

Silane-Modified PVC Pervaporation Membranes for Bromoform/Water Separation

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ABSTRACT: The transport properties of a unique family of silane-modified poly(vinyl chloride) (PVC) pervaporation membranes for the separation of halogenated hydrocarbons from water were investigated. The PVC was modified by using a vinyl silane to improve its resistance to attack by halogenated hydrocarbons and to increase the flux. Two preparation routes were used: Route i included an initiator to promote the vinyl reaction before the hydrolysis and condensation of the methoxy silane group, whereas Route ni did not. The structures of the membranes were characterized and related to the transport properties, as derived from batch pervaporation experiments. The permeability of unmodified PVC membranes increases with exposure to haloorganics at low concentrations. Initially, the modified membranes exhibited a higher permeability than PVC and a lower selectivity. At long pervaporation times, the silane-modified membranes exhibited a higher selectivity than PVC. The different preparation routes led to different morphologies, which affected the performance of the membranes; Route ni membranes exhibited higher permeabilities and selectivity than Route i membranes. Rubbery polydimethylsiloxane membranes were resistant to haloorganics but their high water permeability and low selectivity make them unsuitable for this pervaporative separation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1429–1438, 2001

Key words: PVC; vinyl silane; pervaporation; haloorganics; bromoform

INTRODUCTION

Pervaporation is a liquid/liquid separation process in which the more volatile component of a solution is separated by its selective permeation through a nonporous (dense) membrane and its more rapid evaporation at the downstream sur-

face. The transport of the permeate through the dense permselective membrane involves three successive steps: (i) partition of the components between the bulk and the layer at the upstream membrane surface; (ii) diffusion through the permselective membrane; (iii) desorption at the downstream membrane surface.¹

Trihalomethanes (THMs) are a major drinking water contaminant group and the U.S. Environmental Protection Agency lists them among the 100 most hazardous contaminants.² THMs originate in the chemical reaction of chlorine or bromine with organic matter. They are usually intro-

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duced into drinking water as disinfection by-products (DBP) during drinking water disinfection using chlorine. The suspected carcinogenic nature of THMs has led to strict regulations.³

The techniques used to eliminate THMs include the following: active carbon filtration, anion exchange, air stripping, membrane filtration, coagulation, and changing of the disinfection agent.^{2–10} None of these techniques is suitable for all situations and a comprehensive solution to the problem has yet to be found. Research on the separation of THMs by pervaporation has concentrated mainly on chloroform,^{11–14} but brominated compounds may present an even bigger problem in areas where bromine is found naturally.^{2,15,16}

The criteria for choosing a membrane include its selectivity toward the volatile compound and its resistance to dissolution and cracking.^{10,11,17–22} One method of predicting selectivity is based on the difference in the solubility parameters (δ) of the membranes and solute.²⁰ Membranes for the separation of volatile halogenated hydrocarbons from water should have a solubility parameter close to that of halogenated hydrocarbons.²³ Poly(vinyl chloride) (PVC), with its solubility parameter of 19.2–22.1 (J/cm^3)^{1/2}²⁴ could, therefore, be of interest for the separation of haloorganics such as bromoform (BF) [$\delta = 19.5$ (J/cm^3)^{1/2}]²⁴ from water. PVC, however, has a low chemical resistance to such solvents. In addition, the liquid flux through the glassy PVC would be relatively low. Modified PVC for such membrane applications should exhibit enhanced chemical resistance and a higher flux. Crosslinking the PVC should improve solvent resistance.²⁵ Incorporating a high free-volume moiety within the PVC should increase the flux through the enlargement of the molecular sieving diameter.

Previous research has shown that silane modification of PVC yields unique physically entrapped semi-interpenetrating polymer networks (IPN). By using different preparation routes, the film morphology could be altered by controlling the phase separation of domains rich in reacted silane (r-silane).²⁶

In this research, the use of silane-modified PVC membranes for the pervaporative separation of haloorganic-contaminated water was investigated.

MATERIALS AND METHODS

A commercial 0.05-mm-thick PVC film containing approximately 10% of a rubbery acrylonitrile–

butadiene–styrene (ABS) derivative impact modifier (Poliraz Inc., Kibbutz Moaz Haim, Israel) was modified by using a vinyl silane, γ -methacryloxypropyl trimethoxysilane (MPTS, Silquest® A-174, Witco). The following chemicals were used in the modification process: acetic acid (AA) (analytical grade, Merck) to catalyze the hydrolysis and condensation reactions and benzoyl peroxide (BP) (97%, Merck) to initiate vinyl polymerization. The following haloorganic contaminants (Analytical, Fluka) were used: chloroform, bromodichloroethane, dibromochloroethane, bromoform (BF), and tetrachloroethylene. All chemicals were used as received without further purification.

A 0.5-mm-thick crosslinked poly(dimethyl siloxane) (PDMS) control membrane was prepared by casting a prepolymer (Gvolut Polymers, Kibbutz Gvolut, Israel) (molecular weight ~ 3700) with a crosslinking agent and an initiator on glass fiber filter paper, degassing for 30 min, and curing at 120°C for 20 min.

Membrane Preparation

The PVC films were modified with MPTS by using one of two different routes. The major difference between the routes was that in Route i an initiator was used to facilitate vinyl polymerization before the exposure to water for methoxy hydrolysis and condensation (HC). In Route ni, no initiator was used and, therefore, the HC reaction predominated.

Route i consisted of three steps:

Absorption: the PVC film was immersed for 20 min in a silane solution (10% MPTS in toluene) containing 1% BP at 80°C;

Polymerization: the silane-swollen PVC was placed in a press for 2 h at 80°C under minimal pressure, to prevent curling;

HC: the pressed film was then immersed for 48 h in a 2% AA aqueous solution at 70°C to hydrolyze the Si—O—CH₃ groups and to condense the resulting Si—OH groups into siloxane crosslinks.

Route ni consisted of two steps:

Absorption: the PVC was immersed for 20 min in MPTS (containing no initiator) at 80°C;

HC: the silane-swollen PVC film was then exposed to steam for 30 min at 120°C in a

pressure cooker at 200 kPa to promote hydrolysis and condensation.

Film Morphology and Topography

The film surface topography and atomic composition of the membrane surface was characterized by using scanning electron microscopy (Jeol JSM 840) with energy dispersive spectroscopy (EDS; Link Isis, Oxford Instruments). Secondary electron (SE) and backscattered electron (BSE) images, as well as Si and Cl EDS maps, were taken of carbon-coated specimens by using an accelerating voltage of 10 kV. High-resolution scanning electron microscopy (HRSEM, Leo Zeiss) was used to characterize the cryogenic fracture cross sections of the membranes. The cryogenic fracture surfaces were coated with a thin layer of gold and viewed by using an accelerating voltage of 1–4 kV. In addition, the topography and root mean square (RMS) roughness of the membrane surfaces were characterized by using atomic force microscopy (AFM; Autoprobe CP AFM, Park Scientific) operated in the contact mode, with a 10-nm nominal tip radius (Si Ultralevers).

FTIR

Fourier transform infrared spectroscopy (FTIR; Brüker Equinox 55) was used to characterize the molecular structure of the silane-modified PVC.

DSC

The glass transition temperature (T_g) was determined using differential scanning calorimetry (DSC; Mettler DSC821) under a nitrogen atmosphere. The specimen (approximately 9 mg) was placed in a standard aluminum crucible, cooled to -100°C , and heated to 150°C at $10^\circ\text{C}/\text{min}$ (first heat). Entrapped water was evaporated and the thermal history erased during this first heat. The samples were then cooled to -100°C and reheated to 150°C at $10^\circ\text{C}/\text{min}$ (second heat). The T_g 's were determined from the second heat.

Batch Pervaporation

Batch pervaporation experiments were performed using the cylindrical batch pervaporation cell illustrated schematically in Figure 1. The membrane was supported by a porous metal plate and sealed using Viton O-rings. The cell was filled with haloorganic contaminated water. The sampling opening was also sealed with Viton rubber.

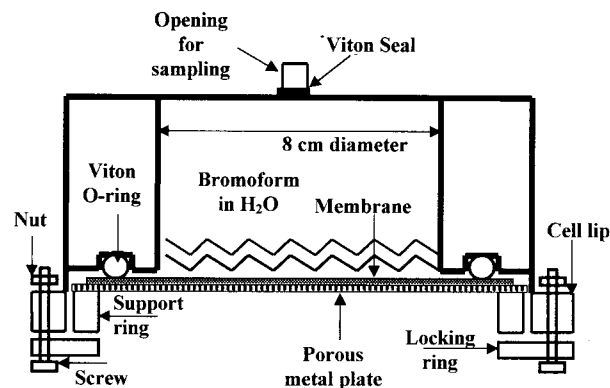


Figure 1 Schematic illustration of batch pervaporation cell.

The pervaporation cell was placed in a vacuum oven at 30°C and 40 Pa. At specific time intervals, the cell was weighed and then samples for gas chromatography analysis (2 mL) were taken with a syringe. The average total flux over the time period was calculated from the weight change divided by the time and membrane area.

The haloorganic concentration was determined using liquid–liquid extraction and gas chromatography²⁷ [a Packard 427 gas chromatograph equipped with a 2-mm ID \times 2-m-long glass column packed with 1% SP-1000 on Carbowax B (60/80) and an electron capture detector (ECD)].

The average haloorganic flux over the time period was calculated by using a mass balance. The selectivity, α , was calculated according to eq. 1:

$$\alpha = \frac{C'_A/C'_B}{C_A/C_B} \quad (1)$$

where A is the haloorganic; B is water; C is the weight concentration in the feed (kg/kg); and C' is the weight concentration in the permeate (kg/kg). The permeability of water through the membranes, P (m^2/s) was calculated according to eq. 2. The water permeability was calculated by taking the total flux for the pervaporation experiment as the water flux, because the BF flux was negligible.

$$P = J \cdot L \quad (2)$$

where J is the water flux [$\text{m}^3/(\text{m}^2 \text{ s})$] and L is the membrane thickness (m).

Two types of feed were used:

Feed I: A mixture of five haloorganics (chloroform, bromodichloromethane, dibromochloromethane, BF, and tetrachloroethylene), each at a concentration of 0.2 mg/L. The feed solution was weighed and sampled at 0, 1, 8, 14, 31, and 55 h. The results for BF will be discussed in detail.

Feed II: 2.3 mg/L BF in water. The feed solution was weighed and sampled at 0, 17, 41, and 71 h.

Multistep Pervaporation

The effects of haloorganics on the transport characteristics of the membranes were studied by performing five experiments in succession using different feeds: (1) water permeability (5 h); (2) feed I pervaporation (12 h); (3) water permeability (24 h); (4) feed I pervaporation (48 h); and (5) water permeability (72 h). The first water permeation experiment was used to establish a baseline for water permeability. The first feed I experiment was used to determine the effects of a relatively short exposure to haloorganics. The second feed I experiment was used to determine the effects of a relatively long exposure to haloorganics.

RESULTS AND DISCUSSION

Phase Separation

Fracture surfaces of the PVC and Route ni and Route i membranes are seen in Figure 2(a), (b), and (c), respectively. The submicrometer phase-separated domains in the cross section of the commercial PVC film [Fig. 2(a)] represents the 10% ABS-derivative impact modifier added to the PVC by the manufacturer. There is an additional phase in the Route ni membrane (Fig. 2b) that was not observed in the PVC. Solid-state NMR indicates that this additional phase, with domains up to 400 nm in size, is rich in reacted MPTS (*r*-silane).²⁶ There is also an *r*-silane-rich phase on the membrane surface. A combined SEM/EDS image of the Route ni membrane surface is seen in Figure 3. The four sections of this figure represent an SE image, a BSE image, an Si concentration map, and a Cl concentration map. For the elemental maps, the elemental concentration is represented by white dots. The SE and BSE micrographs in Figure 3 show a smooth sur-

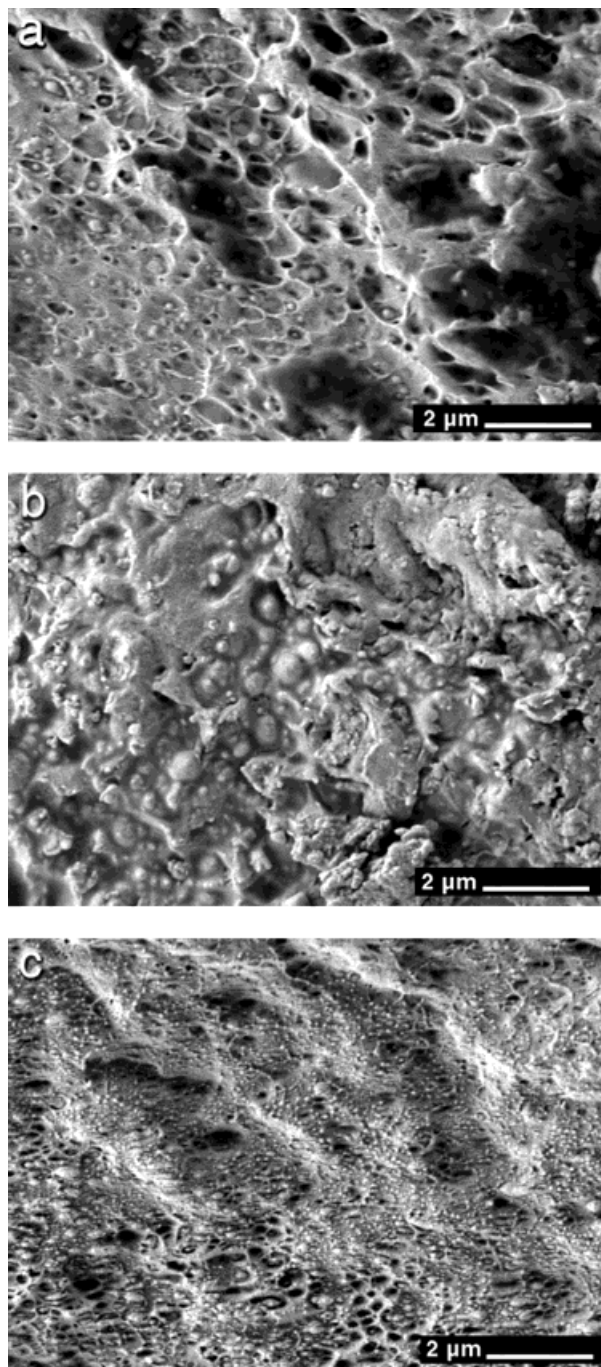


Figure 2 HRSEM micrographs of cryogenic fracture cross sections for the membranes: (a) PVC; (b) Route ni; (c) Route i.

face with a crack across the center. There is an abundance of Si and a paucity of Cl on the Route ni membrane surface, indicating that a phase-separated silane-rich layer has formed. The underlying material, exposed through the crack, displays lower Si and higher Cl concentrations, representing a combination of PVC and *r*-silane.

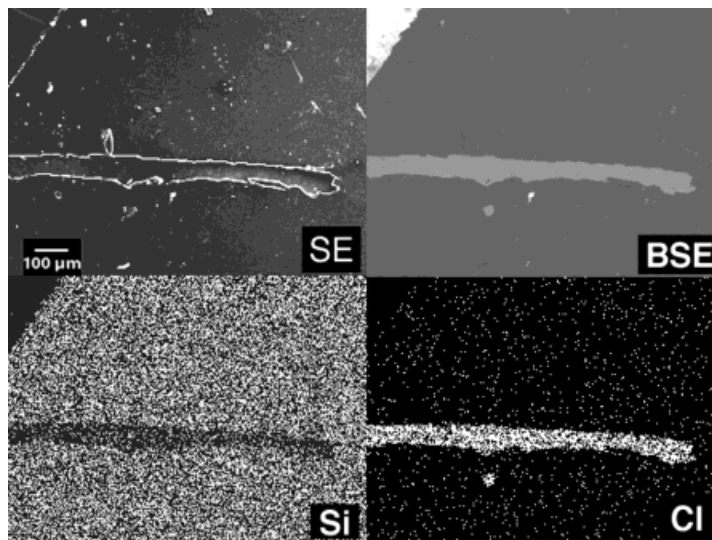


Figure 3 Micrographs of a Route ni membrane surface: (SE) secondary electron image; (BSE) backscattered electron image; (Si) Si concentration map; (Cl) Cl concentration map.

The Route i membrane also displays a phase-separated structure [Fig. 2(c)]. The phase-separated domains in the Route i membrane are approximately 50 nm in diameter, roughly an order of magnitude smaller than those in the Route ni membrane. The finer distribution of *r*-silane-rich domains in the Route i membrane is a direct result of the difference in the preparation routes. The almost complete reaction of the MPTS vinyl groups limits the mobility of the *r*-silane mole-

cules and prevented extensive phase separation. The extent of the vinyl reaction was investigated by FTIR (Fig. 4). The strong FTIR peak at 819 cm^{-1} , associated with the vinyl groups in MPTS, is barely discernible in the Route i membrane. The Route ni membrane, on the other hand, has a prominent peak at 816 cm^{-1} , representing unreacted vinyl groups.

DSC thermograms for the PVC, Route i, and Route ni membranes are seen in Figure 5. The

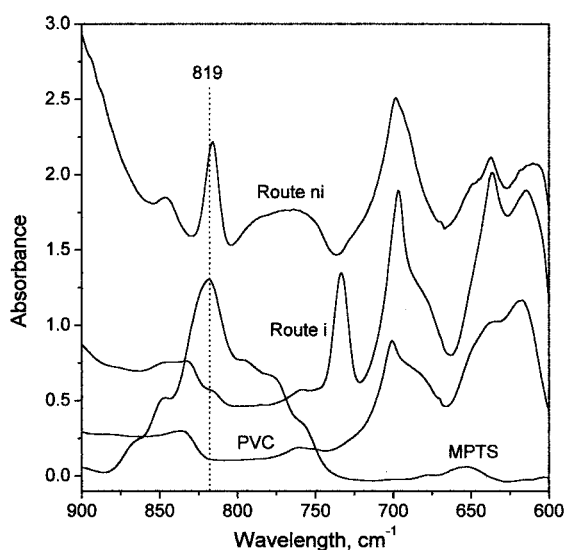


Figure 4 FTIR spectra of PVC, MPTS, and Route i membranes.

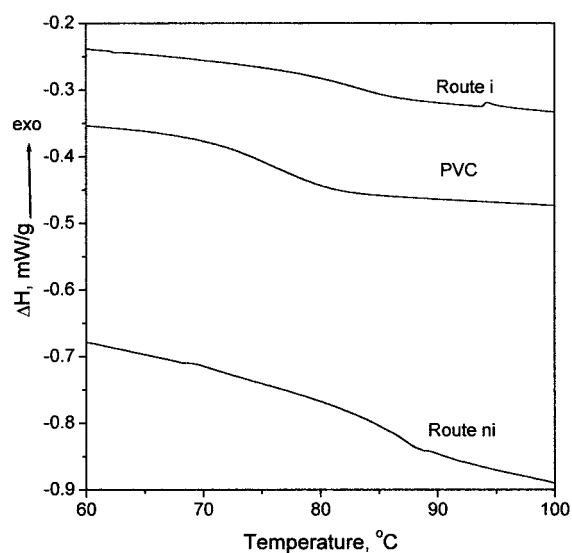


Figure 5 DSC thermograms for PVC, Route i, and Route ni membranes.

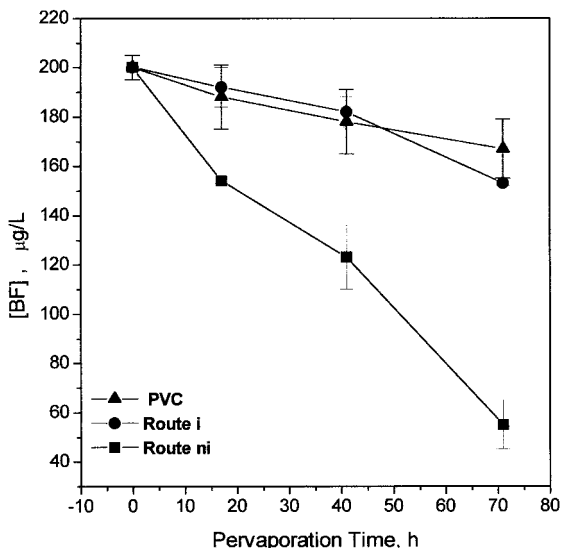


Figure 6 Variation of BF concentration in feed with time during batch pervaporation (initial feed: 0.2 mg/L BF in 1 mg/L haloorganics).

PVC T_g , derived from the DSC thermogram, is 75.0°C. The T_g associated with PVC increases by 5 and 7.5°C for the Route i and Route ni membranes, respectively. This increase in the T_g associated with PVC is attributed to the intimate mixing between the PVC and the stiff, crosslinked, r-silane network. The semi-IPN structure hinders the movement of the PVC molecular segments, raising the T_g .

Batch Pervaporation of 0.2 mg/L BF in 1 mg/L Haloorganics

The initial concentration of BF was 0.2 mg/L in a feed that contained a total of 1 mg/L haloorganic contaminants. The results for the other compounds (not reported) were similar to those of bromoform.

PVC

The BF concentration in the feed decreases with time, as seen in Figure 6. This decrease continues until the end of the experiment; a limiting BF concentration was not reached. The total flux is several orders of magnitude greater than the BF flux and, thus, the water flux, which is the difference between them, is practically identical to the total flux. The total flux through PVC increases during the first 40 h and then reaches a plateau of $4\text{E}-4 \text{ kg}/(\text{m}^2 \text{ h})$ (Fig. 7). The flux in Figure 7 is an average based on a mass balance between two

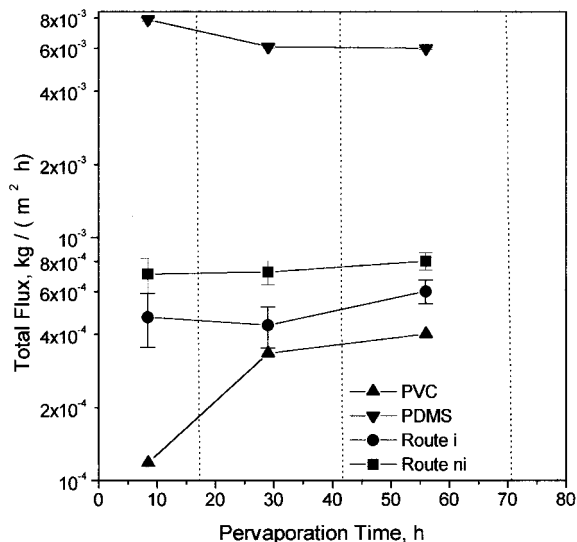


Figure 7 Variation of total flux (\approx water flux) with time during batch pervaporation (initial feed: 0.2 mg/L BF in 1 mg/L haloorganics).

points in time (the dotted lines). The average BF flux through PVC decreases by more than 50% during the experiment, from $9\text{E}-9 \text{ kg}/(\text{m}^2 \text{ h})$ to $4\text{E}-9 \text{ kg}/(\text{m}^2 \text{ h})$ (Fig. 8). The BF selectivity of PVC decreases with time (Fig. 9), reflecting the increase in water flux coupled with the decrease in BF flux.

PDMS

The total flux through PDMS is over an order of magnitude greater than that through PVC (Fig. 7).

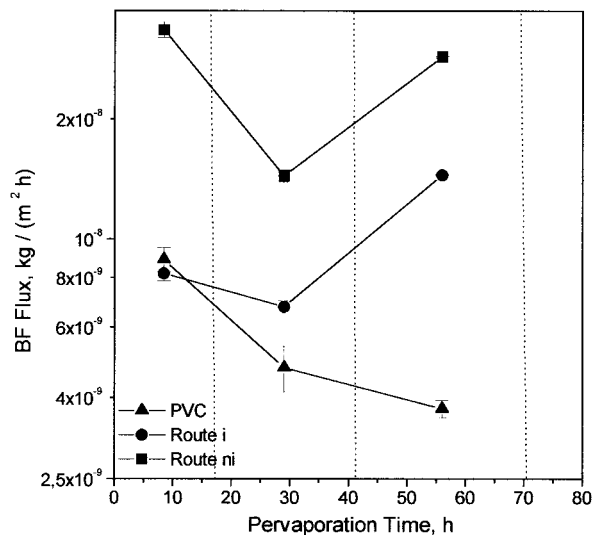


Figure 8 Variation of BF flux with time during batch pervaporation (initial feed: 0.2 mg/L BF in 1 mg/L haloorganics).

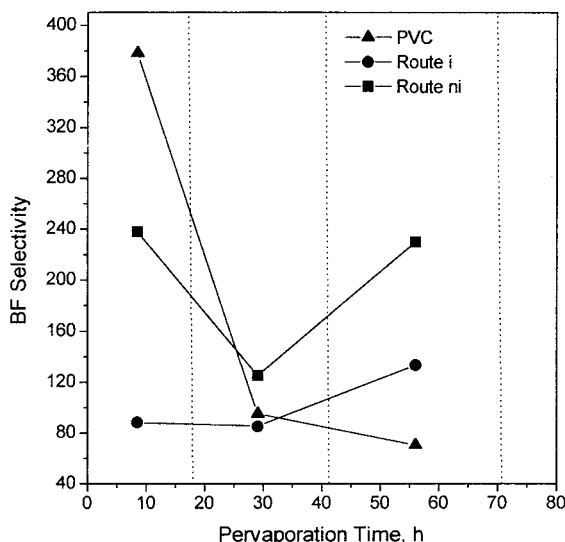


Figure 9 Variation of selectivity with time during batch pervaporation (initial feed: 0.2 mg/L BF in 1 mg/L haloorganics).

The BF flux through PDMS in this experiment was so high that within 20 h the BF concentration in the feed was less than the detection limit of 10 $\mu\text{g/L}$. The flux through PDMS is high, but its selectivity is low in the investigated concentration range.

Route i Membrane

The BF concentration in the feed decreases with pervaporation time through Route i membranes (Fig. 6). The BF concentration in the feed is similar to that for PVC for the first 40 h and is slightly less than that for PVC after 70 h of pervaporation. The total flux is relatively constant, greater than the flux through PVC and less than the flux through PDMS (Fig. 7). Initially, the BF flux is similar to that for PVC. There is a small decrease in BF flux, followed by an increase for the Route i membrane (Fig. 8) as compared to the rapid decrease in BF flux for PVC. The BF flux, after 70 h of pervaporation, is higher than the initial BF flux. This unusual combination, a decrease in BF flux, followed by an increase, is reproducible. Initially, there is a significantly higher water flux through the Route i membrane than through PVC for similar BF fluxes. Therefore, the initial Route i membrane selectivity is lower than that of PVC (Fig. 9). The decrease, and subsequent increase, in BF flux yields similar changes in selectivity, because the water flux is relatively constant. The selectivity of the Route i membrane, after 70 h of pervaporation, is higher

than that of PVC, reflecting the significantly higher BF flux through the Route i membrane. A summary of the three parameters for the Route i membrane, showing the dependence of selectivity on the BF and water fluxes, is seen in Figure 10.

Route ni Membrane

The BF concentration in the feed decreases with pervaporation time for the Route ni membrane (Fig. 6). The BF concentration's rate of decrease is significantly higher than those for PVC or the Route i membrane. The total flux through the film is relatively constant, as seen for the Route i membrane (Fig. 7). The total flux is greater than those through the PVC and Route i membranes and less than that through PDMS. The BF flux, however, is significantly higher than those through the PVC or Route i membranes and varies in the same manner as that through the Route i membrane, a decrease followed by an increase (Fig. 8). The BF flux after 70 h of pervaporation is similar to that at the beginning of the experiment, 2.1E-3 kg/(m² h). Initially, the selectivity of the Route ni membrane (Fig. 9) is lower than that of PVC, reflecting the significantly lower flux of water through PVC. The initial selectivity of the Route ni membrane is higher than that of the Route i membrane, reflecting the significantly lower BF flux through the Route i membrane. The selectivity

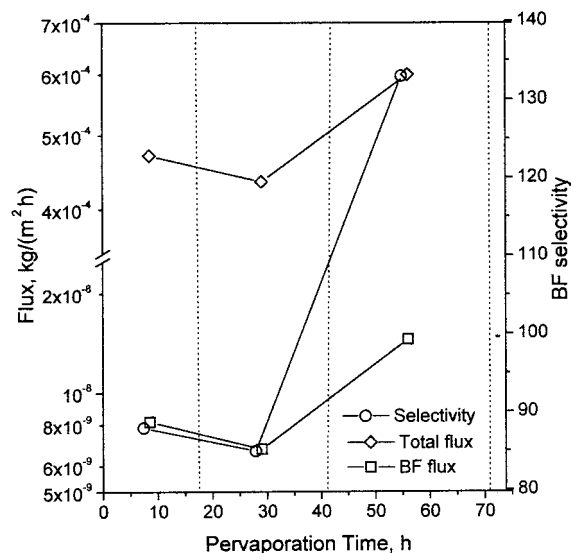


Figure 10 Variation of BF flux, water flux, and selectivity during batch pervaporation using a Route i membrane (initial feed: 0.2 mg/L BF in 1 mg/L haloorganics).

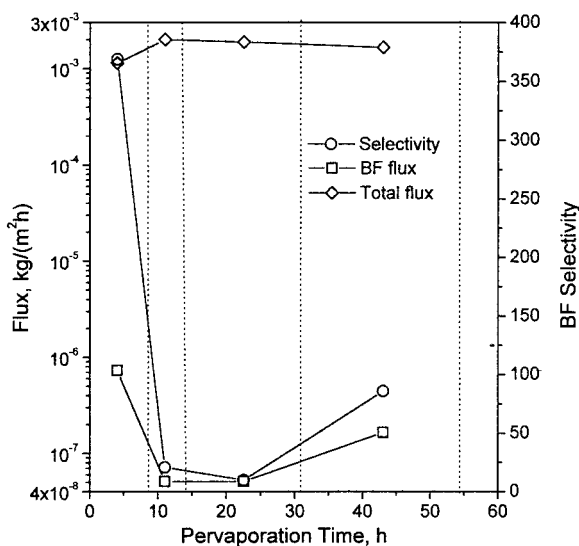


Figure 11 Variation of BF flux, water flux, and selectivity during batch pervaporation using a Route i membrane (initial feed: 2.26 mg/L BF).

of the Route ni membrane, after 70 h of pervaporation (Fig. 9), is higher than those of the PVC and Route i membranes, reflecting the significantly higher BF flux (Fig. 8) for similar water fluxes (Fig. 7).

Batch Pervaporation, 2.26 mg/L BF

The results of pervaporation from an initial feed of 2.26 mg/L BF through a Route i membrane are summarized in Figure 11. The BF flux decreases and, then, increases, similar to the pervaporation from an initial concentration of 0.2 mg/L BF in 1 mg/L haloorganics (Fig. 10). After 41 h of pervaporation, the BF concentration is reduced from 2.26 to 0.8 mg/L. The selectivity decreases and, then, increases, as seen previously (Fig. 10). The $1.6\text{E}-3 \text{ kg}/(\text{m}^2 \text{ h})$ total flux is higher than the flux

of about $5\text{E}-4 \text{ kg}/(\text{m}^2 \text{ h})$ for 1 mg/L haloorganics. The total flux is relatively constant in both cases. Increasing the haloorganic concentration in the feed by about 2.3 fold yields a 3.2 fold increase in total flux.

Effects of Haloorganic Exposure on Membrane Properties

PVC

The permeability of water through a fresh (previously unused) PVC membrane remains a constant $4\text{E}-16 \text{ m}^2/\text{s}$ (Table I, #1) during the first experiment (water alone). The permeability of water during a relatively short haloorganic pervaporation (second experiment) varies with time, reaching a maximum of $48\text{E}-16 \text{ m}^2/\text{s}$ (Table I, #2). The permeability of water in the presence of a haloorganic contaminant is more than an order of magnitude greater than that for water alone. The permeability of water in the third experiment (water alone, Table I, #3) returns to its previous value of $4\text{E}-16 \text{ m}^2/\text{s}$, in spite of the membrane's exposure to haloorganics. The permeability of water during the fourth experiment, a relatively long haloorganic pervaporation, reaches a maximum of $26\text{E}-16 \text{ m}^2/\text{s}$ (Table I, #4). The water permeability does not return to its original value during the fifth experiment (water alone, Table I, #5). Instead, the high water permeability exhibited in the presence of haloorganic contaminants during the fourth experiment is maintained. These observations suggest that haloorganic exposure causes changes in the PVC film and alters the permeation pathway.

One mechanism that could account for such changes in permeability is crazing on exposure to even low concentrations of haloorganics. The crazes may heal, restoring the original permeabil-

Table I Effect of Exposure to Haloorganics on the Membrane's Water Permeability

No.	Feed	Time (h)	Average Water Permeability ($\text{m}^2/\text{s}) \times 10^{16}$			
			PVC	PDMS	Route ni	Route i
1	Water	5	4 ± 2	3000 ± 1900	320 ± 170	86 ± 33
2	Feed I	12	4; 48; 48 ^a	2700 ± 100	291 ± 186	9.5 ± 4.2
3	Water	24	4 ± 2	3100 ± 240	370 ± 130	75 ± 10
4	Feed I	48	4; 26; 14 ^a	2700 ± 380	100 ± 81	51 ± 20
5	Water	72	52 ± 48	3100 ± 240	180 ± 43	76 ± 21

^a PVC: the water permeability changes considerably during pervaporation with Feed I. The permeabilities reported are the initial, maximum, and final.

ity, after a relatively brief exposure to haloorganics. The crazes become permanent, and the permeability remains high, following a sufficiently long exposure to haloorganics. Environmental stress crazing has been observed in mechanically constrained glassy polymers.²⁴ The mechanical constraints of the batch pervaporation cell which prevent the relief of internal stress through deformation may enhance craze formation in these glassy PVC membranes.²⁸

PDMS

The following observations can be made for PDMS:

1. The permeability of water through a fresh (unused) PDMS membrane, $3000\text{E}-16$ (m^2/s) is three orders of magnitude higher than that through PVC (Table I, #1).
2. The permeability of water does not change in the presence of haloorganics.

The high permeability reflects the rubbery nature of PDMS. As glassy polymers undergo crazing and rubbery polymers do not,²⁴ PVC is likely, therefore, to craze in the presence of haloorganics and PDMS is not.

Route ni and Route i Membranes

The permeability of water through the Route ni membrane during the first three experiments lies between $291\text{E}-16$ and $370\text{E}-16$ m^2/s (Table I, #1–3). The permeability decreases to between $100\text{E}-16$ and $180\text{E}-16$ m^2/s during the subsequent experiments (Table I, #4, 5). The water permeability, 60–80 times that for PVC, may reflect the influence of the large, r-silane-rich domains with a high free volume. The presence of haloorganic compounds does not seem to affect the Route ni membrane. The unexpected decrease in permeability with time may be related to the incomplete silane condensation observed using solid-state NMR.²⁶ The condensation of the silanol groups can continue during water permeation, yielding a denser and more densely crosslinked membrane.

The water permeability through an unused Route i membrane ($86\text{E}-16$ m^2/s), about 22 times that of PVC, may reflect its semi-IPN structure. The presence of an r-silane network can enhance the free volume, although not as effectively as the r-silane domains in the Route ni membrane. The

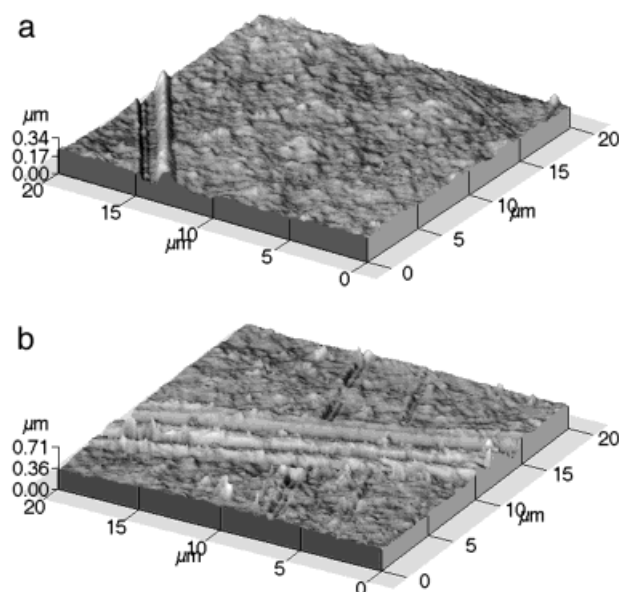


Figure 12 AFM images of PVC membranes (a) before and (b) after the five experiments.

reproducible decrease in the permeability of water during the relatively short pervaporation is unusual.

Film Topography

The PVC surface was characterized by AFM before and after the five experiments in Table I (Fig. 12). The as-received PVC film [Fig. 12(a)] is smooth and uniform, with an RMS roughness of 24.5 nm and few defects. Following the five experiments, the PVC film [Fig. 12(b)] has deep lines etched in the surface and the RMS roughness has doubled (55.0 nm). This change in PVC roughness may reflect the crazing on exposure to haloorganics that yields the increase in the permeability of water.

CONCLUSION

The pervaporation of haloorganics through PVC, silane-modified PVC, and PDMS membranes was investigated and the transport characteristics were related to membrane structure. During the pervaporation of haloorganic contaminated water, the PVC membranes exhibited an increase in the water flux, a decrease in the haloorganic flux, and a decrease in selectivity. The increase in water permeability through PVC was associated with changes in the permeation path resulting

from crazing on exposure to the haloorganic environment. The effects of haloorganic exposure are also reflected in the significant increase in RMS roughness. The water permeability through the silane-modified membranes was significantly higher and remained relatively constant. Initially, PVC's BF selectivity was higher than those of the silane-modified PVCs. The silane-modified PVCs, however, exhibited superior BF selectivity at long pervaporation times. The water permeability of rubbery PDMS is three orders of magnitude greater than that of PVC, making it unsuitable for this pervaporative separation.

Route i yields a semi-IPN membrane with phase-separated r-silane-rich domains limited to 50 nm. The silane's vinyl groups polymerize to near completion in the presence of an initiator and this restricts silane molecular mobility and limits phase separation. Route ni yields a membrane containing larger phase-separated domains (400 nm) which are rich in silane, because the silane molecular mobility is not restricted by vinyl polymerization. The larger domains in the Route ni membrane, rich in the high free volume silane, yield a higher water flux, BF flux, and selectivity than those seen for the Route i membrane.

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