

Effect of Surface-Modifying Macromolecules and Solvent Evaporation Time on the Performance of Polyethersulfone Membranes for the Separation of Chloroform/Water Mixtures by Pervaporation

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SYNOPSIS

Polyethersulfone (PES) membranes using different evaporation periods were fabricated by the phase-inversion method. Pervaporation experiments were conducted for chloroform/water mixtures to determine the selectivity of the PES membranes. It was found that chloroform could be concentrated in the permeate from chloroform/water binary feed mixtures by PES membranes prepared using longer evaporation periods, and that the selectivity of PES membranes in pervaporation could be reversed by shorter evaporation periods. This study also showed that by adding surface-modifying macromolecules (SMM) up to 1 wt % into the casting solution, chloroform enrichment in the permeate could be increased by 50%. Chloroform enrichment increased with increasing SMM concentration until an optimal value, after which the enrichment decreased. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The membrane pervaporation process has become an industrial process in recent years.¹ As this technology is still rapidly developing in terms of membranes, modules, and engineering aspects, more applications of pervaporation are expected in the future.^{2,3} The pervaporation process can be used for the following applications:

1. Dehydration of organic solvents or solvent mixtures (alcohols, esters, ethers, ketones, hydrocarbons, acids, amines, etc.)
2. Continuous removal of water from reaction mixtures
3. Extraction of organics (esters, ethers, chlorinated hydrocarbons, aromatic compounds, etc.) from aqueous solutions
4. Recovery of aroma substances in the food industry.

Among these applications, the removal of organics from aqueous solutions is of particular interest. In the environmental industry, removal of volatile organic compounds (VOC) is becoming more and more important.⁴ In the biotechnology industry, many of the most important separation needs involve recovery of organic compounds from dilute solutions.⁵ Although attempts were made in the early 1980s,⁶ it was not until recently⁷⁻¹⁰ that this subject started to receive much more attention due to its potential impact on those industries.

The transport of the permeant molecules across the membrane is governed by two factors: (i) the permeant molecules/membrane surface chemistry interaction, and (ii) the polymer morphology at the membrane surface.¹¹ This article addresses both aspects in the development of asymmetric pervaporation membranes. In the first part of this study, membranes of different pore sizes were prepared from polyethersulfone (PES) material by changing the solvent evaporation period, and the effect of the solvent evaporation period on the selectivity and the flux was studied in the separation of chloroform/

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water mixtures. This study is important because both experimental data and theoretical discussions on the effect of the pore size on pervaporation performance will improve the understanding of the fundamentals of the pervaporation process.

The second part of this article discusses a new approach to modify the membrane surface. It consists of adding tailor-made surface-modifying macromolecules (SMM) to the PES membrane casting solutions to enhance the removal of volatile organic compounds from water. SMM is introduced in the membrane casting solution. The fluorine tails of the SMM have the ability to make a surface more hydrophobic, to reduce the surface energy, to yield a surface with high chemical resistivity, and to improve surface lubrication.⁷ Therefore, not only would the surface be selective to organic compounds, but the likelihood of contamination build-up at the membrane/feed liquid interface would be minimized.

The objectives of this article are (i) to study the removal of chloroform, a common VOC, from aqueous solutions; (ii) to examine the effect of the pore size at the membrane surface on the membrane performance; and (iii) to examine the effect of a fluorinated surface-modifying additive on the membrane performance. In addition, a liquid and gas chromatography study will be conducted to assess the gas phase and liquid phase adsorption of chloroform and water.

EXPERIMENTAL

Surface-Modifying Macromolecule (SMM) Synthesis

The materials used for the synthesis included methylene bis-phenyl diisocyanate (MDI) (obtained from Eastman Kodak), polypropylene diol of average molecular weight 425 (PPO) (Aldrich Chemical Company), fluorotelomer intermediate (Zonyl BA-L) (Dupont Chemical, distributed by Van Waters & Roger in Montreal) and for solvent N,N-dimethylacetamide (DMAc) (99%) (Aldrich Chemical Company). Prior to use, MDI was vacuum-distilled at 0.025 mmHg. PPO was degassed for 24 h at 0.5 mmHg. The fluorotelomer intermediate was vacuum-distilled to yield three major fractions. The fraction used in this synthesis was a colorless liquid, with boiling temperature in the 50–55°C range at a pressure of 0.025 mmHg. The surface-modifying macromolecules were synthesized using a two-step solution polymerization. The polymerization was carried in a Labconco controlled atmosphere glove box containing dried nitrogen gas. The reaction sol-

vent was distilled at 0.5 mmHg within 24 h of the synthesis. The synthesis procedure was as follows.

PPO was dissolved in 100 mL of DMAc (0.08 wt/wt) and transferred into a 1,000 mL reaction vessel; then 50 mL of an MDI–DMAc solution (0.13 wt/wt) was added at once into the reaction vessel. Once the MDI addition was completed, the reacting solution temperature was brought to and maintained between 40–50°C for 3 h. Stirring and heating were accomplished using a Thermix magnetic stirring hotplate model 210T with the following parameters: magnetic stirring bar length, 2"; stirrer setting, 2; and periodic heating at a low setting to control the temperature. After 2½ h, the reaction solution was allowed to gradually cool, to about 35°C. Then, 50 mL of the fluorotelomer–DMAc solution (0.13 wt/wt) was added at once to the reaction vessel. This reaction step was carried out for about 15 h at room temperature. After the reaction was complete, the macromolecule solution was precipitated in distilled water, and then was washed five more times with distilled water to remove solvent and unreacted components. The macromolecules were then dried in a 50°C oven for 2 days to remove all water and trace solvent. The final steps consisted of reducing the physical size of the macromolecules and washing three times with 1,1,2-trichloro-trifluoroethane (BDH, Inc.); those steps were necessary to remove all unreacted fluorotelomers. The washed materials were then dried in a 50°C oven for 3 days to evaporate trace amount of 1,1,2-trichloro-trifluoroethane. Complete macromolecule nomenclature, reaction stoichiometry, description, and relative molecular weight are presented in Table I; the molecular structure of the SMM is shown in Figure 1.

Gel Permeation Chromatography (GPC)

Molecular weights were determined by GPC. The system consisted of a solvent mobile phase reservoir; a high-pressure solvent delivery system (Waters 510 pump); a Rheodyne 7125 injector with 200-μL sample loop; a thermostatted oven for the columns; three

Table I Reaction Stoichiometry and Macro-Characteristics of the Surface-Modifying Macromolecules (SMM)

Fluoropolymer	MDI/PPO(425)/BA-L	
MDI 3 mol	PPO 2 mol	BA-L 2 mol

Number average, 1.1×10^4 ; weight average, 1.7×10^4 ; polydispersity, 1.5; description, dry white solids.

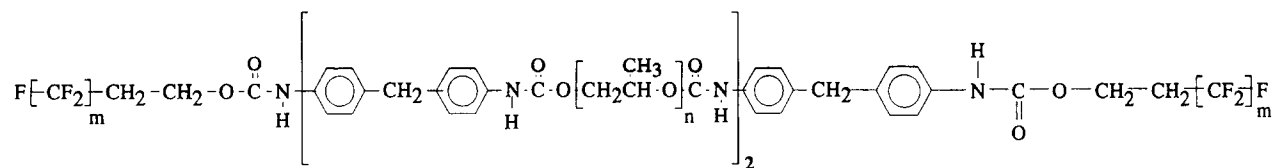


Figure 1 Chemical structure of SMM additive.

Waters ultrastyrigel columns with pore sizes of 10^3 Å, 10^4 Å, and 10^5 Å; a differential refractive index detector (Waters 410); a temperature controller for columns (set at 80°C); a refractive index detector (set at 40°C); and a data-processing station. The solvent phase was DMF containing 0.05 M LiBr, the sample size was 200 μL , and the polymer concentration was approximately 0.2 g/100 mL. The flow rate was set at 1 mL/min, and a typical chromatogram showed a retention volume of 40 mL. All molecular weight data are reported as calibration grade polystyrene molecular weight equivalents.

Membrane Preparation

PES membranes *without* and *with* SMM were prepared. The compositions of the different casting solutions are as follows. The concentration of SMM in the casting solution was changed from 0 to 3.3 wt %, while PES (Victrex 4800P supplied by ICI Advanced Materials) and polyvinylpyrrolidone (PVP) (from Sigma Chemical Co.) concentrations were maintained at 25 wt % and 6 wt %, respectively. The balance was DMAc solvent (from BDH). The PES powder was dried at 150°C in an oven with ventilation for 4 h before use. PVP of molecular weight 10,000 was used as a nonsolvent additive, except for membranes bearing experimental results in Figures 2 and 3, in which PVP of molecular weight 40,000 was used. Membranes were cast on a glass plate to a nominal thickness of 2.5×10^{-4} m. Immediately after the casting, the films were transferred into an oven preheated at 95°C , where they were kept for 2–16 min; this is called the evaporation period. The cast films were then gelled by immersing the glass plate into ice-cold water. The membranes were kept in the gelation medium overnight. Specific conditions for membrane preparation are provided in Table II. All PES membranes were dried by a solvent-exchange technique.

In this technique, the water in the membranes after the gelation process was replaced by ethyl alcohol with successive immersions in ethyl alcohol/water solutions (overnight for each immersion). This

process was repeated with solutions of different ethyl alcohol content using the following order: 25, 50, 75, and 100 vol %. Then, ethyl alcohol was subsequently air-evaporated to yield the final dry membranes.

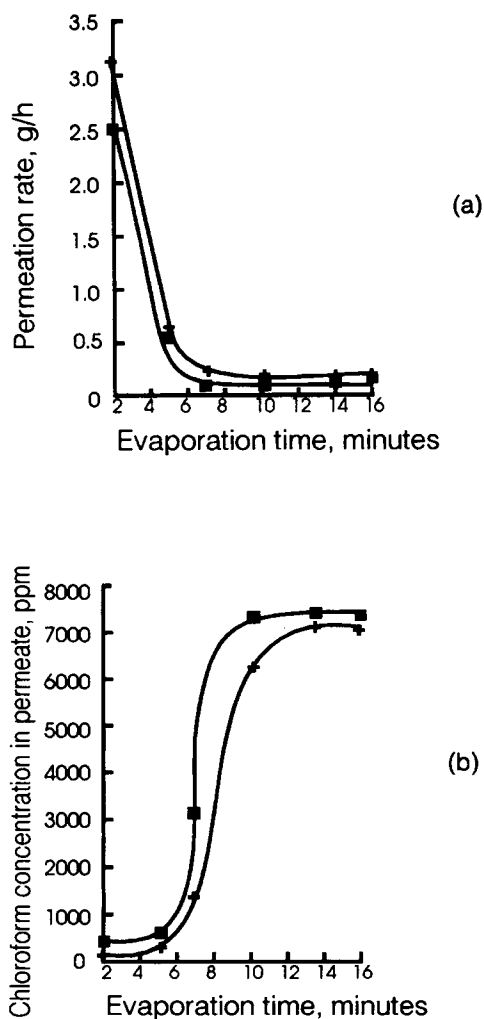


Figure 2 Results of pervaporation experiments using polyethersulfone membranes without SMM additive for the chloroform/water mixtures at room temperature. Downstream pressure, 399.97 Pa (3 mmHg); effective membrane area, 9.6×10^{-4} m². (■) 1,000 ppm feed; (+) 500 ppm feed.

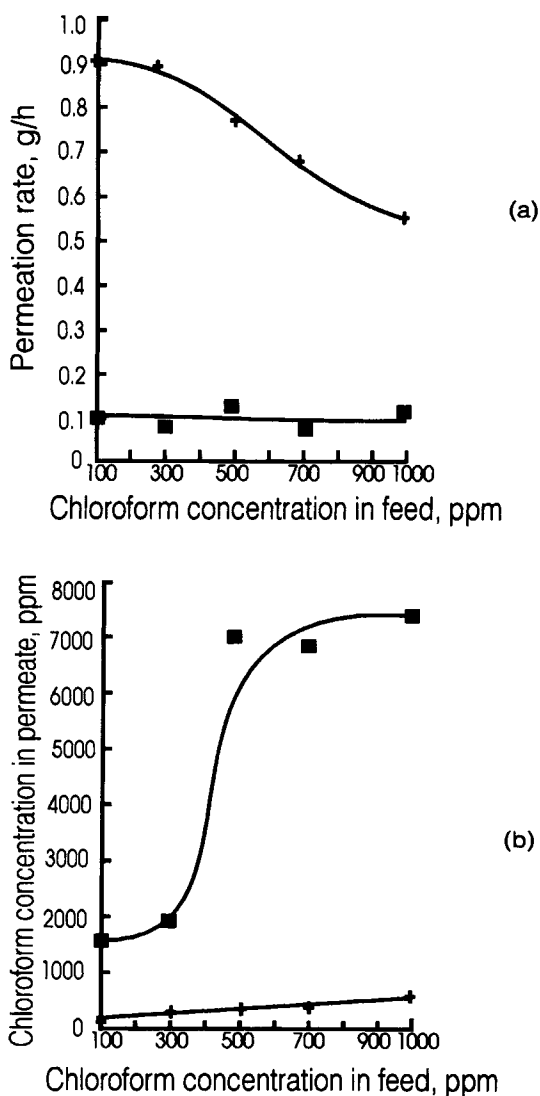


Figure 3 Effect of feed concentration on pervaporation performance using polyethersulfone membranes without SMM additive for the chloroform/water mixtures at room temperature. Downstream pressure, 399.97 Pa (3 mmHg); effective membrane area, $9.6 \times 10^{-4} \text{ m}^2$. (■) Membranes with 14-min evaporation period; (+) membranes with 5-min evaporation period.

Pervaporation Experiments

The pervaporation of chloroform and water mixtures was studied with the various membranes. The cells used for the pervaporation experiment were identical to the static cells used in reverse osmosis experiments.¹¹ The effective area of the membrane was $9.6 \times 10^{-4} \text{ m}^2$. About 0.250 kg of feed liquid were loaded in the feed chamber, and a vacuum was applied at the downstream side of the membrane. The permeant sample was condensed and collected in a cold-

trap cooled with liquid nitrogen. The amount of sample removed by membrane permeation was kept below 5% of the initial feed volume. The permeation rate was determined by measuring the weight of the sample collected during a predetermined period. The temperature was controlled at $23 \pm 1^\circ\text{C}$ throughout the pervaporation experiment. The downstream pressure was controlled within $\pm 1 \text{ mmHg}$. New membranes were used for each pervaporation experiment unless stated otherwise. Chloroform concentrations in the mixtures were analyzed with a Waters differential refractometer R401. The sample size was $10 \mu\text{L}$ for each injection. Distilled water was used as carrier solvent, and its flow rate was set at 2.0 mL/min .

Gas Chromatography and Liquid Chromatography Experiments

Gas chromatography and liquid chromatography experiments were performed to determine the sorption properties of water and chloroform in vaporous and liquid phases. They were conducted using a stainless-steel tube with a length of 0.6096 m (2 feet), an inside diameter of 0.001575 m (0.062 inches), packed with 0.001698 kg of PES powder. The particle size of the powder was kept in the range of 38–53 μm by sieving. The polymer powder was packed dry under a vacuum.

Gas Chromatography Experiments

The column was flushed with helium gas (from Air Products) overnight before testing. A Varian series 1400 gas chromatograph equipped with a thermal conductivity detector was used. The column temperature was kept at 100.5°C . Then, $1 \mu\text{L}$ of pure water or chloroform was injected into the carrier gas stream. The carrier gas was helium flowing at the rate of $5.17 \times 10^{-7} \text{ m}^3/\text{s}$.

Table II Conditions of Polyethersulfone Membrane Preparation

Variable	Condition
Casting temperature	Room temperature, 23–24°C
Thickness	$2.5 \times 10^{-4} \text{ m}$
Evaporation in air	As short as possible, < 1 s
Evaporation in oven	95°C, various times, from 2 to 16 min
Gelation media	Ice-cold water, overnight
Drying method	First solvent exchanged with ethyl alcohol, then air-dried

Liquid Chromatography Experiments

The column was washed with distilled water overnight before testing. A Waters liquid chromatograph model 501 fitted with a R401 refractometer was used. Then, 10 μL of pure chloroform (from BDH) or deuterium oxide (from Aldrich Chemical Co.) in lieu of distilled water was injected into the stream of the mobile phase. Distilled water was used as the mobile phase, and its flow rate was set at $5.0 \times 10^{-9} \text{ m}^3/\text{s}$ (0.3 mL/min). The pressure drop across the column was less than $2.07 \times 10^6 \text{ Pa g}$ (300 psig).

RESULTS AND DISCUSSION

Chromatography Results

Gas chromatography experiments showed that the retention volumes of water and chloroform were 4.79×10^{-5} and $2.20 \times 10^{-4} \text{ m}^3$, respectively. Liquid chromatography experiments showed that the retention volumes of deuterium oxide and chloroform were $1.82 \times 10^{-6} \text{ m}^3$ and $1.88 \times 10^{-6} \text{ m}^3$, respectively. The peak shape was narrow for water, whereas broad peaks were observed for chloroform both in gas and liquid chromatography. Peak shape and retention volume are indicators of the sorption strength.¹² Both wider peak shape and larger retention volume reflect stronger adsorption. The difference in the peak shape and retention volume data between chloroform and water/deuterium oxide demonstrates that chloroform is preferentially adsorbed to the polyethersulfone material in the vapor phase, although it is only slightly preferentially adsorbed in the liquid phase.

Effect of Oven Evaporation Period

As mentioned in the experimental part, the preparation of the membranes involved a solvent evaporation step. During this step, membranes were kept in a preheated oven for various time intervals. The effect of the solvent evaporation period on the PES membrane performance is shown in Figure 2. Note that the feed chloroform composition was either 1,000 or 500 ppm. Figure 2(b) shows that PES membranes prepared with evaporation time less than 7 min were water-selective compared with those with longer evaporation time. As the evaporation period became longer, PES membranes became chloroform-selective.

The above data indicate that the selectivity is reversed when the evaporation period increases. It is common knowledge that ultrafiltration mem-

branes are porous.¹¹ Since the polyethersulfone material and the conditions of membrane preparation used in this study are similar to those for ultrafiltration membranes, the fabricated membranes are believed to be porous. In the case of ultrafiltration membranes, it is understood that an increase in evaporation period will decrease the average pore size on the membrane surface.¹¹ Thus, Figure 2(b) indicates that water permeates preferentially when the pore size is large, while the opposite is the case when the pore size is small. This phenomenon was further confirmed at another feed concentration of chloroform in water, as illustrated in Figure 2.

In general, separation is controlled by two factors: thermodynamic and kinetic.¹¹ The former is caused by the sorption equilibrium of the minor component, while the latter is the reflection of the relative mobility of the minor and major components in the membrane. These two factors may work together to enhance the preferential permeation of the minor component or they may compete with each other. In the pervaporation system discussed in the paper, chloroform is the minor component and water is the major component. Based on the chromatographic experiments, it is known that the minor component (chloroform) is preferentially adsorbed to the membrane material in both liquid and vapor phase. Therefore, the thermodynamic factor favors the preferential permeation of chloroform.

Comparing the size of water and chloroform, the molar volume of water is $18.016 \times 10^{-6} \text{ m}^3/\text{mol}$, while that of chloroform is $80.181 \times 10^{-6} \text{ m}^3/\text{mol}$. Since the friction against the movement of the permeant molecule in a pore increases with an increase in the size of the permeant relative to that of the pore,¹¹ the friction on the water molecule would be less than that on the chloroform molecule. In other words, the kinetic effect favors the preferential permeation of water molecule. Therefore, in this particular system the equilibrium and the kinetic factors compete with each other.

The data indicate that the equilibrium factor is dominating when the pore size is small, whereas the kinetic factor is dominating when the pore size is large. Hence, the inversion in selectivity takes place. Presumably, when the pore size is small, the pore is filled with chloroform that is sorbed preferentially to the polymer wall, forming a multilayer. Thus, the presence of water molecules in the pore is restricted, resulting in the preferential permeation of chloroform.

On the other hand, it can be hypothesized that when the pore size is large, more water molecules can coexist with chloroform molecules because the

adsorption layer of chloroform does not fill the pore. Because water flows faster than chloroform, preferential permeation of water can take place. The data in Figure 2(a) also indicate that a dramatic decrease in the flux occurs for membranes cast with 2-min evaporation time in comparison to 5-min evaporation time. This corresponds with the expected decrease in the pore size with an increase in evaporation time.

Effect of Feed Concentration

Pervaporation results at different feed concentrations for PES membranes (without SMM) at two different evaporation times are shown in Figure 3. In terms of separation, the membrane that was evaporated for 5 min remained water-selective in the feed concentration range of 100 to 1,000 ppm. An increase in the feed concentration of chloroform resulted in a relatively small increase in the chloroform concentration in the permeate. On the other hand, the membrane with a 14-min evaporation period showed a significant increase in chloroform concentration in the permeate. The permeation rate of the membrane with a 5-min evaporation period decreased from 0.9 g/h for a 100 ppm feed solution to 0.5 g/h for a 1,000 ppm feed solution, while the permeation rate of the membrane with a 14-min evaporation period changed only slightly.

Effect of SMM Additive

The effect of SMM additive concentration is illustrated in Figure 4. It shows that the separation increases with an increase in the amount of SMM added to the membrane casting solution when the weight of SMM is between 0 and 1 wt % of the casting solution. At 1 wt % SMM, membrane exhibits the highest separation (50% increase compared to PES membrane without SMM). As SMM% further increases, the separation decreases. It is also interesting to note that the flux keeps increasing with an increase in SMM concentration.

The profile of the plots shown in Figure 4, and the enhancement of chloroform enrichment in the permeate can be explained as follows. The SMM used has a molecular weight of 1.7×10^4 and contains a surface-active segment involving fluorine, while the molecular weight of PES is 1.0×10^5 . It is hypothesized that these two features lead to the migration of SMM to the surface when mixed with PES. Since the SMM is highly hydrophobic, the migration of the SMM to the membrane-air interface makes the hydrophilic PES membrane surface more

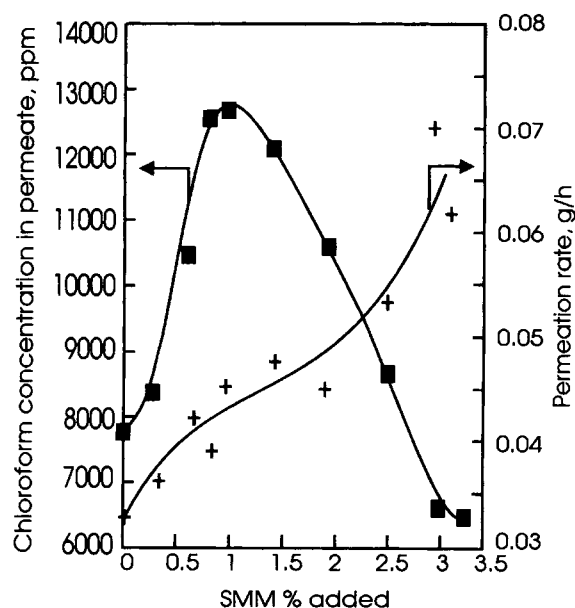


Figure 4 Effect of SMM additive concentration in the casting solution on pervaporation performance for the chloroform/water mixtures at room temperature. Feed concentration: 1,000 ppm; downstream pressure, 399.97 Pa (3 mmHg); effective membrane area, 9.6×10^{-4} m²; evaporation period, 7 min.

hydrophobic. As a result of this, enrichment of chloroform in the permeate is enhanced. When elevated amounts of SMM are added to the membrane casting solutions, the SMM itself may cause perturbations in the surface morphology of the substrate PES membrane, and subsequently lead to a decrease in separation. This explains the maxima in permeate concentration near 1 wt % of SMM. The increase in permeation rate remains unexplained at this time, and further investigations into the characterization of membranes containing SMM will have to be carried out to elucidate the mechanism of these changes.

CONCLUSIONS

Based on the above results, the following conclusions can be drawn:

1. An enrichment of chloroform from chloroform/water binary mixtures by pervaporation can be achieved with PES membranes by both increasing evaporation time and adding optimal amounts of fluorinated SMM material.
2. The solvent evaporation period in the membrane preparation is an important variable

governing the membrane performance in pervaporation. The selectivity in the separation of chloroform/water mixtures by PES membranes can be reversed by changing the evaporation period. This phenomenon is explained by the interplay of the kinetic and thermodynamic factors.

3. Chloroform is strongly preferentially adsorbed, in comparison to water, to the PES material in the vapor phase and slightly preferentially sorbed in liquid phase.
4. The addition of 1 wt % fluorinated SMM in the casting solution enhances the enrichment of chloroform in the permeate by more than 50%.
5. The addition of fluorinated SMM can increase the flux of PES membranes.

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