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E. S. Peterson[a]; M. L. Stone[a]; R. R. McCaffrey[a]; D. G. Cummings[a]
[a] Idaho National Engineering Laboratory, Idaho Falls, Idaho, USA

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MIXED-GAS SEPARATION PROPERTIES OF PHOSPHAZENE POLYMER MEMBRANES

E. S. Peterson, M. L. Stone, R. R. McCaffrey, and D. G. Cummings
Idaho National Engineering Laboratory
Idaho Falls, Idaho, USA 83415

ABSTRACT

In this paper the mixed-gas separation properties of poly[bis(phenoxy)phosphazene] based polymers are reported. Transport behavior was determined using the variable volume technique. Test gases were run as mixed-gas pairs including SO_2/N_2, H_2S/CH_4, and CO_2/CH_4. Transport of these gases was found to be a sorption controlled process since these gases significantly deviated from the diffusion controlled permeability-size correlation. Membranes were prepared using solution casting techniques. Solvent evaporation rate during the casting and subsequent curing processes was controlled to provide a consistent membrane microstructure. We have observed that polyphosphazene membranes can effectively be used to separate acid gases from various waste streams in harsh, chemically aggressive environments.

INTRODUCTION

Rising energy costs and environmental concerns in recent years have resulted in increasing efforts in both the industrial and government sectors for development of energy efficient separation processes. One of these ongoing efforts at the Department of Energy's Idaho National Engineering Laboratory (INEL), is the Inorganic Membrane Technology Research Program (IMTRP). At present, the IMTRP is supported by the DOE's Office of Industrial Technology. The current thrust of the IMTRP, based upon the Office of Industrial Technology's and industrial concerns which have been identified in a recent DOE report (1), is the development of energy efficient separation processes.

One apparent answer to these processing needs is the use of membranes. Since membrane processes are non-energy intensive compared to traditional phase separation processes, they could offer significant energy savings for extraction processes (2). The immediate problem, however is that many of the available commercial organic membrane systems degrade in the adverse thermal (>100 °C) and chemical (extreme pH's) environments frequently encountered in industrial applications (1,3).

An alternative proposed by the INEL is the use of phosphazene polymers as membranes. The phosphazene polymers were proposed since they have the required thermal and chemical stabilities. The objective of the present program is to develop, characterize, and test a variety of inorganic based, high temperature, separation membranes applicable to waste gas and aqueous stream conditioning. The results presented in this paper address the acid gas problem. Initial emphasis has been directed to the separation of sulfur dioxide, hydrogen sulfide, and carbon dioxide from roasting off-gas streams. The mixed gas transport behavior of poly[bis(phenoxy)phosphazene] based polymers is reported in this paper. Membranes were prepared using solution casting techniques, and the rate of solvent evaporation was found to have a profound influence upon the microstructural details of the membrane (4). Consequently, in these studies the rate of solvent evaporation was maintained at a constant rate. Optical and electron microscopic techniques were used to characterize the membrane microstructure. The pure gas transport properties of the membranes have been previously reported (4, 5). Data for the mixed gas pairs reported here included 10% SO_2/N_2, 10% H_2S/CH_4, and 10% CO_2/CH_4.

Background

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 (6)). 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 polyphosphazene is synthesized by ring cleavage polymerization of a cyclic trimer (usually hexachlorocyclotriphosphazene) 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 dependant upon the mole ratios of the reactants and reactive sites

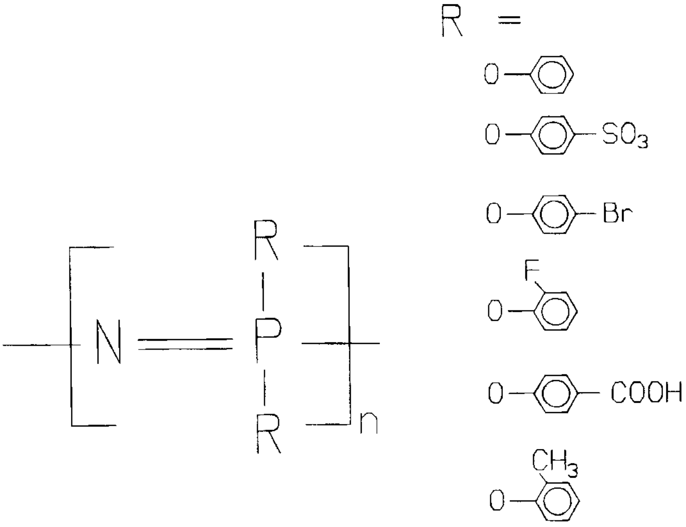

FIGURE 1. The chemical structures of the polyphosphazenes.

on the trimer. Chemical and thermal properties of the polymers are related to both the polymer backbone structure and side groups (7).

Membrane Studies

There are two methods for evaluation of the transport properties of a membrane material; one is a mixed gas study and the other is a pure gas study. The pure gas studies using the time-lag method have been performed and previously reported (4). The pure gas transport measurements show no interaction effects with other gases, but provide very useful information to guide the mixed-gas membrane transport studies. We concluded that examining the mixed gas systems would provide a significant demonstration of the separation properties of polyphosphazenes in harsh environments. Thus a fully automated mixed gas permeation test cell was designed, constructed, and tested in our laboratory. A system diagram is shown in Figure 2.

In the mixed gas experiments reported here the variable volume technique of Todd (8) was used. This method has found extensive use in a number of modifications. In principle one measures the flow of

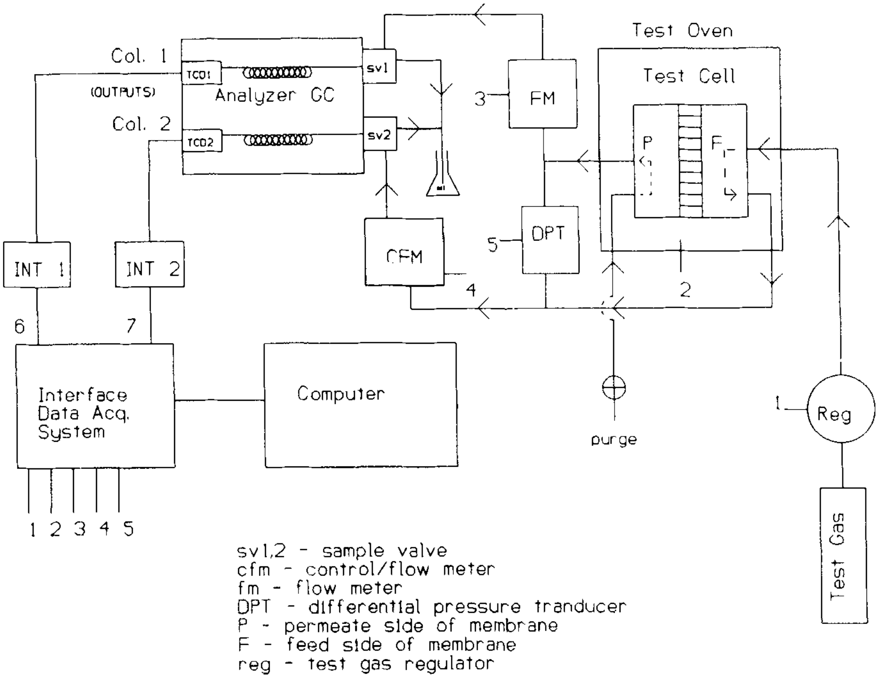

FIGURE 2. Fully automated mixed gas experiment.

a gas or vapor (under non-condensible conditions) through a polymer film using a sufficiently sensitive flow meter. The gas transport parameters determined in this experiment include permeability (P) for a material. Selectivity (S) was determined using an in-line gas chromatograph. The mixed gases used for the testing are pre-analyzed standards (Air Products), thus giving a set of well characterized gases for the performance testing of the membranes. Additionally, the system is calibrated with a series of analytic standards (Air Products) to insure good accuracy and precision of the experiment.

A simplified pictorial representation of the mixed gas experiment is presented in Figure 3. The premixed test gas is sampled and analyzed by gas chromatography just prior to each experiment, and the gas concentrations were called the "feed" concentrations. After the premixed gases were introduced to the

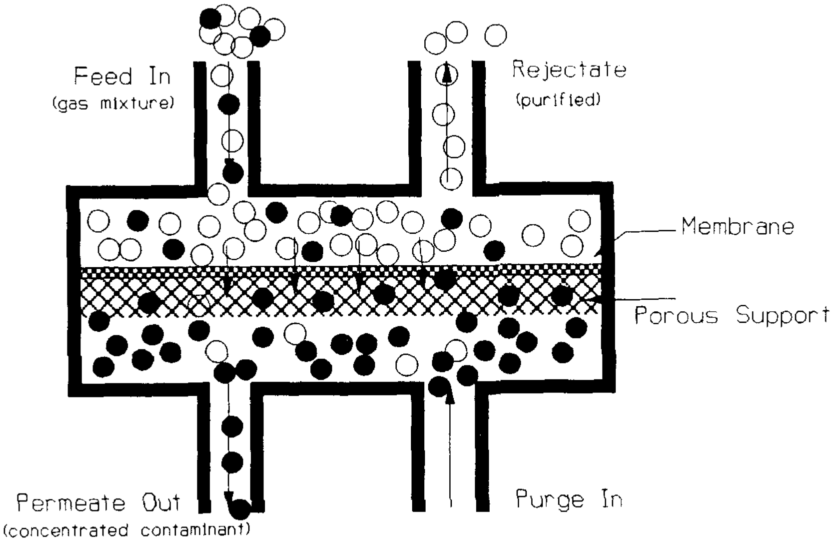

FIGURE 3. Simplified mixed gas experiment.

feed side of the membrane, the gas flow across the membrane was measured on the permeate side as an increase in net sweep flow, then sampled and fed into a gas chromatograph. The membrane rejectate was also sampled and analyzed by gas chromatography. Typically, gas flow measurements were made using a soap bubble meter on: a.) the feed side of the system; b.) the permeate side; c.) the rejectate side. The separation factors (α) for the membrane can be calculated from the ratios of gas concentrations in the feed, and the ratios of the gas concentrations in the permeate:

$$\alpha = \frac{\dfrac{[A]_{permeate}}{[B]_{permeate}}}{\dfrac{[A]_{feed}}{[B]_{feed}}} \qquad (1)$$

or as rejectate separation factor:

$$\alpha = \frac{\dfrac{[A]_{rejectate}}{[B]_{rejectate}}}{\dfrac{[A]_{feed}}{[B]_{feed}}} \qquad (2)$$

When the mixed test gas is first introduced into the feed side of the membrane, a short build up period occurs prior to the flow reaching a steady state (in the time-lag type of experiments, this would correspond to the non-linear region of the p-t plot (9, 10)). Thus, one must wait for the steady state to be achieved prior to continuing with the experiment. This experiment allows the calculation of the percent of acid gas removed from the feed to give the rejectate gas (the actual amount of gas removed is equal to the permeate concentration).

The determination of the permeability follows from the calculation of the permeability/thickness ratio:

$$\frac{P_i}{l} = \frac{\dfrac{\Delta V_i}{\Delta t_{STP}}}{A \Delta P_i} \qquad (3)$$

The partial volume flow ($\Delta V_i/\Delta t$) can be calculated from the measured flow by:

$$\frac{\Delta V_i}{\Delta t_{STP}} = \frac{\Delta V_i}{\Delta t_{EXP}} \times \frac{T_s \times P_{EXP}}{T_{EXP} \times P_s} \qquad (4)$$

Simplifying:

$$\frac{\Delta V_i}{\Delta t_{STP}} = \frac{\Delta V_i}{\Delta t_{EXP}} \times K \qquad (5)$$

Under standard conditions:

$$K=\frac{T_s\times P_{EXP}}{T_{EXP}\times P_s}=0.779 \tag{6}$$

Since our conditions are variable K remains a part of the equation, rearranged as follows:

$$\frac{P_i}{l}=\frac{\left.\frac{\Delta V_i}{\Delta t}\right._{EXP}}{A\Delta P_i} \tag{7}$$

Experimentally, the partial volume flow can be calculated if one considers the flow as the product of the total permeate flow and the volume fraction of gas "i" in the permeate, then:

$$\frac{\Delta V_i}{\Delta t}=\frac{\Delta V_T}{\Delta t}\times X_i \tag{8}$$

where X_i is the volume fraction of gas "i" in the permeate. Since selectivity is the quotient of the permeabilities, the thickness factors cancel. A BASIC program consisting of three parts has been written to perform these calculations and allow the full automation of these experiments.

EXPERIMENTAL

Synthesis

Poly[bis(phenoxy)phosphazene] (PPOP) was prepared using a modification of Singler's procedure (11). A typical synthetic route for PPOP is:

$$[-N{=}P(Cl)_2-]_n + 2n\ NaOC_6H_5 \xrightarrow[\text{dark 42 hrs}]{\text{reflux 110°C}}$$

$$[-N{=}P(OC_6H_5)_2-]_n + 2n\ NaCl$$

Details of the procedure have been previously reported (12, 13). Yields of 50-60% have been achieved with this method. The resulting polymer solid was a white, fibrous, flexible, film-forming material which dissolved easily in tetrahydrofuran or dioxane.

Several phosphazene polymers with varying functionality and therefore varying polarity were tested. The substituents on the phenyl ring included sulfoxide (SO_3), bromine, fluorine, methyl, and commercially supplied polymers. The various structures are shown in Figure 1.

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 (14). Those samples of polymer supplied by Elf Atochem 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.

Membrane Casting

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. Leak checking was performed under a pressure differential of 40 psig (twice that which would be experienced by the membrane in any of our 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.

Testing

The mixed-gas transport behavior of the PPOP membrane was determined using a test system fabricated at INEL. A 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 written in BASIC, consisted of three parts: a control section, data acquisition section, and data analysis section. The control section was used to open and close three solenoid actuator valves during the experiment; namely, 1) feed gas valve, 2) rejectate gas valve, 3) permeate gas valve. These valves feed gas into the auto sampler sample loops on the HP 5830 gas chromatograph for TCD analysis. The membrane cell pressures were measured before, during, and after data acquisition using a calibrated GENISCO PB427B-101 pressure transducer. Membrane cell temperatures were controlled by using a second HP 5890A gas chromatograph oven. Systematic time lags, measured for the test gases were as great as 0.8 seconds. Membrane time lags for the fast diffusing gases in the polyphosphazene membranes were measured previously (4), and found to be of the same order of magnitude. For the slower diffusing gases (SO_2/N_2, H_2S/CH_4, and CO_2/CH_4), the time lags were found to be 1-2 orders of magnitude greater. Thus an adequate amount of time needed to be provided for each measurement, therefore reducing errors in the measurements due to non-equilibrium conditions at the time that measurements were made. Selectivities and permeabilities were calculated from these data.

RESULTS AND DISCUSSION

The physicochemical properties of a polymeric material affect the membrane's transport properties. Additionally, the membrane morphology or microstructure has a profound effect upon the transport properties. This morphology can largely be defined and controlled in the membrane preparation technique. Depending upon the casting conditions, several types of membrane morphology can be formed, each of which exhibits a discrete set of transport

TABLE 1. POLYPHOSPHAZENE MEMBRANE MIXED GAS PERMEABILITIES*

Polymer	SO_2 in the 10% SO_2/N_2 mixture.		H_2S in the 10% H_2S/CH_4 mixture.		CO_2 in the 10% CO_2/CH_4 mixture.	
	30°C	80°C	30°C	80°C	30°C	80°C
PPOP	52	177	17	--	11	--
SO3-PPOP	42	146	13	77	7	30
8%Br-PPOP	48	251	20	120	12	52
m-F-PPOP	104	348	29	176	15	76
8%-COOH-PPOP	48	121	21	109	14	42
CH3-PPOP	163	516	51	--	22	168
PPOP-Ethyl	56	101	20	92	--	678
PPOP-ATO	--	413	--	228	--	80

Permeability units are barrer 10^{-10}[cc(STP)*cm]/[cm^2*sec*cm(Hg)]

characteristics. Examples include dense non-porous membranes formed from single solvent systems (as we used in these studies), porous systems formed from solvent systems doped with pore-forming salts, or asymmetric membranes formed from solvent/non-solvent systems and solvent quenching. The objective of this study was to gain an overall understanding of the transport behavior of the polyphosphazene membranes. To accomplish this, a dense non-porous homogeneous membrane structure was chosen. The non-porous structure was chosen because it was hoped that complications in transport behavior due to Pousieulle and Knudsen contributions would be eliminated and that transport behavior would be due only to a solution-diffusion process in the membrane.

Gas Transport Properties

The results of time-lag studies (4) of the PPOP's were the basis for the initial set of gas pairings. The experimental results presented in this paper are based upon three separate experiments with membranes of the same starting batch. The mixed gas transport behavior of the polyphosphazenes was examined at several temperatures, Table 1. The general trend for PPOP transport behavior is the same for each of the experiments; permeability

TABLE 2. TEMPERATURE DEPENDENCE OF SEPARATION FACTOR

Temperature (°C)	Pressure (psig)	Separation Factor[1]
SO_2/N_2		
30	20	101.3
70	20	16.9
110	20	18.6
150	20	17.0
190	20	17.2
H_2S/CH_4		
30	20	16.4
70	20	8.6
110	20	4.4
150	20	3.3
190	20	2.8
CO_2/CH_4		
30	20	6.2
70	20	3.9
110	20	2.5
150	20	1.9
190	20	1.0

[1] Separation Factor is a ratio of concentrations

$$\alpha = \frac{[gas1]/[gas2]_{permeate}}{[gas1]/[gas2]_{rejectate}}$$

typically decreased with increasing test gas molecular size, and selectivity increased with greater differences in test gas molecular sizes of gases used. Sulfur dioxide, (hydrogen sulfide, and carbon dioxide to a lesser extent) is a notable exception to the general trend, and these results probably are due to the high solubility of sulfur dioxide in the membrane (4).

Gas transport or permeation across a polymer membrane can be considered to occur in three distinct stages: sorption into the membrane, diffusion through the polymer matrix, and desorption out of the membrane. Sorption into and out of the membrane is directly

TABLE 3. PRESSURE DEPENDENCE OF SEPARATION FACTOR

Temperature (°C)	Pressure (psig)	Separation Factor[1]
SO_2/N_2		
30	9.7	159.0
30	19.4	161.5
30	39.5	151.9
H_2S/CH_4		
30	10.0	20.6
30	20.0	21.5
30	39.5	21.8
CO_2/CH_4		
30	10.1	8.1
30	19.6	8.3
30	39.1	8.3

[1] Separation Factor is a ratio of concentrations

$$\alpha = \frac{[\text{gas1}]/[\text{gas2}]_{\text{permeate}}}{[\text{gas1}]/[\text{gas2}]_{\text{rejectate}}}$$

related to solubility, while transport through the polymer matrix is dependent upon diffusion. Factors which affect gaseous diffusion primarily involve membrane microstructure and actual gas molecular size. For solubility, the gas/membrane, and gas/gas physicochemical properties are important. Without strong solubility effects, overall transport (permeation) is diffusion limited and related to molecular size (15). This type of transport-size trend is typically observed with noble-atmospheric and non-polar gases (15, 16, 17). Our previously observed permeability-size correlations suggested that sulfur dioxide transport is solubility controlled, and therefore SO_2 passes through the membrane more quickly via a different mechanism than He, N_2, or Ar (4). Thus our results, presented here, further confirm these subtle differences in transport phenomena, and give us the opportunity to capitalize upon the differences for various separations. Table 1 shows the results of the permeability temperature dependence studies. Since permeability is a measure of how easily the gas passes through the

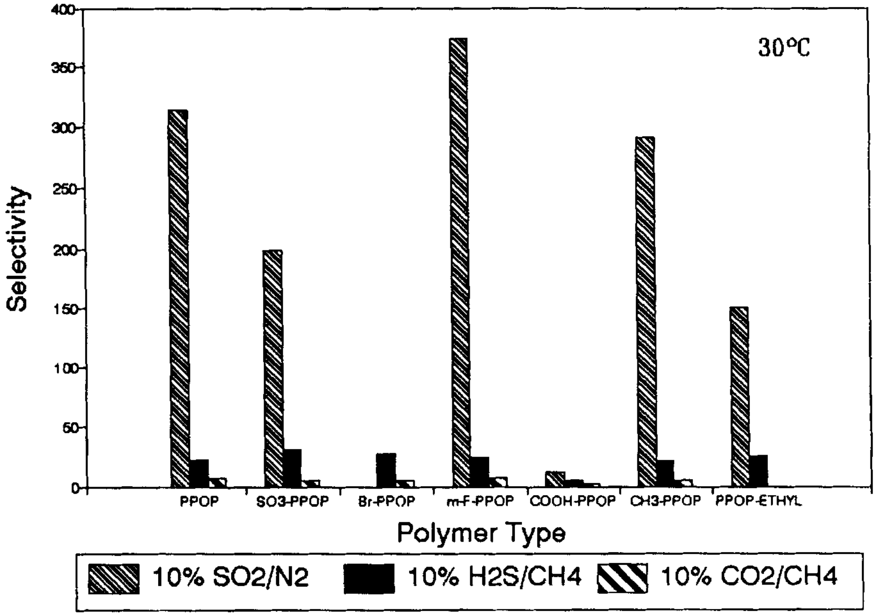

FIGURE 4. Separation factors for mixed gas experiment at 30°C.

polymer matrix an indication of the transport mechanism is also provided. Our general observation for the three gas pairs is that the membrane permeabilities increase with temperature (Table 2). Additionally, we found that the separation factors were independent of pressure (Table 3). Thus, these data suggest a solubility/diffusion based mechanism of transport.

Selectivities of the membranes resulting from separations performed at 30°C are shown in Figure 4, the results of the experiments at 80°C are shown in Figure 5. The figures illustrate the difference in performance with the three mixed gas pairs. Additionally, the efficiency of the sulfur dioxide/nitrogen separation is demonstrated thus helping to confirm a solubility based transport mechanism. The separation factors for hydrogen sulfide and carbon dioxide are considerably lower, due to the differences in their solubility in the membranes, and probably some plasticization effects.

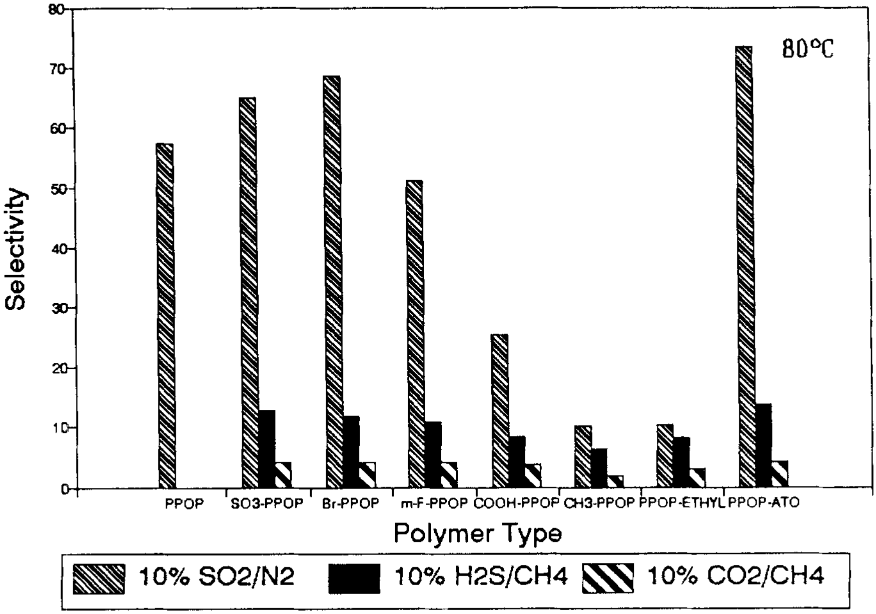

FIGURE 5. Separation factors for mixed gas experiment at 80°C.

One significant point to acknowledge is the fact that these membranes tolerate concentrations of at least 10% or more acid gas. Furthermore, the polymer's upper limit of tolerance to acid gases has not been determined. Some of the commercial membrane manufacturers specify that 5% acid gas is the maximum of what their membranes will tolerate. As one might expect a significant temperature dependence is observed for these systems and selectivity decreases as the temperature is increased. This dependence is shown in Figure 6 for the 10% SO_2/N_2 system. Nonetheless, these data demonstrate that the polyphosphazene membranes show remarkable stability in harsh chemical environments.

We have found that the polarity of the substituent group on the polymer backbone has a significant effect upon the membrane's permeability properties. The results in Table 1 show that the more polar gas (i.E. SO_2), the more easily it permeates a polar polymer (i.e. m-F-PPOP). In contrast, a less polar gas (i.e. CO_2) shows a lower permeability to the more polar systems (i.e. SO3-PPOP). These

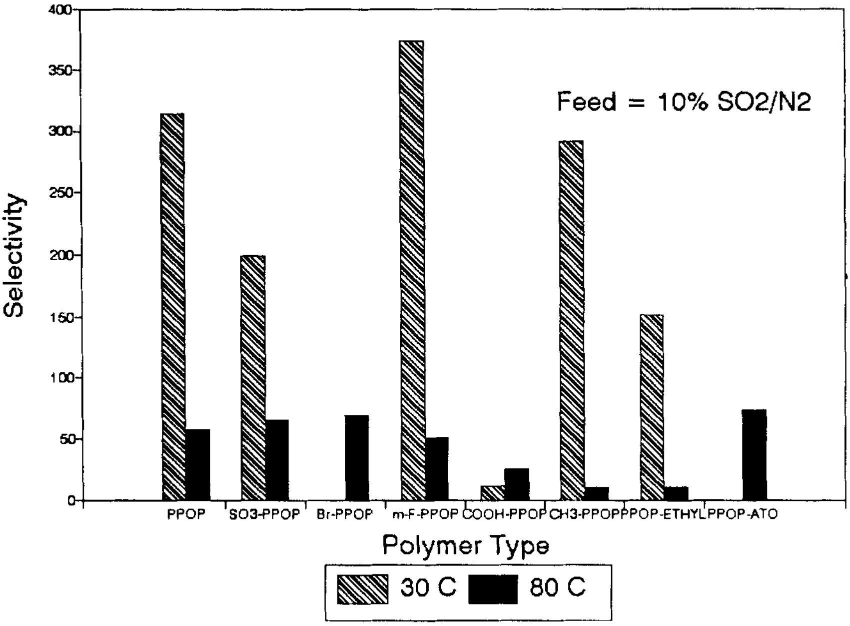

FIGURE 6. Effect of temperature upon separation factors.

results suggest that the polyphosphazenes offer a significant opportunity for chemically customizing a membrane for an individual separation.

SUMMARY AND CONCLUSIONS

Poly [bis(phenoxy)phosphazene] based polymers have been successfully cast into dense homogeneous membrane films using solution casting techniques. Presented in this paper have been the results of our gas-gas separations experiments using polyphosphazene derived membranes. The following conclusions can be drawn from these studies:

1.) The polyphosphazenes exhibit chemical and physical characteristics which are favorable for applications in harsh chemical environments.

2.) 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 factors in the gas transport processes of polyphosphazenes.

3.) The transport properties of the membrane materials studied show evidence for a solubility/diffusion mechanism suggesting that the systems can be chemically tailored to achieve the desired gas separation.

4.) The transport properties of the membranes are highly dependent upon the polarity of the chemical substituents present upon the polymer. The more polar the substituent, the more polar the material which is soluble in the polymer, and vice versa. Thus, in principle, one can custom tailor the membrane to the needed application, from reverse osmosis to organic chemical transport.

DEFINITION OF TERMS

PPOP = Poly[bis(phenoxy)phosphazene

SO3-PPOP = Poly[bis(sulfoxidophenoxy)phosphazene]

Br-PPOP = Poly[bis(bromophenoxy)phosphazene]

m-F-PPOP = Poly[bis(metafluorophenoxy)phosphazene]

COOH-PPOP = Poly[bis(paracarboxilato-phenoxy)phosphazene]

STP = Standard Temperature and Pressure

ΔP_i = Differential partial pressure for gas "i".

A = Membrane area in cm^2.

P_i/l = Permeability/thickness ratio for gas "i".

$\Delta v_i/\Delta t$ = Partial volume flow at STP of the gas ("i") in the permeate.

T_{EXP} = 298°C, Experimental Temperature

T_S = 273°C, Standard Temperature

P_S = 1 atmosphere, Standard Pressure

P_{EXP} = 0.8503, Experimental Pressure

α = Separation Factor

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