Evaluation of Membranes Containing Surface Modifying Macromolecules: Determination of the Chloroform Separation from Aqueous Mixtures via Pervaporation

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ABSTRACT: The pervaporation performance of polyethersulfone (PES) membranes prepared by incorporating surface modifying macromolecules (SMMs) was evaluated via experiments with chloroform/water mixtures as the feed. Isolation and chemical analysis of the organics in the permeate revealed that the permeate contained virtually no chloroform. The bulk of the isolated organic compounds was ethanol. This differed from previous reports, which claimed that the organic component isolated via gas chromatographic analysis was chloroform (Y. Fang et al., *Journal of Applied Polymer Science,* 1994, Vol. 54, pp. 1934–1943; Y. Fang et al., in *Proceedings of the Seventh International Conference on Pervaporation Processes in the Chemical Industry,* R. A. Bakish, Ed., Bakish Materials Corporation: Englewood, NJ, 1995, pp 349–362). It was demonstrated that ethanol, used during the solvent exchange drying step of membrane preparation, was retained in the membrane and leached out during membrane use. However, while it was observed that SMMs in PES membranes contributed to no enrichment of chloroform, there was a significant depletion of chloroform achieved in the permeate. The increased separation of chloroform from the SMM-modified membranes is hypothesized to be related to the unique fluorinated surface character endorsed within the material by the novel modification process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 183–189, 2001

Key words: pervaporation; volatile organic chemicals; polyethersulfone membrane; surface modifying macromolecules

INTRODUCTION

Separation of volatile organic chemicals (VOCs) from liquid streams via membrane pervaporation followed by their concentration in the permeate via compression-induced condensation is economically and technically comparable alternative to the existing technologies for the removal/recovery of VOCs from aqueous streams.[1] In this process, VOCs from a liquid stream are driven across a permselective membrane and exit as an enriched vapor due to the vacuum maintained in the downstream side of the membrane.[2]

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In general, membranes made from hydrophobic elastomeric polymers have been known to be highly organophilic and effective in VOC removal from water by pervaporation.[3] Hydrophobic polydimethylsiloxane (PDMS) and its copolymer membranes are widely used for pervaporation; however, they suffer from limitations of mechanical stability.[4]

Polyethersulfone (PES) membranes have inherently good mechanical and thermal properties[5] but are intrinsically water selective.[6] Fang et al.[7] and Pham[8] found that the addition of surface modifying macromolecules (SMMs) in the casting solution of PES membranes increased the hydrophobicity of the membrane surfaces. It was shown that both advancing and receding contact angles values, which increased with increasing SMMs content. Fang et al.[7] also reported that the separation of organics from a 1000 ppm chloroform/water feed mixture increased with increasing the concentration of the fluorinated SMM in the SMMs/PES casting solution, and exhibited the highest separation at 1.0 to 1.5 wt % of SMMs and then decreased. The highest chloroform permeate concentration was reported to be 15,000 ppm. Fang et al.[7] isolated the organic compounds by gas chromatography and used a Waters differential refractometer as a means of quantifying their amounts. A single peak was associated with an organic compound and was assigned to chloroform without further characterization of the isolated product. The flux increased with increasing SMMs concentration.

The current study reinvestigates the performance of these PES/SMMs membranes on the separation of chloroform from aqueous solutions via pervaporation, using more refined chromatographic separation methods in order to confirm the identification of the separated organic compounds.

EXPERIMENTAL

The experiments carried out in this work involved four steps: (a) preparation of casting solutions, (b) membrane casting and gelation, (c) membrane drying by the solvent exchange method, and (d) pervaporation experiments. A general description of the methods involved in each of these steps was presented elsewhere[9], however some specific conditions were varied and these are briefly described below. The nomenclature for the membranes is represented by an alpha numeric label, i.e., "Q1a," which defines its casting solution, time of casting, and label for the specific membrane. For example, in the sample Q1a, the first α symbol, i.e., "Q," indicates the casting solution type, the numeric symbol, i.e., "1," indicates the timing of casting a specific batch from solution Q, and the final α symbol "a" indicates the label of the specific membrane casted at time 1.

Casting Solutions

A casting solution, labeled "Q" was prepared. Specifically solution Q, was made up with polyvinylpyrrolidone (molecular weight 10,000, Aldrich Chemical Company, Inc., Milwaukee, WI), PES (Victrex 4800P, ICI Advanced Materials, Billingham, Cleveland, England), SMM, and dimethylacetamide (DMAc) (BDH, Inc., Toronto, ON). The concentrations of the above components were 1.5, 25.0, 1.0, and 72.5 wt %, respectively. SMM was synthesized by Pham[8] from methylene di-phenyl diisocyanate: polypropylene diol:fluorotelomer intermediate {BA-L (low fraction)} in stoichiometric proportions of 3:2:2.

Membrane Casting, Evaporation, and Gelation

Solution Q was stirred for 13 days at 55°C, and then degassed for 48 h at 55°C, and stored in a refrigerator at 0°C for 268 h before the first membranes (Q1a and Q1b) were cast. The remaining casting solution was stored in a refrigerator at 4°C for 2 weeks before degassing for the second batch of casting. The second batch of membranes (Q2a and Q2b) was prepared from solution Q, after redegassing for 48 h and then cooling at 0°C for 48 h. Just prior to each casting, the solutions were taken out from the refrigerator and immediately used for membrane preparation. Immediately after casting on pyrex plates, the films along with the plates were placed for 7 min into an oven preheated at 95°C, then gelled by immersing into ice-cold water. The membranes were kept in the gelation media for 24 h.

Membrane Drying

Membranes were dried by a solvent exchange technique following the gelation process. In this technique, the water/solvent remaining in the membranes after the gelation process was exchanged with an alcohol solution (ethanol 85% and methanol 15%, BDH, Inc., Toronto, ON) through successive immersions in alcohol/water

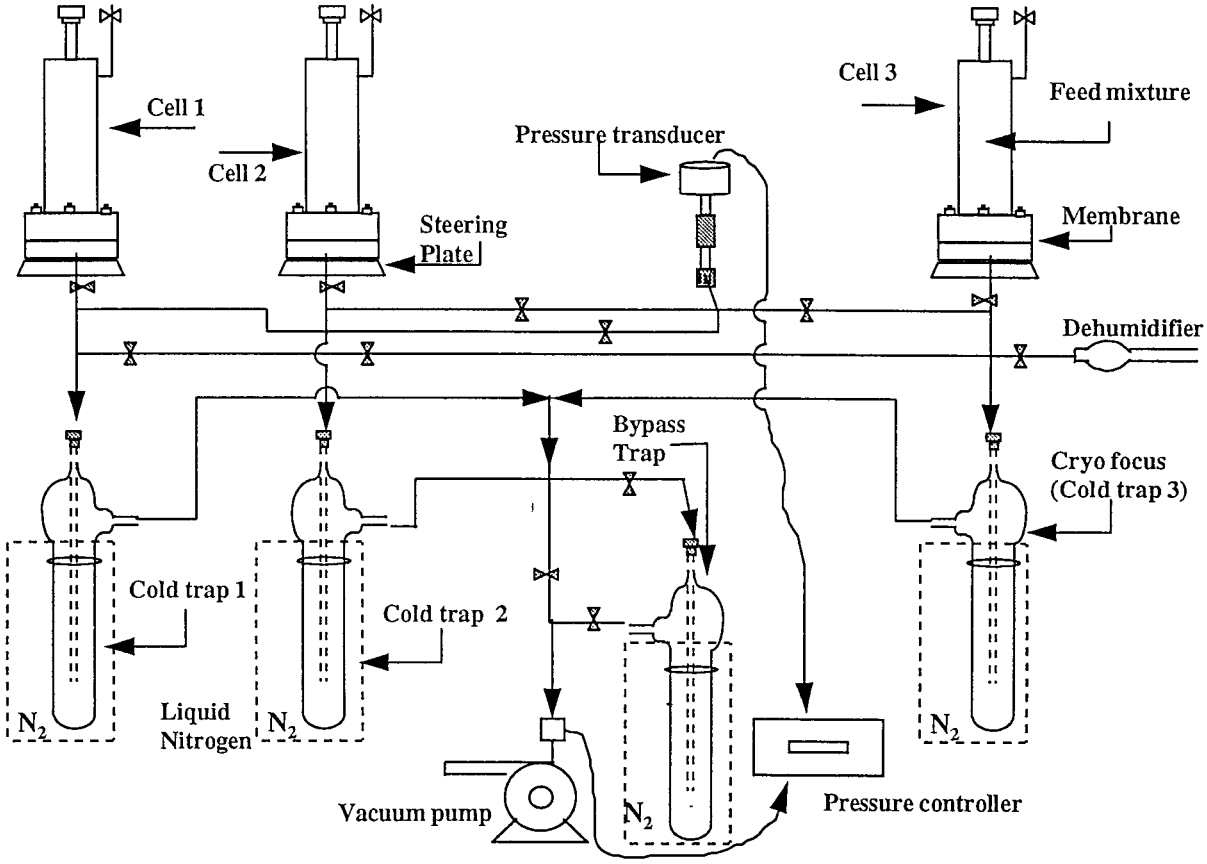

Figure 1 Membrane pervaporation experimental setup.

solutions of 25, 50, 75, and 100% by volume. The duration of each immersion was 24 h. The membranes were then removed from the alcohol and were subsequently air dried at room temperature for 24 h to yield the final membranes. Membrane Q2b was dried in air for an additional 8 days and vacuum dried (−100 kPa) for 4 days at room temperature. Each dried membrane was individually stored in a sealed polyethylene bag at room temperature.

Pervaporation Experiments

All the membranes used in pervaporation experiments for separation of $CHCl_3$/water solution were tested with a 11 ± 1 ppm $CHCl_3$ (99.8% $CHCl_3$, BDH, Inc., Toronto, ON) aqueous feed solutions. A second coupon of Q2a membrane, namely Q2a′, was tested with deionized water as a feed. This latter test was conducted as a control run to evaluate the possible contamination of the filtrate solution from other organic contaminants associated with the membrane.

The experimental setup used for the pervaporation studies is shown in Figure 1. The system consists of three independent membrane testing lines, which permit the simultaneous evaluation of three membranes for their respective feed solutions. The basic structure of the pervaporation cell was similar to that of reverse osmosis and ultrafiltration static cells, which had previously been reported by Sourirajan and Matsuura.[10] This consisted of stainless steel chambers with two detachable segments. The segments were clamped and sealed tight using rubber O-rings. The membrane was placed in between these two detachable segments on a stainless steel sintered support embedded in the lower part of the cell. The vapor/gas permeate was withdrawn through this support under a vacuum. The upper section of the cell contained the feed solution at atmospheric pressure. The feed solution was kept homogenous and concentration polarization was minimized by continuous stirring during the experiment. Mixing was accomplished by a magnetic stirrer fitted in the cell approximately 0.6

Table I Permeate Analysis Results from GC (P&T) and GC-MS

Membrane (% SMM)	Feed	Cumulative Operating Hours	GC (Purge & Trap)		GC-MS[b]	
			$CHCl_3$ (ppm)	Ethanol[a]	$CHCl_3$	Ethanol
Q1b (1.0 wt)	11 ppm $CHCl_3$	13.50	OR[c]	DD[d]	ND[e]	DD
		27.00	1.5	DD	ND	DD
		40.50	0.5	DD	ND	DD
Q1a (1.0 wt)	11 ppm $CHCl_3$	13.50	3	DD	ND	DD
		27.00	1.5	DD	ND	DD
		40.50	0.7	DD	ND	DD
Q2b[f] (1.0 wt)	11 ppm $CHCl_3$	13.50	ND	ND	ND	DD
		27.00	ND	ND	ND	DD
Q2a (1.0 wt)	11 ppm $CHCl_3$	13.50	1.2	DD	ND	DD
		27.00	1.5	DD	ND	DD
		40.50	0.8	DD	ND	DD
		54.00	0.6	DD	ND	DD
		67.50	ND	DD	ND	DD
		81.00	ND	DD	ND	DD
Q2a′ (1.0 wt)	Deionized water	13.50	ND	DD	ND	DD
		27.00	ND	DD	ND	DD
		40.50	ND	DD	ND	DD
		54.00	ND	DD	ND	DD
		67.50	ND	DD	ND	DD
		81.00	ND	DD	ND	DD

[a] The quantity of ethanol could not be determined as ethanol is not good purgeable compound.
[b] GC-MS identified chloroform and ethanol in qualitative terms only.
[c] OR: out of range. The concentration was lower than expected, so dilution factor was high for the range used.
[d] DD: detected.
[e] ND: not detected.
[f] Additionally dried membrane.

cm above the membrane surface. The effective area of the membrane in the cell was 9.6 cm^2. The cells had a capacity of 300 ± 10 mL and were connected to their individual liquid nitrogen cold traps for collection of the permeate. The traps were connected via a by-pass trap to a vacuum pump (Welch Vacuum Technology, Inc., Skokie, IL), which drove the process. The pressure was controlled by a pressure controller (MKS Type 651, MKS Instrument, Inc., Andover, MA).

The entire system including the membranes was tested for leaks by applying a vacuum prior to each run. The downstream pressure of the membrane was less than 1 mm Hg, unless otherwise stated. To allow the system to reach steady state, during the initial 90 min, only the by-pass trap was submerged in liquid nitrogen, so the permeate was only collected in this trap. After 90 min, the permeate was collected in cold traps 1, 2 and 3 from their respective cells by submerging them in liquid nitrogen and disconnecting the by-pass trap. The permeate of the by-pass trap was discarded. Each test run had a duration of 13.5 h. At the end of each test run, the cold traps along with the permeate were removed from the liquid nitrogen, both ends of the traps were sealed with parafilm, and then immediately immersed into ice cold water for 8–10 min to defrost the permeate. The permeate, which was still primarily (frozen) solid, was then pushed out of the control tube of the trap with a clean metal wire into a preweighed sample collection vial. The permeation rate was determined by measuring the mass of sample collected during the testing period. Immediately after weighing, the vial was reimmersed into ice cold water to completely melt the permeate. The liquid permeate was then immediately analyzed. Precautions were taken during permeate handling to minimize air contact. All pervaporation experiments were carried out at room temperature (23–25°C). Pervaporation tests were conducted with a number of different membranes (Table I) and each membrane was kept in the pervaporation apparatus and retested several

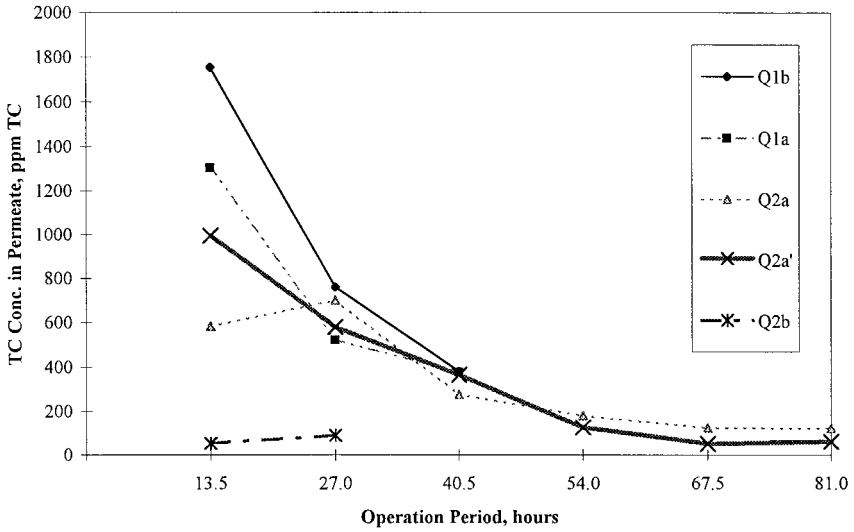

Figure 2 Effect of operation period on permeate TC concentration.

times. After each run, the feed was drained and reloaded on the following day with a fresh feed prior to the start of the test.

Analysis

The feeds and retentates were analyzed using a total organic carbon (TOC) analyzer (DC-190, Rosemount Analytical, Santa Clara, CA) and gas chromatograph (GC) with a purge and trap concentrator [GC (Purge & Trap)] to determine the concentration of purgeable organic carbon and chloroform, respectively. GC (Purge & Trap) includes a Tekmar Liquid Sample Concentrator LSC-2 (Tekmar Company, Cincinnati, OH), a Varian-Vista Series 6000 Gas Chromatograph (Varian Instrument Group, Walnut Creek, CA). The GC system had a Flame Ionization Detector, operated with a packed column (Carbopack B 60/80 Mesh, 1% SP-1000, 8 feet by 1/8 inch SS) (Supelco Canada Ltd., Oakville, ON), and a Waters 820 Chromatography Data Station as an integrator (Waters, Water Chromatography Division, Millipore Corporation, Milford, MA). The permeates were also analyzed by TOC analyzer for total carbon (TC), by GC (Purge & Trap) and gas chromatograph—mass spectrometer (GC-MS) to determine their composition. The GC-MS consists of a gas chromatograph (Model HP 5890, Series II, Hewlett Packard, Palo Alto, CA) and a Kratos Mass Spectrometer, Model Concept, Series II H. The gas chromatograph was fitted with 30 m long capillary column (DBS, J & W Scientific, Folsom, CA). Ethanol is highly soluble in water as well as difficult to strip completely from water at room temperature. Repeated analysis of ethanol standards via GC (Purge & Trap) yielded highly visible peaks; however there was poor reproducibility. This may have been the result of uneven purging. Thus, GC (Purge & Trap) analysis for ethanol will be considered on a qualitative basis only although the peaks were well above the

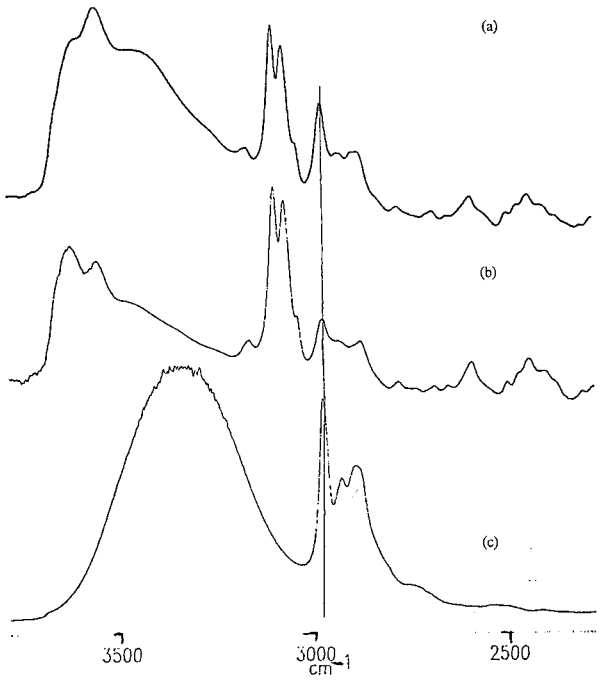

Figure 3 Fourier transform infrared spectra of the membranes.

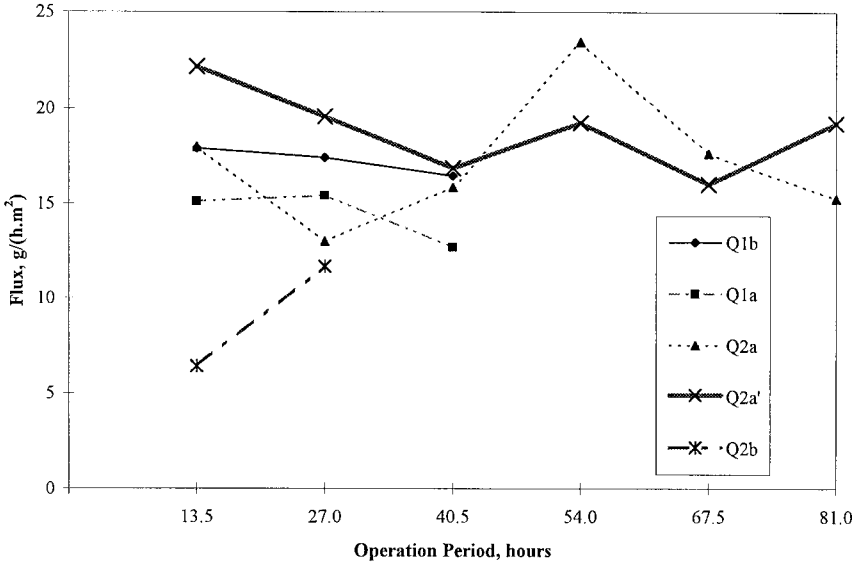

Figure 4 Effect of operating period on flux.

detection limits. The GC-MS analysis results were also qualitative and not quantitative.

Analysis of Residual Solvent in Membrane

Two specimens of the Q2a membrane, each having undergone different degrees of drying, were assessed for the presence of residual ethanol from the solvent exchange steps during membrane preparation. The analysis was conducted using a Fourier transform infrared spectrophotometer (Bomem, Vanier, PQ). One of these sample membranes was air dried for 24 h, as per the protocols described earlier and the another specimen was vacuum dried (room temperature, −100 kPa) for an additional 48 h.

RESULTS AND DISCUSSION

Figure 2 shows that the TC concentration in the permeate decreased with the period of use of the membrane except for membrane Q2b, which was well dried (8 days in air and 4 days in vacuum). This pattern was even observed for the coupon (Q2a′) of membrane Q2a that was tested with deionized water as feed.

The results of the permeate analysis by GC (P&T) and GC-MS are shown in Table I. The data from GC (P&T) indicate that the presence of chloroform in the permeate was significantly lower than that in the feed. The less sensitive GC-MS analysis could not detect chloroform in the permeate. Thus the PES-SMM membranes seem to separate chloroform from chloroform water mixture.

The GC (P&T) showed clear peaks of ethanol but its concentration could not be determined as discussed in the experimental section. The GC-MS analysis also showed the presence of ethanol in the permeate. These results suggest that the ethanol, which was used in the solvent exchange step, was partially retained in the membrane and leached out during use. Thus ethanol represents a much greater fraction of the TC in the permeate than chloroform. The decreasing trend in TC concentration in the permeate with the increase of accumulated operating period possibly relates to the fact that the leaching of ethanol was obviously higher for a fresh membrane and decreased with period of membrane use. The presence of ethanol in the membranes was further confirmed by the Fourier transform infrared (FTIR) spectra (Fig. 3). The principal ethanol peak occurs near 3000 cm^{-1} and it is marked by a vertical line in this figure. The spectra presented in Figure 3(a) shows the presence of residual ethanol after 24 h of normal drying. The spectra for the membrane subjected to the additional vacuum drying showed a substantially lower (but still measurable) ethanol concentration [Fig. 3(b)]. This indicates that the 24 h of membrane drying in air following the dehydration step is not sufficient for total removal of residual ethanol. The possibility of the carbon

originating from other sources, such as DMAc, could not be eliminated based on this work.

Flux data illustrated in Figure 4 show that the total permeation rates did not change significantly with use. It was noted that the initial flux of membrane Q2b, which was dried for a longer period, was lower but appeared to recover with a longer operating period. This requires further verification.

CONCLUSIONS

1. Residual ethanol comprises a much larger fraction of TC in the permeate than chloroform.
2. Ethanol was mistaken as chloroform enrichment in the earlier work reported by Fang et al.[7,9]
3. The PES membranes prepared by incorporating SMM do not enrich chloroform in the permeate as reported earlier.[7,9] However, the data do show that the PES membranes containing SMMs appear to be water selective as a significant depletion of chloroform was achieved in the permeate.

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