Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Peterson, E. S. , Stone, M. L. , Orme, C. J. , Stewart, F. F. and Cowan, R. L.(1997) 'Preparation and Characterization of Membranes with Adjustable Sep Aration Performance Using Polyphosphazene Membranes', Separation Science and Technology, 32: 1, 541 — 556

To link to this Article: DOI: 10.1080/01496399708003214
URL: http://dx.doi.org/10.1080/01496399708003214

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 541-556, 1997

PREPARATION AND CHARACTERIZATION OF MEMBRANES WITH ADJUSTABLE SEPARATION PERFORMANCE USING POLYPHOSPHAZENE MEMBRANES

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ABSTRACT

Preparation of polymeric membranes with dynamically adjustable separation properties is a new area of research. The approach described herein involves adjusting the permeate pressure of a swollen polymeric membrane to alter its separation properties. For example, during the separation of methylene blue from isopropyl alcohol, pressure on the permeate side was increased such that both methylene blue and alcohol were passed, resulting in no separation. The permeate pressure then was decreased and only colorless isopropyl alcohol passed through the membrane. A subsequent increase in the pressure on the permeate side results in no separation once again demonstrating that the effects were fully reversible. In a mixed dye experiment in isopropyl alcohol, methylene blue and rose bengal were separated with the lower-molecular-weight methylene blue permeating with isopropyl alcohol while the rose bengal was retained in the feed. The new membranes are distinguished by improved control of separation parameters as well as improved flux rates and have been experimentally characterized for their separation abilities using both flat sheets and tubular systems. This approach can be used for virtually any polymer which swells, but does not dissolve in the solvents which are being used.

INTRODUCTION

Increased awareness of both environmental and energy needs has resulted in significant efforts in both industrial and governmental sectors to develop energy efficient separations processes (1, 2). The Idaho National Engineering Laboratory's Inorganic Membrane Technology Research Program (INEL-IMTRP) is an ongoing Department of Energy (DOE) effort to develop such energy efficient membrane processes in collaboration with industry. Membranes are energy efficient separation systems when compared to traditional phase separation processes such as distillation. The immediate problem for membranes is that many of the available commercial polymeric materials degrade in the harsh thermal and chemical environments frequently encountered in industrial settings. Phosphazene polymers have been suggested as alternatives to organic polymers available today due to their higher thermal and chemical stabilities. The INEL-IMTRP has focussed upon understanding the behavior of the phosphazenes as membranes for the past several years (3, 4, 5, 6, 7, 8, 9, 10, 11, 12).

Membrane technology requires skills in chemical synthesis, analytical chemistry, and chemical engineering. Ongoing research strives to improve processes by enhancing the selectivity and flux rates by altering the chemical functionality of polymers in the membranes. Transport of a solution component through a membrane is often accomplished by establishing a pressure differential at opposite faces of the membrane, causing hydraulically driven permeation. The solution-diffusion model(13) suggests that the trans-membrane pressure differentials result in a concentration gradient of the components through the membrane. Such pressure differentials may be related to membrane permeability:

$$P = J\ell/\Delta\phi \qquad (1)$$

where P = membrane permeability, J = permeant flux, ℓ = membrane thickness, $\Delta\phi$ = difference in hydrostatic pressure across the membrane. To date, membrane fluxes have remained modest and selectivities of membranes have remained problematic (14). This paper describes a membrane with variable separation properties (15) which make it possible to perform molecular level separations that can easily be adjusted using simple pressure changes on the permeate side of the membrane.

BACKGROUND AND PREVIOUS WORK

The INEL-IMTRP's initial research emphasis was the separation of acid gases and removal of organics from water using flat sheet systems. Gas, vapor, fluid transport, and laboratory scale membrane module separation behaviors have been reported in previous publications (3-12).

The thermal and chemical stabilities of the phosphazene polymers are due to the polymer backbone which consists of a phosphorus-nitrogen chain with alternating single and double bonds. Two pendant groups, either organic or inorganic, are attached to the pentavalent phosphorus atoms by nucleophilic substitution reactions. Three types of polyphosphazene structures (linear, cyclolinear, and cylomatrix) provide variety in the chemical, thermal, and mechanical properties. The cyclolinear and cylomatrix polymers are prepared by reacting hexachlorocyclotriphosphazene (chloro-trimer) with difunctional monomers. The type of polymer obtained is dependent upon the mole ratios of the reactants and reactive sites on the chloro-trimer.

Linear organo-substituted polyphosphazenes, as utilized in this work, are synthesized by ring cleavage polymerization of the chloro-trimer at 250°C under vacuum(16) to yield poly(dichlorophosphazene), which is then substituted by the desired pendant group (17). A variety of alternate synthetic methods for the polymers have been developed by several authors; most recently, a method for synthesizing poly(dichlorophosphazene) employing condensation of trichloro(trimethylsilyl)phosphoranimine with phosphorus pentachloride at ambient temperature was demonstrated(18). Chemical and thermal properties of the polymers are related to both the polymer backbone structure and side groups (5).

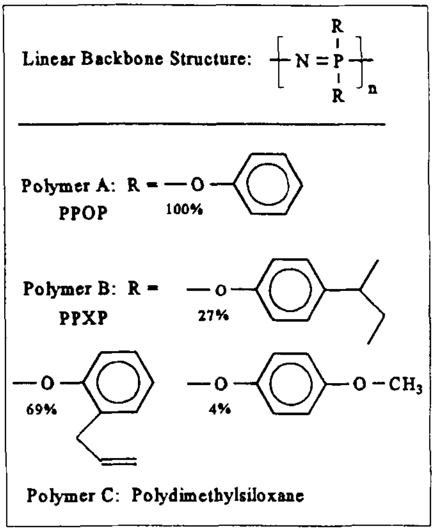

FIGURE 1. Chemical names and structures

EXPERIMENTAL

Polymer Characterization

The polymers used for this study were: (A) poly(bisphenoxy phosphazene) ORGAFLEX JP 200, (PPOP), molecular weight (number average) 600,000, T_g= -0.9°C, Thermal T_1 transition at 125°C; and (B) crosslinkable polyphosphazene ORGAFLEX AMF 100, (PPXP), molecular weight (number average) 1,200,000, T_g= -3.1°C; supplied by ELF ATOCHEM, SA (ELF). Membrane C (a polydimethylsiloxane membrane) was supplied by General Electric Corp. Molecular weight determinations were supplied by ELF for PPOP and PPXP. Thermal analyses were performed using a TA Instruments model 2910 differential scanning calorimeter. The structures and approximate degrees of substitution of the polymers used in these studies are shown in Figure 1. Isopropyl alcohol was obtained from Fisher and used without further purification.

Flat Sheet Membrane Preparation

As previously reported (3-6), the membranes were prepared by solution casting techniques using a centrifuged 4.5% PPOP tetrahydrofuran (THF) solution. Membranes were cast on glass plates, dried (24 hours), floated off the glass substrates onto water, transferred to a porous ceramic (ANOTEC™) 0.02 micron support, and placed inside a stainless steel test cell equipped with a VITON™ "O" ring forming a seal around the edge of the cell. The silicone membranes were commercially supplied as thin films cast on a non-woven support, and were used as supplied.

Membrane leak checking was performed under a pressure differential of 40 psig (about four times that which would be experienced by the membrane in any of the experiments). Film thicknesses and surface structures were determined by liquid nitrogen freeze fracturing followed by scanning electron microscopic (SEM) examination. Film swelling was measured gravimetrically as a function of solvent uptake in a simple immersion test. The immersion test consisted of casting films, weighing the films, and placing them into a pure solvent followed by gravimetrically monitoring of the solvent uptake over time.

Transport Studies-Membrane Testing

The procedure for testing membranes with variable separation performance is a modification of our previously described pervaporation systems (10). The test cell used in these studies was a 47 mm diameter (17 cm^2) modified Millipore ultrafiltration cell. The single change in the system is that permeate pressure can be varied using an air bleeder valve. Solute rejections were calculated from concentrations of each material in the feed and permeate, determined by visible light spectroscopy (Hewlett-Packard Model 8452A Photodiode Array Spectrophotometer). Concentration standard curves using the dye (rose bengal and methylene blue [Aldrich]) were constructed in the appropriate ranges and used for these measurements. Fluxes were collected in liquid nitrogen traps and masses of liquids per predesignated time period recorded. Active surface membrane thickness was estimated based upon the photographs taken during the characterization studies described below. Calculation of fluxes and modeling of the active system were performed using fundamental filtration equations.

Transport Mechanism Elucidation Experiments

The principal goal of these studies was to obtain a better understanding of transport phenomena in these unique membranes. Real-time evaluation of membranes' performances were made in two ways: a) by freezing the membrane with liquid nitrogen while it was performing a separation, and b) plugging the membrane with a catalyzed fast setting epoxy resin suspended in isopropyl alcohol (IPA) solvent. The epoxy was allowed to polymerize and the resulting hard mass was freeze fractured with liquid nitrogen. The materials were then potted in epoxy blocks to give them physical stability. Examination and evaluation of the samples were made using optical microscopy. All of the polymer samples prepared for SEM evaluation were coated with either gold or palladium films (~10 nm) to reduce surface charging on the polymer during exposure to the electron beam. Typical polymer film thicknesses were 10 - 25 microns.

RESULTS AND DISCUSSION

It is well known that as one increases the transmembrane pressure differential, selectivities and fluxes may change in some manner. The direction and magnitude of the changes depend upon several factors including feed mixtures, membrane chemistry and morphology, and separation mechanism. In the case of pervaporation, Bining, *et al* (19) suggested that the selectivity takes place in a boundary layer between the liquid zone and the vapor zone within the membrane. Micheals, *et al* (20) added that selectivity is a result of sieving by polymeric crystals. A contribution by Schrodt, *et al* discussed polymer-solvent hydrogen bonding as playing an important role (21), and Long and Yoshikawa have employed various sieving and bonding mechanisms for pervaporation processes (22, 23). Huang and Rhim discuss separation characteristics of the pervaporation process (24). In their discussion they point out that the permeate pressures can be varied to present some unusual behavior. This work takes advantage of the unusual behavior which occurs with changing the permeate pressures. The work presented in the above references provides several interaction mechanisms that require a phase change of the permeant.

The original intent of the work presented in this paper was to examine the nature of polymer-solvent interactions in a pervaporation process as a means to increase process fluxes. Typically, for pervaporation processes, non-porous or diffusive flow is observed. Convective flux typically is observed with porous systems. Evaluation of the data, however, suggested that another transport mechanism (or combination of mechanisms) was occurring. Strong polymer-solvent interactions and no phase change of the permeating solvent appear to be the requirements for the separation to take place. The data suggest that a membrane which is selective against a 1017-dalton molecule can also be made selective against a 374-dalton molecule simply by varying the modest pressures on the membrane's permeate side.

Lonsdale's (25) solution-diffusion model, coupled with Wijmans's (26) modifications, suggests that each permeant dissolves into the membrane material and transports through pores in response to the resulting chemical potential gradient. According to Lonsdale and Wijmans, the solute flux is independent of pressure while the solvent flux increases proportionately with pressure; thus selectivity must increase with pressure, which we observed experimentally (Tables 1 and 2). In our work, this relationship exists up to the limit of approximately one atmosphere of trans-membrane pressure, then the flux curve reverses and drops off (Table 3). It is believed that this is due to a reversible compression of the membrane structure which results in a shift to a diffusive transport mechanism.

A significant increase in solute flux with pressure is typically associated with small leaks in the membranes causing nonselective Poiseuille flow of the solute through the membrane. Typically, this flow minimally affects the larger solvent flow, but it influences the solute flux considerably due to the small diffusive flow (dense film-like) of the solute. A number of approaches have been suggested to account for the convective flow (porous-like), and are extensively reviewed in references 24 and 27. Because we observe non-Poiseille flow, we have chosen to use an evaluation approach similiar to that suggested by Guizard, *et al* (14).

Tables 1 and 2 summarize the effects that both pressure and temperature have upon the PPXP membrane's ability to perform separations. These data suggest that the process is solvent viscosity dependent. Since both convective and

TABLE 1. FLUX AND PERMEATION OF ROSE BENGAL:VARYING VACUUM AND TEMPERATURE.

Time (hrs)	Permeate Color	Flux (cc $sec^{-1}cm^{-2}$) (10^{-4})	Permeate Pressure (mmHg)	Temp. (°C)
0.5	Red	1.6	200	40
0.15	Pink	5.5	2	40
1.0	Clear	24.5	2	70

TABLE 2 . SELECTIVE DYE RETENTION VERSUS PRESSURE AT CONSTANT TEMPERATURE.

	Permeate Pressure (mmHg)				
	650	400	250	150	2
Rose Bengal (% retained)	0	67	48	100	100

diffusive fluxes are present in a nanofiltration process, equations 2 and 3 (14) describe transport of solvent and solute respectively:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \tag{2}$$

$$J_s = P\Delta\pi + (1-\sigma)J_vC \tag{3}$$

where J_v is the solvent flux, J_s is the solute flux, L_p is the permeability of the solvent, P is the solute permeability, ΔP is the transmembrane pressure differential, C is the concentration of solute in the solvent, π is the solvent hydrostatic pressure, and σ is the reflection coefficient. Because each of the above quantities are measureable, with the exception of sigma, one is then able to algebraically determine sigma and gain an understanding of the magnitude of the reflection coefficient. The magnitude of the reflection coefficient, sigma, allows one to evaluate the membrane as an ultrafilter, reverse osmosis system, or as a nanofilter. Sigma values of nearly 1, typically at higher transmembrane pressures, provide a measure of diffusive or dense film-like fluxes. Sigma values approaching 0, typically at lower transmembrane pressures, provide a measure of convective or more porous film-like fluxes. Intermediate sigma values of approximately 0.2 - 0.8 suggest a mixed convection/diffusion mechanism.

Contrary to our expectations that the alcohol/dye separations would be of the pervaporation type, our results are consistent with a mixed convection/diffusion mass transfer mechanism typically characteristic of nanofiltration processes. The results which are described below are similar to those found with Boye' *et al's* zirconia filled composite films (28). Our model has been confirmed by measuring the rejection of two model solutes and their respective reflection coeffecients. The increase of rejection with very modest feed side pressure is unusual for a nanofiltration membrane, Table 3. The increase of rejection at modest feed pressures leads us to speculate that there is a reversible polymer compression in these experiments. Thus, the reflection coefficient, sigma, also varies with the degree of compaction -- approaching 1 at high transmembrane pressure (diffusive flux) and approaching 0 at the lower transmembrane pressures (convective flux). The fact that we observe a larger than 0.2 reflection coefficient for the IPA ($\sigma = 0.43$) indicates a mixed transport mechanism which is dominated by convective flux but includes diffusive properties (possibly dual-mode behavior for highly plasticized rubbery polymers). Additionally, we have observed this phenomenon to be reversible using the silicone membrane, see Table 4. These data show two things: a reversible effect, and that the method which we have described is probably general to other polymers (the silicone membrane's active layer is a polydimethylsiloxane, not a phosphazene-based material).

TABLE 3. REVERSIBLE EFFECT OF VACUUM ON MEMBRANE AT 22°C.

Time (hrs)	Permeate Color	Feed Pressure (psig)	Flux (cc $sec^{-1}cm^{-2}$) (10^{-4})	Permeate Pressure (mmHg)
1.0	Blue/Violet	0	2.5	650
1.5	Clear/Colorless	30	0.54	2
2.0	Blue/Violet	0	8.2	650
4.0	Clear/Colorless	0	4.1	2

TABLE 4. RESULTS OF SILICONE MEMBRANE EXPERIMENTS.

Collection Time (hrs)	Color	Flux (cc $sec^{-1}cm^{-2}$) (X 10^{-4})	Vacuum (mm Hg)	Temperature (° C)
1.0	Blue/Violet	2.5	650	22
1.5	Clear/Colorless	0.54	2	22
1.0	Blue/Violet	0.33	650	22
2.0	Clear/Colorless	0.82	2	22
2.0	Blue/Violet	0.82	650	64
4.0	Clear/Colorless	2.3	2	59

TABLE 5. NON-SWELLING POLYMER PERFORMANCE.

Time (hrs)	Permeate Color	Flux (cc $sec^{-1}cm^{-2}$) (10^{-4})	Permeate Pressure (mmHg)	Temperature (°C)
3.0	NA	0.0	650	22
6.5	Clear/Colorless	Trace	650	22
8.0	Clear/Colorless	0.01	2	80

TABLE 6. Summary of Permeabilities of Membranes.

Polymer	Permeant	Temp. °C	Delta P (cm Hg)	Flux (cc $sec^{-1}cm^{-2}$)	Thickness (um)	Permeability*	sigma	Dye Rej. %
PPXP	IPA	22	64.8	$1.634 X 10^{-4}$	30	$7.565 X 10^{-9}$	0.43	99.9
PPXP	Rose Bengal	22	64.8	$1.63 X 10^{-11}$	30	$7.17 X 10^{-15}$	0.97	
PPXP	IPA	70	64.8	$4.90 X 10^{-3}$	30	$2.27 X 10^{-7}$	0.43	99.9
PPOP	IPA	22	64.8	0	30	N/M	N/M	N/M
PPOP	Rose Bengal	22	64.8	0	20	N/M	N/M	N/M
PPOP	IPA	80	64.8	$5.45 X 10^{-6}$	20	$1.68X10^{-10}$	0.64	99.9
PPOP	Rose Bengal	80	64.8	0	20	N/M	N/M	N/M
PDMS	IPA	22	64.8	$1.63 X 10^{-4}$	35	$8.83 X 10^{-9}$	0.37	99.9
PDMS	IPA	59	64.8	$4.49 X 10^{-4}$	35	$2.43 X 10^{-8}$	0.37	99.9

* units of permeability are: cc (STP) cm cm^{-2} sec^{-1} $cmHg^{-1}$

N/M= Not Measured

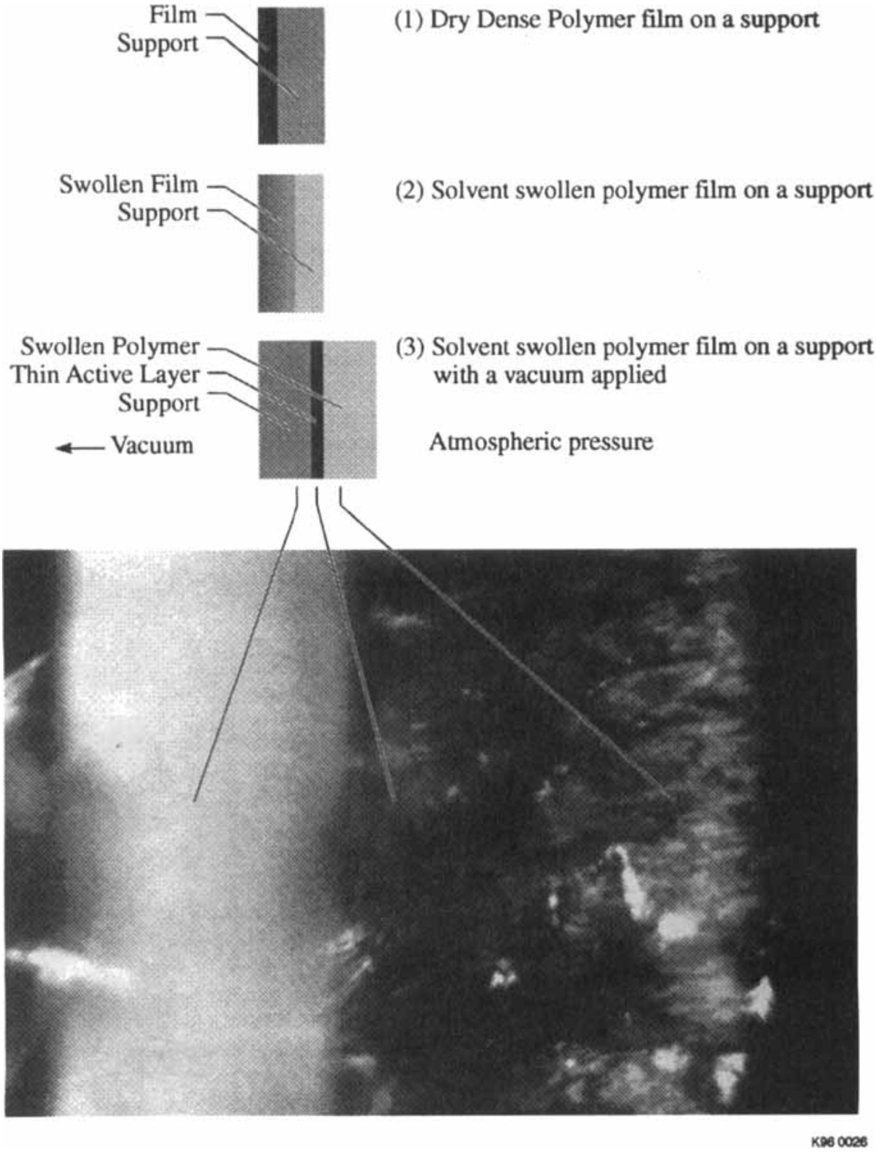

Figure 2. Physical picture of dynamically variable polymer film's behavior on solvent

The requirement of polymer swelling was experimentally examined and confirmed using a non-swelling (swells 2.5wt% in IPA) polymer (PPOP), and compared to the swellable polymer PPXP (swells 8 wt% in IPA). Table 5 summarizes the results of non-swelling polymer membrane experiments. Clearly, the minimally swollen PPOP allows only small permeation of IPA and only at temperatures above ambient. Permeabilities for IPA and the dyes were determined assuming single component Fickian flow for the liquids and are reported in Table 6.

A physical description of the phenomenon can also be presented based upon our photographic and pressure dependence studies. Three distinct steps can be visualized for the generation of the active membrane: **Step 1** is to place the film on a support, either by coating or by simply laying a film over a support, **Step 2** swelling of the film in a solvent, and **Step 3** pull a modest vacuum on the swollen film which is already passing both solvent and solute. It is during Step 3 that a solvent-depleted layer is probably formed in the film, possibly with molecular sized pores. Efforts to characterize the film morphologies during peak performance have proven difficult because the polymer is in a dynamic state in the solvent. However, some insight into the mechanism using the simple methods described above has proven interesting, see Figure 2.

SUMMARY

This paper describes development of a novel means of generating a new membrane with variable selectivities that can be controlled in real-time during the separation process. The requirements to make the variable membrane process work are that the polymer film swell in a given solvent, and that a pressure differential be applied by lowering the permeate pressure slightly. We have been able to model the system and obtained a simple set of equations which adequately describe the system. The effect appears to be reversible and generally applicable to multiple varieties of polymers.

ACKNOWLEDGMENTS

The authors wish to thank Ms. Jacqueline Fonnesbeck for her generous help with the polymer swelling studies. This work was supported by the U.S. Department of Energy, in part by the Office of Industrial Technologies, in part by the Assistant Secretary for Conservation and Renewable Energy-Office of Basic Energy Sciences, and in part by the Idaho National Engineering Laboratory - Laboratory Directed Research and Development Program under Contract DE-AC07-76ID01570.

NOMENCLATURE

P = Permeability (cc cm/cm Hg sec cm^2)
J = Permeate Flux (cc/cm^2 - sec)
l = Membrane Thickness (cm)
$\Delta\varphi$ = Transmembrane hydrostatic pressure diffference
J_v = Flux of Solvent (cc/cm^2 - sec)
J_s = Flux of Solute (cc/cm^2 - sec)
L_p = Permeability of solvent (cc cm/cm Hg sec cm^2)
ρ = Permeability of solute (cc cm/cm Hg sec cm^2)
ΔPr = Transmembrane pressure differential (cm Hg)
C = Concentration of solute in solvent (moles/liter)
Π = Effective solvent hydrostatic pressure (cm Hg)
σ = Reflection Coefficient
IPA = Ispropyl Alcohol

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