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SEPARATIONS OF HAZARDOUS ORGANICS FROM GAS AND LIQUID FEEDSTREAMS USING PHOSPHAZENE POLYMER MEMBRANES

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ABSTRACT

In this paper the liquid-liquid and gas separation properties for the separation of hazardous organic feed streams using pervaporation and gas separation methods with poly[bis(phenoxy)phosphazene] based membranes are reported. Liquid transport behavior was determined using pervaporation techniques. The preliminary gas separations were studied using a mixed gas separation method which we have described previously. Using the membrane pervaporation technique, separation factors of 10,000 have been routinely achieved for the separation of methylene chloride from water. Other tests have shown similar results for the removal of hydrocarbon vapors from air. Membranes were prepared using solution casting techniques. Solvent evaporation rates during the casting and subsequent curing processes were controlled to provide a consistent membrane microstructure. These results suggest that polyphosphazene membrane technology could effectively be used in cleaning up air and ground water that has been contaminated with chlorinated hydrocarbons.

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INTRODUCTION

One of the environmental issues of major concern today is the contamination of ground water by halogenated hydrocarbons. For example many of the Department of Energy (DOE)-Defense Program Sites have reported problems with chlorinated hydrocarbons in their ground water (1,2). Historically, air sparging and carbon adsorption techniques have been used to remove volatile organics from water (3,4). Air sparging involves the pumping of ground water to the surface and sparging it with air. The contaminated air was sometimes treated and the organics removed, but a more common practice was to dilute the waste stream with outside air until the contaminant values were low enough to dump to the atmosphere.

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Carbon adsorption requires the water to be circulated through an activated carbon bed. The organics are adsorbed by the carbon and then the carbon filter is disposed of by burial or regeneration. Disposal presents the problem of a large volume of hazardous waste and results in high burial or incineration costs since the bulk of the waste is benign carbon. Regeneration of the carbon beds is very expensive.

Membrane separation techniques offer an attractive alternative because the waste is removed from the aqueous waste stream and collected in a single step (5). An additional advantage is that the volume of waste is small since the organic fluids are collected as a concentrated liquid. In principle, a large volume of contaminated water can be treated and the resulting hazardous waste will be a very small volume of concentrated organic liquid which may be incinerated, buried, or recycled at a relatively low cost.

Two of the more common uses of membrane technology occur in the desalination of sea water and in the removal of protein metabolites from blood by hemodialysis (6). Both of these techniques are well established due to their proven success and cost competitiveness compared with other approaches. Some research has been done in developing membranes for separating chlorinated hydrocarbons from aqueous solutions (7,8). Many of the organic polymeric membranes do not survive when exposed to organic solvents. Our experience with phosphazene based polymer systems has demonstrated these materials to be immune to attack by many organic solvents and applicable to organic/water separations (9,10).

The phosphazene polymer used in these studies, poly[bis(phenoxy)phosphazene] (PPOP), is stable over a wide pH range (pH's of 1-12) and is insoluble in many organic liquids (aliphatic hydrocarbons, ketones, esters, alcohols, and ethers) (11,12). The structure of PPOP is shown in Figure 1. We have been investigating this polymer as a membrane material and have discovered that it is useful in separating acid gases from atmospheric gases (13,14,15,16). The results of our previous investigations have shown that the PPOP membranes have an affinity for rather polar gases and could be used for their separation. The work reported in this paper extends the application of PPOP membranes to the separation of chlorinated hydrocarbons from water and air.

Phosphazene polymers consist of alternate phosphorus-nitrogen single and double bonds in the polymer backbone with two side groups attached to the phosphorus atoms (9), Figure 1. These polymers are described in the preceding paper.

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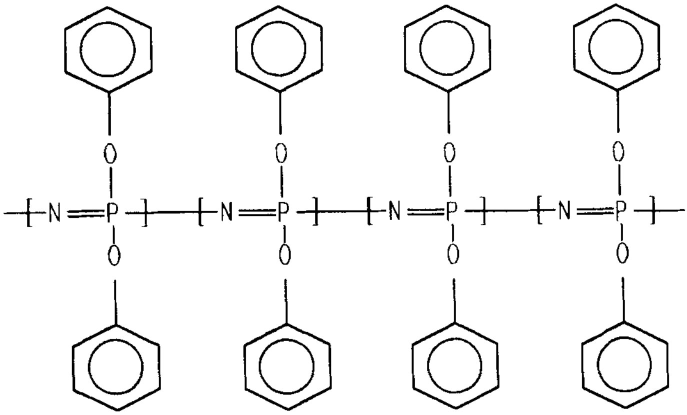

FIGURE 1. The structure of poly[bis(phenoxy)phosphazene].

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EXPERIMENTAL

Synthesis

Poly[bis(phenoxy)phosphazene] (PPOP) was prepared using a modification of Singler's procedure (11) which has been described previously (17,18).

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 (19). Those samples of polymer supplied by 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 as described in the immediately preceding paper.

Testing

The procedure for the testing of the PPOP membranes has been described previously (5).

Separation factors (α) were calculated from the ratios of gas concentrations in the feed and the ratios of the gas in the concentrations in the permeate (equation 1):

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

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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 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. A thin (10-30 microns) dense film was the structure chosen for these studies since it is both easily formed and a very tough system.

Gas Permeation Studies

Gas permeation studies were performed with a 1% methylene chloride/99% nitrogen, and 1% carbon tetrachloride/99% nitrogen standardized (Air Products) gas mixtures. The feed gas mixture was

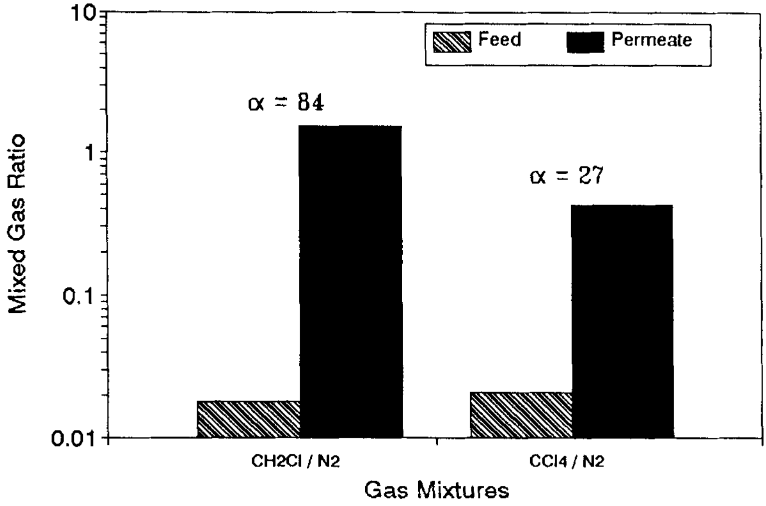

FIGURE 2. The separation of chlorinated hydrocarbon vapors from nitrogen in gas permeation tests.

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pressurized and allowed to flow across the membrane. A helium purge gas was used on the downstream side of the membrane to remove any gas permeates, thus maintaining a constant concentration gradient across the membrane during the experiments. An actual process would utilize either vacuum coupled with condensation or a destructive catalytic reactor to remove the permeate.

Analyses of the feed and permeate gases were performed using gas chromatography. The results of the permeation studies with chlorinated hydrocarbon gas mixtures are summarized in Figure 2. Higher chlorinated hydrocarbon/nitrogen ratios were observed in the permeate stream for both gas mixtures which we evaluated, suggesting a positive membrane affinity for the chlorinated hydrocarbons. The separation factors for separation of methylene chloride and carbon tetrachloride from nitrogen were 84 and 27 respectively. These results are consistent with our previous studies (13) which have demonstrated that the PPOP membranes' transport mechanism is based upon a sorption/solubility process. This hypothesis is also supported by the molecular size correlations for the PPOP membranes (13). Experiments as a function of pressure (70 to 700 KPa) were also performed. No significant changes in separation factors were observed with increasing pressures.

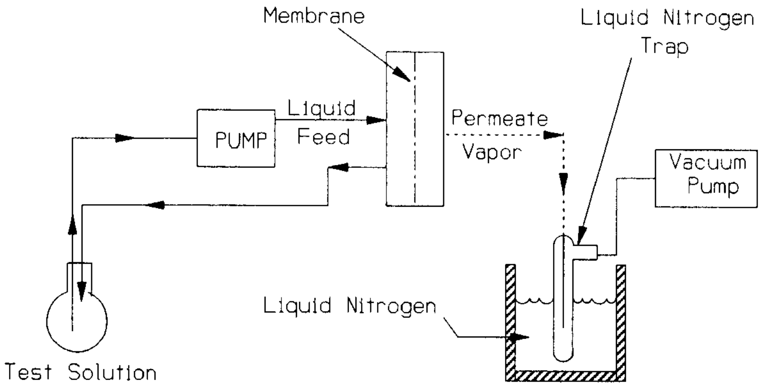

FIGURE 3. The pervaporation experimental diagram (taken from reference number 5).

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Liquid-Liquid Separations

The encouraging results of the gas permeation studies suggested the potential for the membranes to effectively separate halogenated hydrocarbons from water. The liquid/liquid separation studies were performed using the pervaporation technique which is a special application of membranes. On the feed side of the membrane a mixture of liquids are circulated, while on the permeate side, either a low pressure sweep gas is circulated, or a gentle vacuum is maintained. A diagram of the experiment is shown in Figure 3. Volatile molecules permeate through the membrane and enter the gas phase on the "back side" of the membrane as a vapor while the liquid (in these studies water) solvent is rejected. Experiments were performed using a feed solution consisting of a 1% methylene chloride/99% water mixture. The permeate was condensed with a liquid nitrogen trap and analyzed by gas chromatography. Separation factors in the range of 10,000 were obtained. Actual data are presented in Figure 4. The very high selectivities which were achieved in these experiments are due to the combined high hydrophobicity of the membrane, and the high affinity of the membrane for methylene chloride. The flux values obtained for these experiments are provided in Table 1. It should be noted that the comparison of the data found in Table 2 with those of Blume, et

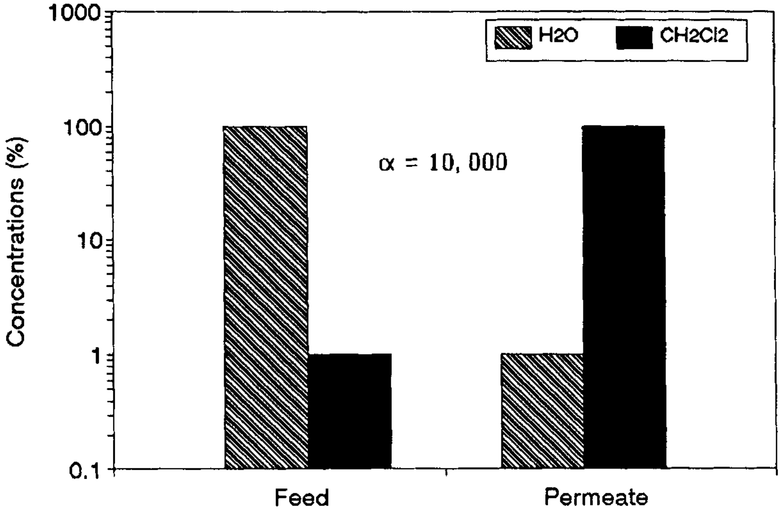

FIGURE 4. The separation of methylene chloride from water using the pervaporation experiment.

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al.(7), suggest that polyphosphazene membranes are a very competitive system with dimethylsiloxane membranes especially when one notes the differences in thickness of the membranes, and the level of vacuum applied to the systems (20,21,22).

Pervaporation Pressure and Temperature Dependence Studies

The results of temperature and pressure dependence studies of the PPOP membranes are shown in Table 2. These results indicate that the pervaporation behavior of the PPOP membranes can be significantly enhanced if one raises either or both the temperature or the pressure applied to the system. The amount of water coming through the membrane was small since no phase separation was observed after the experiment was completed. The membrane's ability to separate was preserved, the flux was enhanced by approximately eight fold (Table 2), and the amount of the halocarbon recovered from the solution was normally 60 to 70%; the best recovery obtained was approximately 90% after two passes over the flat membrane. Thus we feel that these membranes show significant potential for the separation of halocarbons from water in either setting: ambient temperature, or slightly increased temperature and pressure.

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TABLE 1. EXPERIMENTAL PERVAPORATION RESULTS/COMPARISON

	PPOP[1]	PMSO[2]
Surface Area	13.8 cm^2 (flat)	0.1 - 5 m^2 (spiral)
Component	$CH_2Cl_2/CHCl_3$	$C_2H_3Cl_3$
Permeate Pressure (Torr)	~200	~4
Flux (L/M^2*H)	0.003 - 0.05	0.02 - 0.2
Membrane Thickness (μm)	2 - 17	0.2 - 0.5

[1] PPOP = Poly[bis(phenoxy)phosphazene].

[2] PMSO = Poly(dimethylsiloxane); (Reference 7).

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TABLE 2. PRESSURE AND TEMPERATURE DEPENDENCE STUDIES

	Ambient	Increased Feed[1] Pressure	Increased Feed Pressure and Temperature	Increased Feed Pressure and Temperature
Temperature (°C)	24	24	62.5	97
Pressure (psi)	ambient	200	200	200
Flux[2]	0.05	0.13	0.24	0.39
Separation Factor (α)	~10,000	NM[3]	~9,700	~9,200

[1] Feed: 0.5% mixture of methylene chloride and chloroform in water.

[2] Flux units = [liters/m^2*hr]

[3] NM = Not measured.

Membrane = Poly[bis(phenoxy)phosphazene]

SUMMARY

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 from water. Our results are quite encouraging for the potential application of membrane technology to environmental restoration and process waste minimization problems. We emphasize that little is known about several of the systematic parameters which affect separation efficiency and flux; accordingly, we anticipate that an improved understanding of membrane microstructure and transport mechanisms will result in enhancement of the separation process.

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