and the permeation rate of water decreased with the variation of the feed concentration, as shown in Figure 13. The reduction of the separation factor with increasing feed composition was attributed to the fact that the increase in 1,2-DME in the feed was faster than that of 1,2-DME in the permeate.

Effect of the membrane thickness

The effect of the top-layer thickness of composite membranes on the pervaporation performance was investigated, and the results are given in Figure 14. With a reduction of the top-layer thickness of a composite membrane, the total permeation rate increased, but the separation factor decreased. An increase in the top-layer thickness increased the total mass-transfer resistance, and so the total permeation rate decreased. The diffusion of water through the composite membranes became more difficult than that of 1,2-DME as the top-layer thickness increased because of the hy-

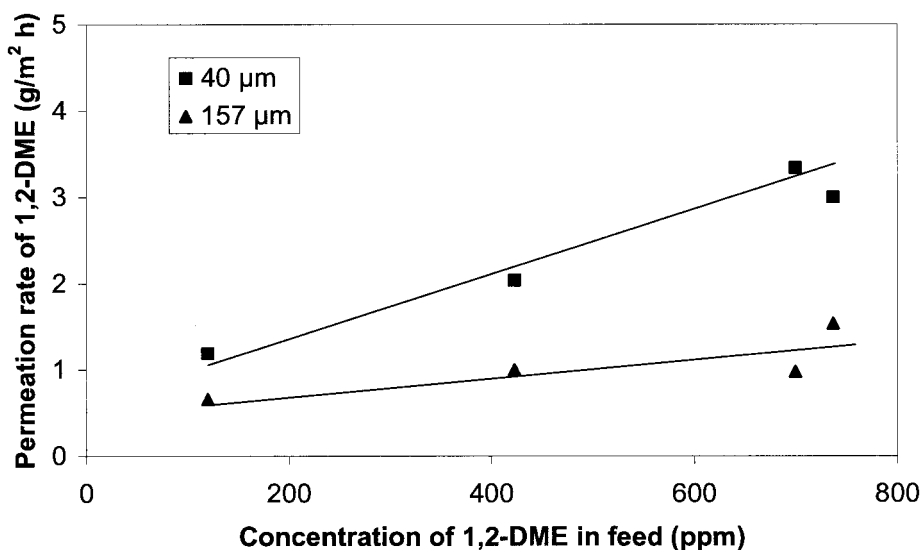


Figure 12 Effect of the feed composition on the permeation rate of 1,2-DME [feed temperature = 30°C, downstream pressure = 5 mmHg, thickness of top layer = (■) 40 or (▲) 157 μm].

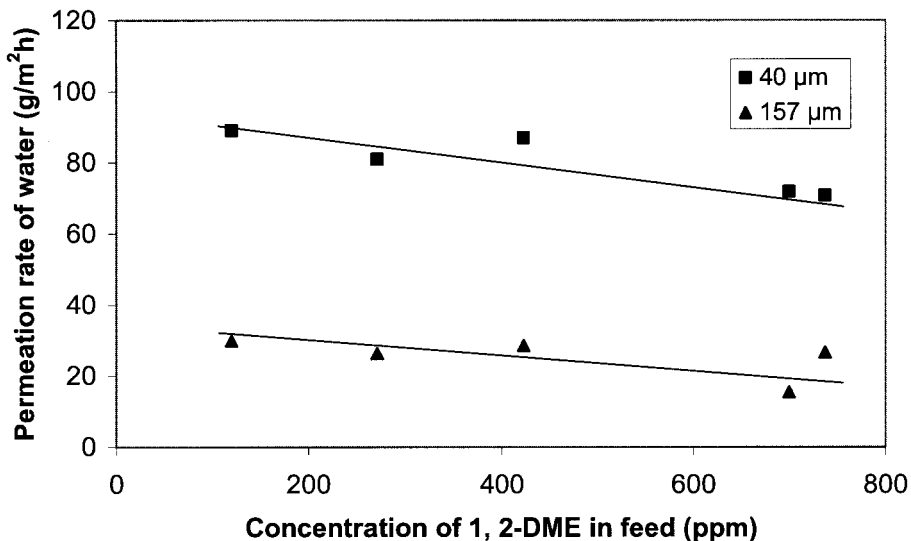


Figure 13 Effect of the feed composition on the permeation rate of water [feed temperature = 30°C, downstream pressure = 5 mmHg, thickness of top layer = (■) 40 or (▲) 157 μm].

drophobic characteristics of PDMS; therefore, the separation factor increased.

CONCLUSIONS

Composite membranes from crosslinked oligosilylstyrene-PDMS exhibited preferential selectivity to 1,2-DME for the entire range of operation conditions. The range of the separation factor was 55–184, and the range of the permeation rate of 1,2-DME was 0.31–3.3

g/m² h, depending on the feed temperature, feed composition, downstream pressure, and membrane thickness. The permeation rates of both water and 1,2-DME decreased as the downstream pressure and membrane thickness increased, but the separation factor increased with increasing membrane thickness and decreased with increasing downstream pressure. An increase in the amount of 1,2-DME in the feed solution resulted in an increase in the permeation rate of 1,2-DME and a decrease in the separation factor. An op-

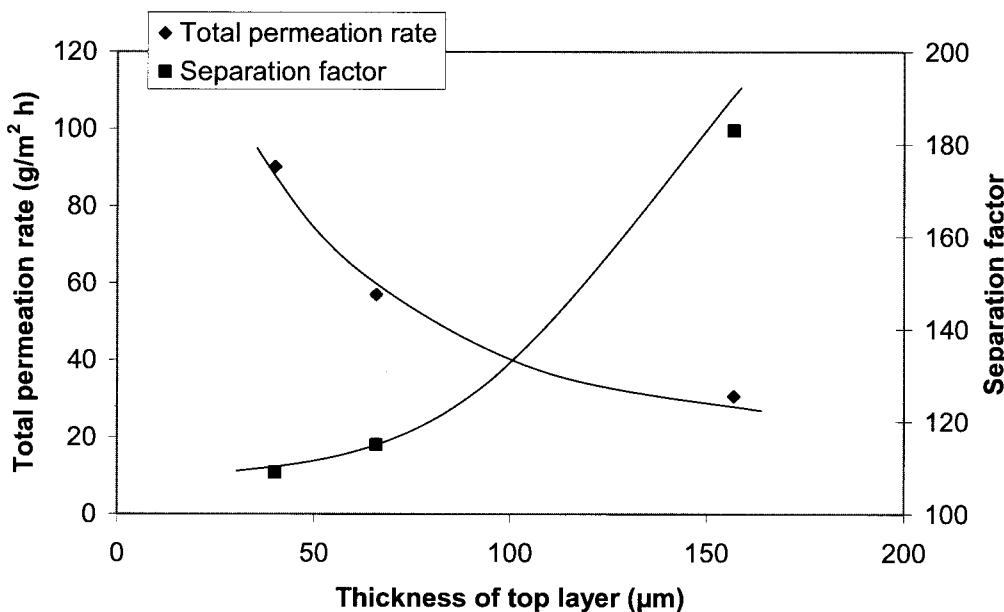


Figure 14 Effect of the top-layer thickness on the total permeation rate and separation factor (feed temperature = 30°C, downstream pressure = 5 mmHg, feed composition = 120 ppm 1,2-DME in water).

timum performance with a permeation rate of 1,2-DME of 1.66 g/m² h and a separation factor of 100 was achieved with a feed temperature of 40°C, a downstream pressure of 5 mmHg, and a feed composition of 700 ppm 1,2-DME.

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