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CHEMICAL SEPARATIONS USING SHELL AND TUBE COMPOSITE POLYPHOSPHAZENE MEMBRANES

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ABSTRACT

Several applications of modular shell and tube polyphosphazene coated membrane units are reported in this paper. These modules were used to measure the mixed-gas separation properties of poly[bis(phenoxy)phosphazene] based polymers on a larger scale. Transport behavior was determined using the variable volume technique. The test gas mixture was SO_2/N_2 at temperatures between 80°C and 270°C. Transport of these gases was found to be a sorption controlled process. Several organic-aqueous and organic-organic separations have been performed using the polyphosphazene coated shell and tube modules. The separations include: methylene chloride/water, acetic acid/water, isopropyl alcohol/water, glycerol/water, and hexane/soy oil. The membranes were prepared using slip casting techniques. The results of these studies show that polyphosphazene membranes can effectively be used to separate acid gases and organic chemicals from various waste streams in harsh, chemically aggressive environments.

INTRODUCTION

Increasing energy needs and environmental concerns in recent years have resulted in increasing efforts in both the industrial and government sectors to develop energy efficient separations processes. The Idaho National Engineering Laboratory's (INEL) Inorganic Membrane Technology Research Program (IMTRP) is one of the Department of Energy's ongoing efforts to develop such energy efficient membrane processes with industry. Currently, the IMTRP is supported by DOE's Office of Industrial Technologies (OIT), industrial partners, and internal INEL funding. The current thrust of the IMTRP, based upon the concerns of our industrial partners and those identified in recent DOE reports(1,2), is the development of energy efficient separation processes.

Membranes appear to answer some industrial concerns (1). Membranes offer low-energy consuming systems when compared with traditional phase separation processes. The immediate problem however, is that many of the available commercial polymeric membrane systems degrade in adverse thermal (>100°C) and chemical (pH, organics) environments frequently encountered in industrial applications (1,2).

An alternative polymeric system for membrane applications, proposed by the INEL-IMTRP, is the polyphosphazene polymers. The polyphosphazene polymers were suggested due to their thermal and chemical stabilities. The objective of the present program is to develop, characterize, and scale-up a variety of chemically and thermally stable inorganic membrane based separation systems applicable to waste gas and aqueous stream conditioning. The IMTRP's initial research emphasis was the separation of acid gases and the removal of organics from water using flat sheet systems. Gas, vapor, and fluid transport behavior have been reported in previous publications (3-6). Membrane module separation data (at the laboratory scale) are reported in this paper. Included here are the mixed gas pair SO_2/N_2, organic-water separations, and organic-organic separations performed on ceramic supported shell and tube polyphosphazene coated modular systems.

BACKGROUND AND PREVIOUS WORK

Phosphazene Polymers

Phosphazene polymers consist of alternate phosphorous-nitrogen single and double bonds in the polymer backbone with two side groups attached to the phosphorous atoms (Figure 1)(4). These polymers can easily be modified with a variety of side groups by nucleophilic substitution and exchange reactions. Three types of polyphosphazene structures (linear, cyclolinear, and cylomatrix) provide variety in the chemical, thermal, and mechanical properties. Linear organo-substituted polyphosphazenes are synthesized by ring cleavage polymerization of a cyclic trimer (usually hexachlorocyclo-triphosphazene) at 250°C under vacuum, coupled with subsequent substitution by the desired side group. The cyclolinear and cylomatrix polymers are prepared by reacting the cyclic trimer with difunctional monomers. The type of polymer obtained is dependent upon the mole ratios of the reactants and reactive

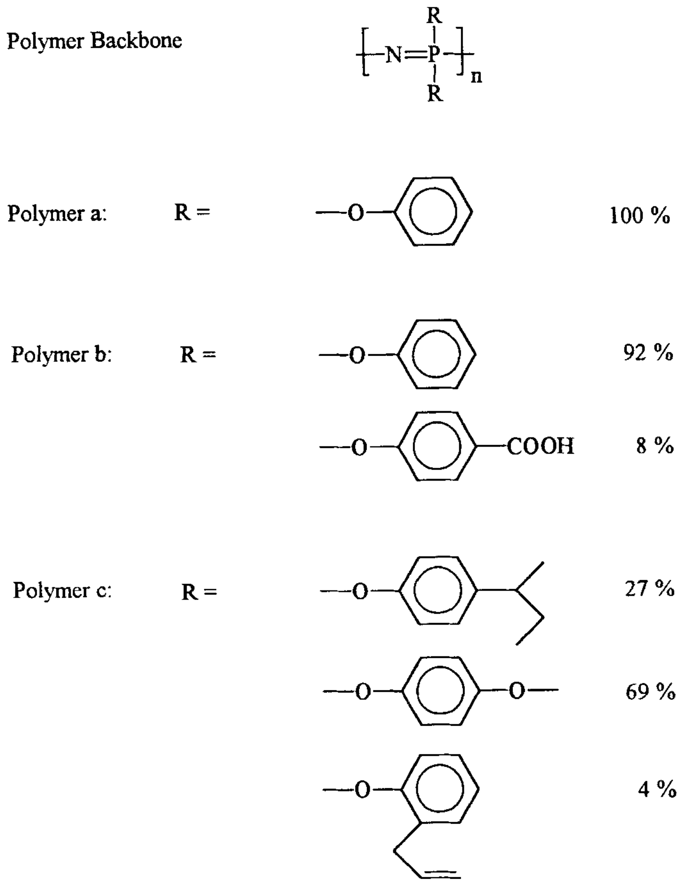

FIGURE 1. Backbone and substituent structures of polymers used in these studies.

sites on the trimer. Chemical and thermal properties of the polymers are related to both the polymer backbone structure and side groups (5).

Previously Reported Acid Gas Separations Performed at INEL

Historically, the IMTRP's work has demonstrated that poly-[bis(phenoxy)phosphazene] based polymers can be successfully cast into dense homogeneous membrane films using solution casting techniques. The polyphosphazenes exhibit chemical and physical characteristics which are favorable for applications in harsh chemical environments. Certain acid gases SO_2, and H_2S, (and CO_2 to a lesser extent) deviate from the diffusion controlled permeability-size correlation. These observations clearly indicate that solubility factors are important in the gas transport processes of polyphosphazenes. The transport properties of the membrane materials studied show evidence for the solution/diffusion mechanism suggesting that the systems can be chemically tailored to achieve the desired separation (3,6).

Previously Reported Organic/Aqueous Separations

Poly[bis(phenoxy)phosphazene] membranes offer an effective alternative approach for cleaning up halocarbon contaminated air and water streams. These studies have shown high separation factors for removing chlorinated hydrocarbon contaminants from air and water; 84 for methylene chloride from nitrogen, 27 for carbon tetrachloride from nitrogen, and about 10,000 for methylene chloride from water (6,7). These results are quite encouraging for the potential application of membrane technology to environmental restoration and process waste minimization problems.

EXPERIMENTAL

Polymer Synthesis

Poly[bis(phenoxy)phosphazene] (PPOP) was prepared using a modification of Singler's procedure (8) which has been described previously (3,4).

Polymer Characterization

Molecular weights of the polymeric products were determined by gel permeation chromatography (GPC) using an Hewlett Packard HPLC system with a refractive index detector. Two DuPont trimodal silanized PS columns connected in series were used with a tetrahydrofuran flow rate of 1.0 mL/min. The columns were calibrated using narrow distribution polystyrene standards obtained from DuPont. Molecular weights were calculated using the ASTM universal calibration method (9). Those samples of polymer supplied by Elf Atochem, North America, Inc. were characterized by the manufacturer and no further characterization was performed. The number and weight average molecular weights for PPOP were 75,000 to 1,000,000 daltons, respectively.

The structures and approximate degrees of substitution of the polymers used in these studies are shown in Figure 1. Polymers a and b were supplied by ELF ATOCHEM, North America and polymer c was synthesized in the INEL laboratories using known syntheses (8). The thermal and physical properties of the polymers are provided in Table 1.

Membrane Preparation

As previously reported (3-6,11), the membranes were prepared by solution casting techniques with a prefiltered 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 (ANOTEK) 0.02 micron support and placed inside of a stainless steel test cell equipped with a VITON "O" ring forming a seal around the edge of the cell.

In this work, the membranes were prepared directly on the inner surface of ceramic tubes using slip casting techniques. Crosslinking, of the materials for which it was possible, was accomplished using dibenzoylperoxide at about 140°C for up to eight minutes. Leak checking was performed under a pressure differential of 40 psig (twice that which would be experienced by the membrane in any of the experiments). Film thicknesses and surface structures were determined by freeze fracturing followed by scanning electron microscopic (SEM) examination. All polymer samples were coated with either gold or palladium films (~10 nm) to reduce surface charging on the polymer during SEM examination. Typical polymer film thicknesses were 10-25 microns.

All materials used for feed solutions were analytic or HPLC grade. Water used was treated with a NANOPURE® deionizer. The SO_2/N_2 mixtures were supplied by Mattheson gases as mixed gas standards, and used as received.

Mixed Gas Studies

The mixed-gas transport behavior of the polyphosphazene membranes was determined using a test system fabricated at INEL. The shell and tube membrane module, Figure 2, was inserted into the system. Gas detection was performed using a

TABLE 1. POLYMER THERMAL AND PHYSICAL PROPERTIES

Polymer	Density (kg/m^3)	Molecular Weight	T_g (°C)	T_{Decomp} (°C)
A	1250	1,000,000	-5	415
B	1250	750,000	N/M*	400
C	1250	1,000,000	-2	415

*N/M = Not Measured.

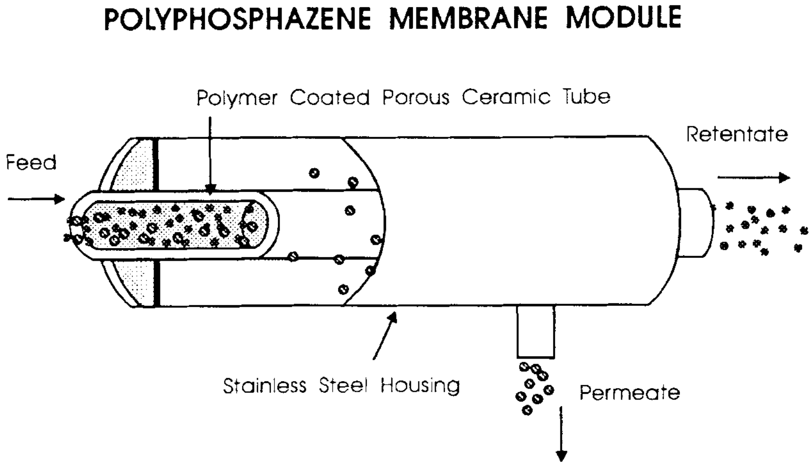

FIGURE 2. The polyphosphazene coated shell and tube composite membrane configuration used in these experiments.

Hewlett Packard 5890A gas chromatograph equipped with two Thermal Conductivity Detectors (TCD's) and an Hewlett Packard 3396A integrator was interfaced through a Hewlett-Packard 19405A Sampler Event Control Module to the mixed gas test apparatus for data acquisition, and data analysis control. The software and the mixed gas test facility have been described previously (5). System operations, calibrations, and data manipulation methodologies have been described previously. Pure gas time lags for the fast diffusing gases in the polyphosphazene membranes were measured previously (3), and found to be of the same order of magnitude. Time lags for SO_2 were found to be 1-2 orders of magnitude greater. The pure gas experiments provided the basis of our experimental conditions to assure that the membrane was in an equilibrium condition, therefore reducing errors in the measurements. Permeabilities of the polymers were determined using the partial volume method during the mixed gas separation experiment as shown in Equation 1 (5).

$$\bar{P}=\frac{\Delta P_2}{\Delta t}\,\frac{V_2}{RT}\,\frac{l}{P_i A} \qquad (1)$$

where:

P = permeability

ΔP_2 = pressure drop of second gas

Δt = time change

V_2 = partial volume of gas "2" in permeate

l = membrane thickness

P_i = volume fraction of gas "i" in permeate flow

A = membrane area

Selectivities were determined during the mixed gas separation using Equation 1. The selectivity is the ratio of permeabilities. Selectivities provide a convenient measure of a membrane's separation capability when the membrane's thickness is not precisely known. The reason for such a calculational approach is that the thickness factors cancel (5). Thus, one should note that the permeability units in Table 2 are Barrers/cm.

Pervaporation Studies

The procedure for the testing of the PPOP membranes has been described previously (6,7). Separation factors (α, or enhancement factors) were calculated from the ratios of gas/vapor concentrations in the feed and the ratios of the gas/vapor concentrations in the permeate (Equation 2):

$$\bar{P}=\frac{\Delta P_2}{\Delta t}\,\frac{V_2}{RT}\,\frac{l}{P_i A} \qquad (2)$$

Membrane thicknesses were determined by freeze fracturing of the ceramic tube membrane composites followed by direct measurement using scanning electron microscopy.

RESULTS AND DISCUSSION

Mixed Gas Testing Results and Discussion

Previous work by INEL and others has described a large amount of testing performed on different phosphazene polymers (3-7,10,11). For this work, one of the better performing polymers, based upon previous INEL studies, was selected because there appeared to be a good match between the polymer solubility parameters and those of the test gas. The module test cell used for these experiments was designed and built in-house, Figure 2.

The results of the high temperature SO_2/N_2 separations which were performed for these studies are shown in Table 2. The selectivity toward SO_2 decreases as the temperature increases. This probably is due to increasing solubility of both gases in the polymer with temperature. Interestingly, the amount of acid gas removed from the feed stream also increased with temperature. Both of these observations are consistent with the sorption-diffusion model of membrane transport. Finally, the flux across the membrane varied with concentration and temperature even though the transmembrane pressure was maintained at approximately 19 psi. The flux differences probably result from either membrane thickness variations, or as other imperfections in the membrane surface. It should be noted that the membrane survived the conditions for several hours while the data were taken.

The membrane temperature was increased for each experiment. No significant amount of hysteresis upon lowering the temperatures of the membrane module was observed. However there was slight discoloration of the membrane upon cooling.
The discoloration probably was due to charring of low concentration impurities in the polymer. There were two instances in which the fluxes increased significantly, first for the higher $S0_2$ concentrations, and secondly for temperatures greater than 240°C. Each case probably has its own set of reasons. In the case of the higher SO_2 concentrations,

TABLE 2. CERAMIC SHELL AND TUBE HIGH TEMPERATURE GAS SEPARATION PERFORMANCE FOR SULFUR DIOXIDE FROM NITROGEN USING POLYMER b

T (°C)	%SO_2	P (N_2) Barrer/cm	P (SO_2) Barrer/cm	Select (SO_2)	Flux L/m^2-h	% Acid Gas Removed
80	10%	4920	108848	22.1	1.75	5.6
130	10%	17245	340587	19.7	4.04	10.0
130	5%	19769	132723	6.7	0.98	17.7
190	5%	43712	149414	3.4	0.55	20.8
210	5%	54767	154916	2.8	0.87	20.9
240	5%	76064	163798	2.1	2.07	21.1
270	5%	118323	170742	1.4	2.84	23.2

the permeability of the polymer to SO_2 is greater, suggesting plasticization of the membrane by the acid gas. For experiments above 240°C, the increased fluxes probably are due to the thermoplastic polymer ($T_g \approx -4°C$) beginning to melt and becoming thinner. Temperatures of greater than 270°C provided significant amounts of off-gassing and loss of membrane continuity. Gas chromatography showed several additional chromatographic peaks which were attributed to polymer degradation. These results suggest that the upper limit operating temperature for the linear polyphosphazenes in acid gas separations is approximately 300°C. Our experience with the polyphosphazenes has shown that the expected life times of the membranes at or below 240°C is on the order of months to years.

The thermal and chemical stability of the polyphosphazenes is attributable to the presence of the inorganic P-N backbone (5,10). Concomitantly, the instability of the polymers is probably due to the degree of organic functionality present on the backbone. The experiments performed in at the INEL have demonstrated that the polyphosphazene polymers are capable of withstanding rigorous acid gas processing conditions which many other polymers will not tolerate.

Pervaporation Testing Results and Discussion

INEL is one of the first groups to evaluate polyphosphazenes as pervaporation membrane materials (5,7,11). Others have pursued this work recently, and have largely substantiated the previous work (10). The results of the pervaporation studies described in this paper, are summarized in Tables 2-6. A variety of separations using the pervaporation methodology to pursue separations which are of interest to industry (1,2) have been examined. A niche market for polyphosphazene polymers is developing for specific harsh environmental applications.

The results of testing polyphosphazene membranes for the removal of methylene chloride from water has resulted in some significant findings. Separation factors of as much as 10,000 on flat sheet membrane systems ranging in size from 17.5 cm^2 to 185 cm^2 were found. However, when ceramic supported tubular membranes of ≈50 cm^2 were used an array of values ranging from 9000 to 3000, Table 3 were observed. We speculate that the variation in values is due to imperfections in the slip-cast membrane surfaces which are laid over the ceramic membrane supports. These studies also have shown that the membranes display no signs of degradation over several weeks of continuous use at temperatures ranging from 24°C to 75°C.

The data indicate that the separation factors are independent of feed temperature and feed flow rate with constant permeate pressures. However, as expected, the fluxes are directly dependent upon feed temperature.

For soy oil/hexane separations, modest separation capabilities were observed for the polyphosphazene polymers. The results of these studies are summarized in Table 4. As with the methylene chloride/water separations separation factors which are independent of feed temperature, and presumably feed flow rate were observed. However, a drop in fluxes of approximately an order of magnitude compared to the methylene chloride/water separations was also found. One might attribute the significant drop in fluxes to the differences in molecular size of hexanes and soy oils when compared to methylene chloride and water. Additionally, vapor pressure differences coupled with lower polarity differences also would provide significant rationale for lower separation factors.

Acetic acid/water separations have been attempted in these investigations. The results are summarized in Table 5. The membranes survived the 50% acetic acid/water

TABLE 3. CERAMIC SHELL AND TUBE PERVAPORATION PERFORMANCE FOR METHYLENE CHLORIDE (1%)/WATER (99%) SEPARATION USING POLYMER a

Feed Flow (mL/min)	T°C	Pressure (mm Hg)	Flux L/m^2-h	Separation Factor
55.0	24	140	0.39	3000
50.0	45	140	----	9000
50.	60	140	0.35	8800
50	75	140	0.45	∞*

*∞ = Only methylene chloride was observed in the permeate.

TABLE 4. CERAMIC SHELL AND TUBE PERVAPORATION PERFORMANCE FOR HEXANE/SOY OIL SEPARATIONS USING POLYMER c

Feed Flow (mL/min)	T°C	Pressure (mm Hg)	Flux L/m^2-hr	Separation Factor
10	22	80	--	4.62
10	80	80	0.025	4.94
10	80	80	0.023	∞*

∞*Only methylene chloride was observed in the permeate.

TABLE 5. CERAMIC SHELL AND TUBE PERVAPORATION PERFORMANCE FOR ACETIC ACID/WATER SEPARATIONS USING POLYMER c

Feed Flow (mL/min)	T°C	Pressure (mm Hg)	Flux (L/m^2-hr)	Separation Factor
10	22	140	0.21	15.1
10	80	140	0.12	9.5

TABLE 6. CERAMIC SHELL AND TUBE PERVAPORATION PERFORMANCE FOR ISOPROPYL ALCOHOL/WATER SEPARATIONS USING POLYMER c

Feed Flow (mL/min)	T°C	Pressure (mm Hg)	Flux (L/m^2-hr)	Separation Factor
70	22	5	0.1	0.51
70	87	5	5.7	1.0
70	88	5	17.1	0.96
70	90	5	11.5	0.98

separation experiments both at 22°C and at 80°C showing no signs of degradation by light microscopic examination. The two separations at 22°C and at 80°C showing separation factors of 15 and 9, respectively, are rather encouraging. The polyphosphazene membranes tested in these studies show potential for performing the acetic acid/water separations using the pervaporation approach.

Polyphosphazene membranes have also been tested for their applicability in isopropyl alcohol/water separations and have been found to offer no significant separation advantages over those membranes commercially available today. However, in an independent set of tests we found that for feed streams containing significant amounts of basic components (e.g. NaOH or LiOH), the polyphosphazenes offer chemical stability which was unequalled by either polyvinyl alcohol or dimethylsiloxane. Results of the isopropyl alcohol/water (without NaOH or LiOH) experiments are summarized in Table 6.

Finally, because of the significant industrial interest in glycerol/water separations some rather preliminary 2" (17.5 cm^2) to 4" (175 cm^2) flat sheet membrane tests are reported here. The results of these investigations are reported in Table 7. Surprisingly, in this case, high separation factors (≥1000) for 30% water/glycerol solutions were found. The separation factors were independent of feed temperature and feed flow rate, however the fluxes, which were rather low, show a direct dependence on temperature changes of the feedstream. We speculate that this result can be assigned to the polarity

TABLE 7. GLYCEROL-WATER SEPARATIONS ON 4-in. FLAT SHEET OF POLYMER c

Feed Flow (mL/min)	T°C	Pressure (mm Hg)	Flux (L/m^2-hr)	Separation Factor*
30	22	140	0.02	1000
30	22	140	0.02	1000
30	80	260	0.05	990
30	80	140	0.05	1000
30	80	140	0.04	990
30	80	10	0.05	1000

*Note: 0.1% glycerol detection limit assumed for glycol in HOH. Checked by NMR, and no glycol observed in the solution.

match between the polymer and the permeate (water). Such a polarity match results in a swollen membrane. The swollen polymer then permits passage of water molecules and rejects the larger glycerol molecules. The observed fluxes are modest in magnitude, however, they appear to present economically feasible opportunities for specific separations and will be scaled up to modules in the very near future.

SUMMARY

Several different separations using polyphosphazene polymers have been studied. The unique ability to match a specific polymer to a specific separation has been explored in this paper, and shown to be quite useful. Three specific examples of matching the polymers to a needed separation are described in this paper:

1. Separation of the polar gas SO_2 from nitrogen using the polar carboxylated membrane, a separation in which the polar component is passed through the membrane;

2. Separation of methylene chloride (nonpolar organic halocarbon) from water, is a separation in which the nonpolar organic component is passed through the polymer with the water being held back;

3. Separation of glycerol from water, a separation in which the polar component is passed through the membrane, and the relatively nonpolar component, glycerol is held back by the membrane.

This work has also demonstrated that the polyphosphazenes will not only survive harsh environments, but perform as membranes in them as well. The subject of lifetimes under continuous operation has been explored, and been found to be acceptable for the described applications.

Overall, the results of these experiemtns are quite encouraging for potential applications of membrane technology in industrial separations and process waste minimization efforts. We emphasize that little is known about several of the systematic parameters which affect separation efficiency and flux: accordingly, it is to be anticipated that improved understandings of membrane microstructure and transport mechanisms will result in enhancement of the separation process.

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