



The separation of oxygen from air using commercial, plasticized, and nonplasticized polymeric membranes
by Mark David Mus

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

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In general, it was found that using phenyl compounds as modifiers increased the separation index of the membrane more than did the use of aliphatic chains.

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POLYMERIC MEMBRANES

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A thesis submitted in partial fulfillment
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of

Master of Science

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Bozeman, Montana

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APPROVAL

of a thesis submitted by

Mark David Mus

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF NOMENCLATURE

A	Area
C	Concentration
CP	Permeability coefficient
D	Diffusivity
D_0	Coefficient in Arrhenius expression for diffusivity
E	Activation energy
H	Henry's Law constant
H_0	Coefficient in Arrhenius expression of Henry's Law constant
L	Membrane thickness
$L_{(2)}$	Molar flowrate of permeate
N	Flux
P	Pressure
R	Gas constant
S	Solubility of gas in membrane
T	Temperature
X	Mole fraction of oxygen in feed
Y	Mole fraction of oxygen in permeate
Z	Length coordinate
r	Pressure ratio

Subscripts

a	Component a
b	Component b

x

d Diffusivity property

m Membrane property

s Solubility property

Superscripts

* Ideal

Greek Letters

α Separation factor = $Y(1 - X)/X(1 - Y)$

ABSTRACT

The oxygen enrichment of a product stream by selective permeation through a membrane was investigated using both commercially available polymeric films and membranes made by including various plasticizing agents (amines, glycols, and ethers) in polyvinylidene fluoride resin. Tests were conducted at various temperatures and constant pressure. The permeate samples were tested for oxygen and nitrogen content using a gas chromatograph.

The selectivity of the various membranes was compared using the traditional separation index, α , where $\alpha = Y(1 - X)/X(1 - Y)$ and Y is defined as % oxygen in the permeate while X is % oxygen in the feed.

The most promising commercial membrane was polystyrene with a separation index of $\alpha = 4.29$ (53% oxygen) at 40°C. The most promising modified membrane contained diphenyl amine as the modifier. This membrane gave a separation index of 3.66 (49% oxygen) at 40°C. Of the ethers, diphenyl ether was the most promising modifier ($\alpha = 2.54$ at 60°C), and of the glycols, diethylene glycol gave the largest separation index ($\alpha = 3.27$ at 42°C).

In general, it was found that using phenyl compounds as modifiers increased the separation index of the membrane more than did the use of aliphatic chains.

INTRODUCTION AND PURPOSE

Oxygen enriched air has a number of important uses including smelting, welding, and increasing the combustion temperature of fuels. With the advent of higher oil and natural gas prices another important use will be in coal liquefaction and gasification. Current U.S. oxygen production is at approximately 60-70,000 tons/day. Future needs of oxygen for coal gasification are estimated at 1/5 to 1/3 ton of oxygen per ton of coal [1, p. 116]. Currently the cheapest method of producing oxygen is the cryogenic distillation of air. In this process air is liquefied, then, due to its lower boiling point, nitrogen is removed in a distillation column [2]. This process is energy intensive.

With the increasing consumption of oxygen and the rise in energy costs, cheaper methods for oxygen production need to be explored. Previous research [3] has indicated that separation of oxygen from air using facilitated transport liquid membranes has the potential of replacing the cryogenic process. This research showed that a permeate containing 88% oxygen could be achieved in a single pass using these liquid membranes. Advantages of these membranes could be smaller process units and less energy. It has been estimated that a membrane producing 90% oxygen from air would require 1/3 the power of cryogenic distillation [4, p. 8]. However, a highly selective membrane is required for high purity oxygen.

Possible reasons for selective permeation through modified and nonmodified polymeric membranes could be a greater solubility of one component versus another and a difference in molecular size of the permeate components.

The goals of this research were as follows:

1. The screening of membranes for selectivity was to be conducted. Commercial polymeric films and modified polyvinylidene fluoride membranes were to be tested.
2. The effect of temperature on the oxygen selectivity of the various membranes was to be studied.

THEORETICAL BACKGROUND

The Theory of the Permeation Process

The permeation of a gas through a polymeric membrane involves three transport processes (see Fig. 1).

These stages are as follows:

1. Diffusion from the bulk phase of the gaseous mixture through the gas film-membrane interface to the membrane surface.
2. Diffusion through the membrane to the opposite face.
3. Diffusion from the membrane surface through the membrane-gas film interface to the bulk gas phase.

Transport Through a Gaseous Film

The flux of gaseous molecules through a gas film can be described by a modification of Fick's first law for steady state diffusion [5, p. 12].

$$N_a = (N_a + N_b) \frac{C_a}{C_a + C_b} - D \frac{\partial C_a}{\partial Z} \quad (1)$$

The first term in the above equation is due to bulk flow while the second term describes molecular diffusion.

The resistance to the flux in a membrane is much greater than that in the gas film [6, p. 11]. Therefore, the resistance in the membrane is the dominant factor of the flux. The resistance in the gas film can be assumed to be negligible.

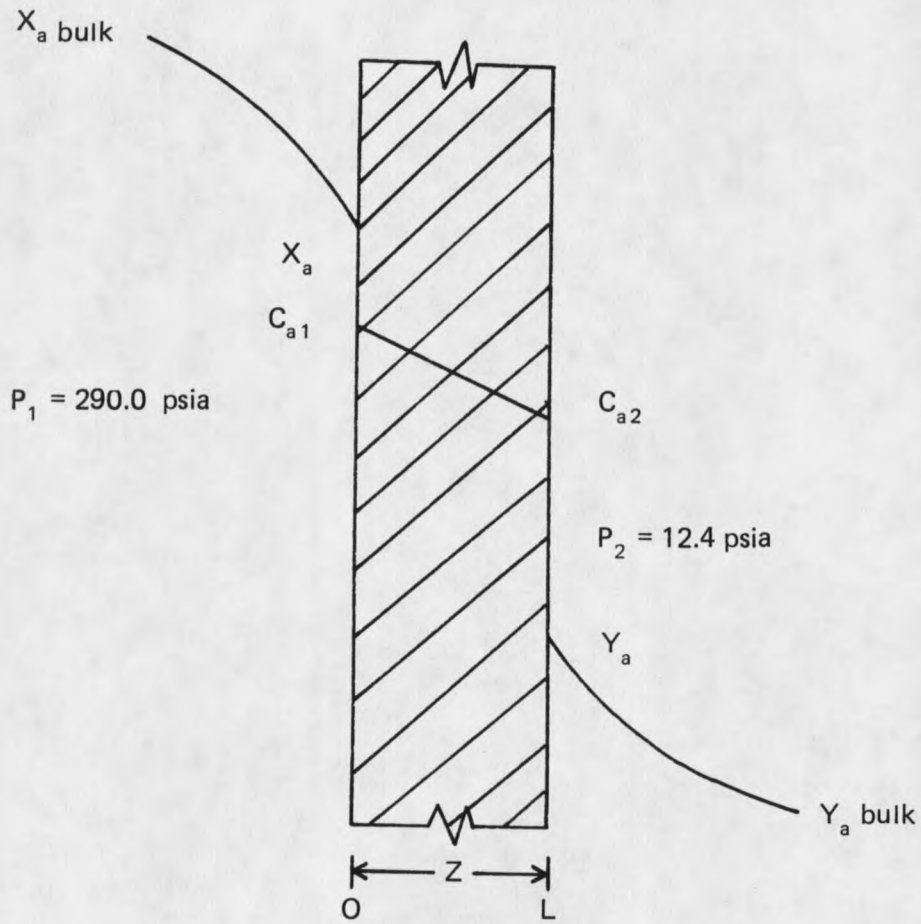


Figure 1. Concentration profile of component a in the membrane and its vicinity.

Note: Y_a bulk $>$ X_a bulk

Transport Through a Polymeric Membrane

The flux of component a in a binary gas mixture through a polymeric membrane can be described by another modification of Fick's first law [6, p. 20]:

$$N_a = -D \frac{\partial C_a}{\partial Z} - \frac{D}{2C_m} \frac{\partial^2 C_a}{\partial Z^2} \quad (2)$$

This equation reflects the assumption that the diffusion process is at steady state. It differs from Fick's first law by the addition of the second term which is needed to describe the nonlinear relationship of the flux to the concentration gradient within the membrane. In gaseous diffusion the effect of the second term is generally negligible [6, p. 21]. The resulting equation is

$$N_a = -D \frac{\partial C_a}{\partial Z} \quad (3)$$

which is Fick's first law for steady state diffusion. Because the concentration is only a function of distance through the membrane, whole derivatives may be used.

$$N_a = -D \frac{dC_a}{dZ} \quad (4)$$

Appropriate boundary conditions are required to solve the equation. The boundary conditions used are

$$\text{at } Z = 0 \quad C_a = C_{a1}$$

$$\text{at } Z = L \quad C_a = C_{a2}$$

where L is the thickness of the membrane. Integrating Equation 4 with these boundary conditions results in

$$N_a \int_0^L dZ = -D \int_{C_{a1}}^{C_{a2}} dC_a \quad (5)$$

With further rearrangement, Equation 5 becomes

$$N_a = \frac{D}{L} (C_{a1} - C_{a2}) \quad (6)$$

Thus, if flux and concentration are measured and the thickness of the membrane is known, the overall diffusion coefficient can be calculated. The overall diffusion coefficient includes the effects of gas diffusion and the effect of the membrane on the diffusion process.

To find the effect of the temperature and membrane type on flux, the solubility of the gas in the membrane must be defined. Since the diffusion of the gas is slow and the pressures are relatively low, Henry's law can be used to describe an equilibrium relationship between component a at the membrane interface and its concentration in the membrane.

$$H_1 X_a P_1 = C_{a1} \quad (7)$$

$$H_2 Y_a P_2 = C_{a2} \quad (8)$$

Defining Henry's constant H as the solubility coefficient S gives

$$C_{a1} = S_1 X_a P_1 \quad (9)$$

$$C_{a2} = S_2 Y_a P_2 \quad (10)$$

Substituting Equations 9 and 10 into Equation 6 gives

$$N_a = \frac{D}{L} (S_1 X_a P_1 - S_2 Y_a P_2) \quad (11)$$

If solubility is a function of temperature only for an individual membrane and both sides of the membrane are at the same temperature, then

$$S_1 = S_2 = S \quad (12)$$

and

$$N_a = \frac{SD}{L} (X_a P_1 - Y_a P_2) \quad (13)$$

From Equation 13 it can be seen that the flux of a gas is dependent on the solubility and diffusivity of this gas in the membrane. Thus, increasing the solubility of one of the components (oxygen) of the feed gas (air) will enhance the separation.

Polymer-Structure Effects on Transport

The transport of gases through an unmodified membrane can be visualized in the following manner: The polymer used in this research (polyvinylidene fluoride) is a highly crystalline material, above 68% [7, p. 1769] with the void spaces being thought of as amorphous regions. In the diffusional process the penetrant molecule travels through these amorphous regions due to the concentration gradient. It has been shown that diffusion through a crystalline polymer depends strongly on two factors [8, p. 53]. The two factors are degree of crystallinity and crystallite size. Larger crystallites in combination with a greater degree of crystallinity causes the diffusional tortuosity to increase. This decreases the diffusion of the penetrant molecule through the polymer. Michaels et al. [7, p. 1772] has shown that the crystallites in vinylidene fluoride polymer have a flat planer structure.

The solubility of a penetrant molecule in the polymer depends primarily on the crystallinity of the polymer [9, p. 412]. With an increase in polymer crystallinity the solubility decreases. This is due to the amount of amorphous material present. For a less amorphous polymer there is less space available for the penetrant molecule which decreases the solubility.

There are several methods to change the degree of crystallinity of a polymer. One way is to change the method of polymer manufacture. Another is to cool the molten polymer to its solid state faster. The polymer becomes less crystalline and the crystallite size decreases. A third way is to add a plasticizer (modifier). An ideal modifier is one in which the desired penetrant molecule is preferentially soluble over the other molecules in the gas mixture. This would increase the flux and the separation of the preferred molecule. A

modifier also serves to increase the amount of amorphous material in the membrane. This increase reduces the diffusional tortuosity and increases the solubility of the penetrant molecule in the polymer. The total effect is to increase the flux of a gas through the membrane.

No particular method was used in choosing the main chemical group (i.e., amines, glycols, etc.) for use as modifiers. Different modifiers within each chemical group were tried in the hope that they would give clues for the direction that future research should take.

Temperature Effects on Transport

Temperature Effects on Gas Solubility

Work done on the permeation of gas into solid polymeric membranes has shown that the solubility of a gas in a membrane follows an Arrhenius behavior with respect to temperature [8, p. 53].

$$H = H_0 \exp\left(-\frac{E_s}{RT}\right) \quad (14)$$

Thus, an increase in temperature increases the solubility of the gas in the membrane.

The effect of temperature on gas solubility in a modified membrane is more complex. Although the solubility of a gas in a liquid modifier is generally higher than its solubility in a solid polymer, the effect of temperature on this solubility is different. The solubility of a gas in a liquid decreases as the temperature increases. Thus the overall temperature effect on gas solubility is a function of modifier and polymer properties.

Temperature Effects on Diffusion

Studies have shown that temperature effects on diffusion in modified polymers also follow an Arrhenius behavior [10, p. 106].

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \quad (15)$$

Equation 15 shows that the diffusivity of a gas increases exponentially with the increase of absolute temperature. The addition of a modifier decreases the diffusional energy of activation in the membrane.

Pressure Effects on Transport

Diffusion constants are a function of temperature and the solubilities of a gas in a liquid and solid follow Henry's law at low to moderate pressures.

The pressure drop across a membrane is also an indication of the concentration driving force present. An increase in the pressure drop will increase the gas flux through the membrane (see Eq. 13).

Definition of the Separation Factor

The separation factor is a measure of the relative selective permeation of the compounds being separated. In a binary gas mixture the local separation factor for component a is defined as:

$$\alpha_a = \frac{Y_a(1 - X_a)}{(1 - Y_a)(X_a)} \quad (16)$$

The local separation factor is equivalent to the overall separation factor if perfect mixing is assumed.

The dependency of the separation factor on temperature is very complex. The solubilities and diffusivities of different gas molecules in a membrane are different. Temperature changes will affect each component differently depending on the membrane and modifier. At some point the increased solubility of the primary penetrant molecule could be outweighed by the increase in diffusivity of the gaseous mixture causing the separation factor to decrease.

The effect of pressure on the separation factor can be seen from the following [11, p. 157]:

Rewriting Equation 13 for both components in a two-component system gives

$$Y_a L_{(2)} = S_a D_a \left(\frac{A}{Z}\right) (P_1 X_a - P_2 Y_a) \quad (17)$$

and

$$(1 - Y_a) L_{(2)} = S_b D_b \left(\frac{A}{Z}\right) [P_1 (1 - X_a) - P_2 (1 - Y_a)] \quad (18)$$

where $L_{(2)}$ is the molar flowrate of the permeate and A is the area of the membrane through which the gas is permeating. Defining the coefficient of permeability of components a and b as $CP_a = S_a D_a$ and $CP_b = S_b D_b$, respectively, and dividing Equation 17 by Equation 18 gives (with rearrangement)

$$\frac{Y_a}{1 - Y_a} = \left(\frac{CP_a}{CP_b}\right) \frac{X_a - \left(\frac{1}{r}\right) Y_a}{(1 - X_a) - \left(\frac{1}{r}\right) (1 - X_a)} \quad (19)$$

where r is the ratio of the high side pressure of the membrane to the low side pressure ($r = P_1/P_2$).

Defining the ratio of the permeability coefficients of components a and b as the ideal separation factor (α^*) and combining Equations 16 and 19 results in the following:

$$\alpha = \frac{(\alpha^* + 1)}{2} - \frac{\left(\frac{1}{r}\right) (\alpha^* - 1)}{2} - \frac{1}{2X_a} \pm \left[\left(\frac{\alpha^* - 1}{2}\right)^2 + \frac{(\alpha^* - 1) - \left(\frac{1}{r}\right) [(\alpha^*)^2 - 1]}{2X_a} \right. \\ \left. + \left[\frac{\left(\frac{1}{r}\right) (\alpha^* - 1) + 1}{2X_a} \right]^2 \right]^{1/2} \quad (20)$$

Equation 18 describes the effect of pressure on the separation factor. As the pressure drop across the membrane increases, the separation factor increases until it reaches the point where any increase in the pressure drop affects the separation only slightly. For r

changing from 20 to 50 and an ideal separation factor of 4.00, the separation factor changes from 3.72 to 3.88 which is less than a 5% change. This change in r is equivalent to the high pressure side changing from 290 psia to 620 psia with the low pressure side maintained at atmospheric pressure (640 mm Hg).

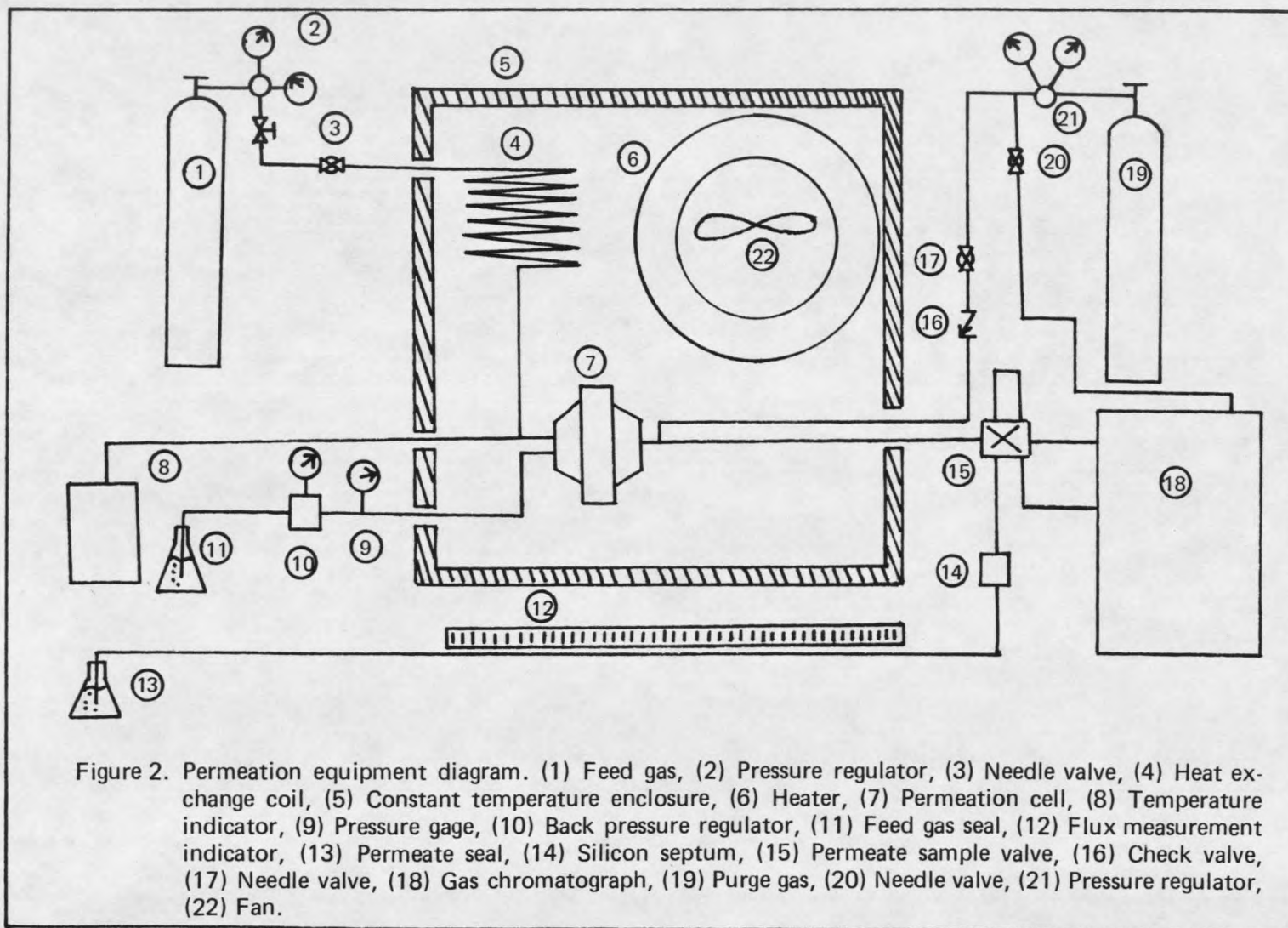
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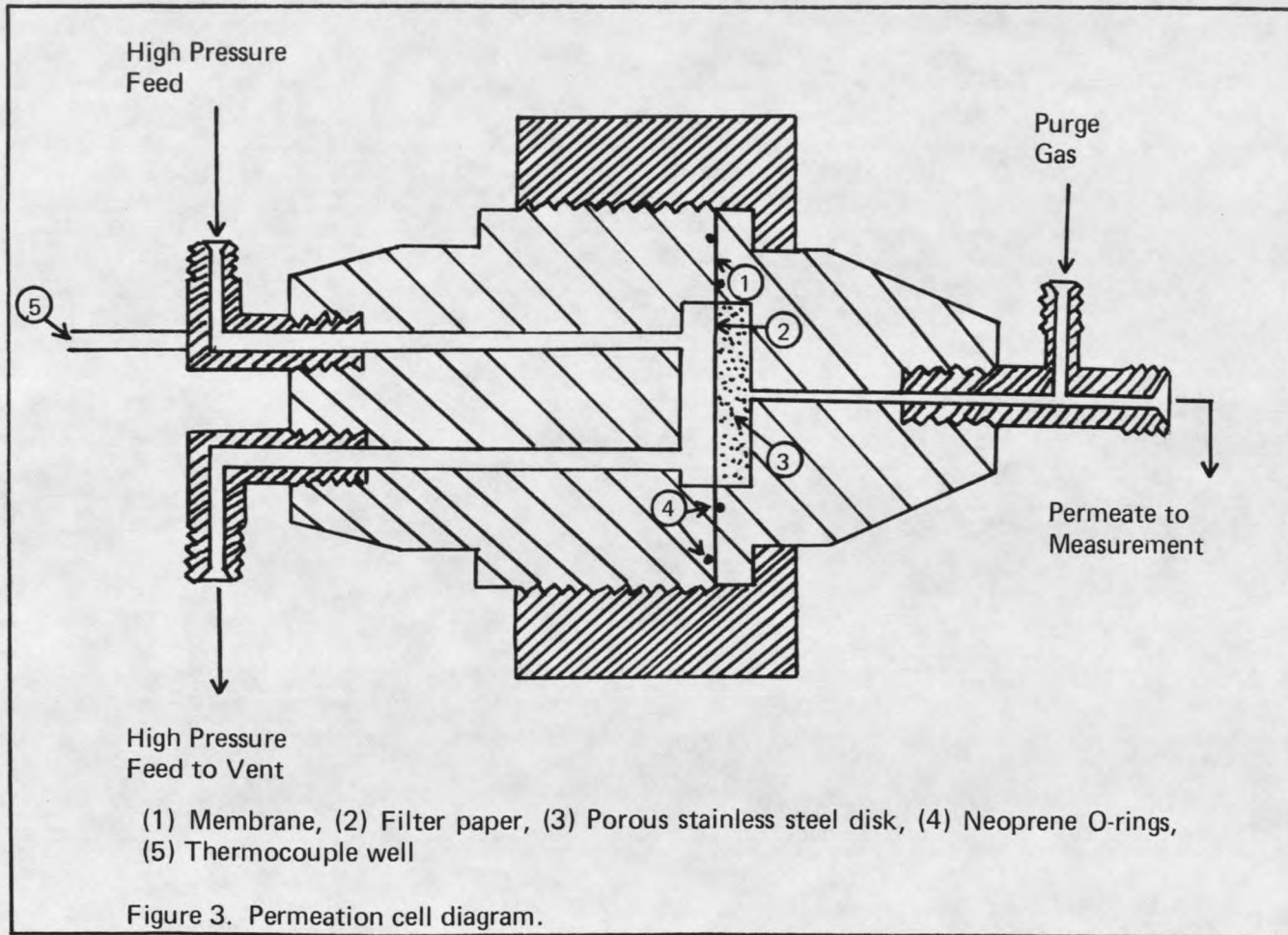
Description of Equipment

The experimental apparatus is shown in Figure 2. The equipment consists of the following: (1) Permeation cell; (2) Constant temperature enclosure; (3) Pressure control equipment; (4) Flux measurement equipment; (5) Purge gas system; and (6) Permeate composition analysis equipment. They are described separately as follows:

Permeation Cell

The schematic of the permeation cell is shown in Figure 3. The cell consists of two 2.75" dia. stainless steel flanges with a hollow interior to hold the membrane and its support. One flange has a lip that fits on the inside lip of a large stainless steel nut. The nut is then threaded on the exterior of the opposite flange. On the interior face of each flange there is a neoprene O-ring to seal the membrane against the opposite face. On the low pressure side of the membrane is a stainless steel, porous pressed metal support to help prevent the membrane from rupturing due to the large pressure differential across it. Next to this support is a Whatman #50 hardened filter paper. This prevents membrane damage by the face of the support. The high pressure side of the cell contains an inlet and outlet for the feed and a thermocouple well. On the low pressure side there is also an inlet and outlet. The inlet allows all permeate, from the previous run, to be swept out using purge gas. The outlet serves a dual purpose, the first being the exit for the purge gas and the second being the exit for the permeate to allow flux measurements and the analysis of permeate composition.





Constant Temperature Enclosure

The constant temperature enclosure, constructed from an old chromatograph oven, is shown in Figure 2. The oven, 12.75" × 12.75" × 6.5", is covered with insulation and the lid contains a layer of insulation between its walls. Gas lines, heater cord and thermocouple wires enter the enclosure through insulated 0.25" diameter holes. Inside the enclosure is a support for the permeation cell and an electric heater with blower. The temperature is monitored with a Fluke digital thermometer, and the heater is controlled by a variable Powerstat transformer hooked into a voltage regulator, allowing temperature control within 1°C.

Feed Gas Storage and Feeding Equipment

The feed gas system is shown in Figure 2. The feed gas is stored in 1.5 cu. ft. size gas cylinders at 2000 psig supplied by Liquid Air Corporation. The flow is regulated by a Matheson pressure regulator. A Grove Mity Mite back pressure regulator located downstream of the membrane cell is used to maintain the proper operating pressure. The pressure is monitored with a U.S. Gage pressure gage. The flow is monitored with the use of a Brooks flow meter. The flow is regulated at approximately 100 SCCM to allow a constant composition feed at the membrane face. To maintain a uniform feed temperature a coil of the feed line is in the constant temperature enclosure next to the heater. All tubing and components of the feed system are made of stainless steel with the tubing having a diameter of 0.125".

Purge Gas System (see Fig. 2)

The purge gas system consists of a cylinder of helium equipped with a pressure regulator, check valve and metering valve. Purge gas is fed into the permeate side of the membrane cell and into the permeate line through the regulator and a block valve allowing all permeate from a previous run to be swept out. Both hydrogen and helium are used as purge gas.

Flux Measurement Equipment (see Fig. 2)

The flux of permeate across a membrane is measured by timing the movement of a column of light machine oil inside a length of calibrated teflon tube. The tube has been determined to have a volume to length ratio of 0.00344 cu. cm./mm. The oil is drawn up to the start of the measurement position by inserting a 0.5 cu. cm. gas syringe into the line through a silicone rubber septum and drawing purge gas out of the line.

Permeate Composition Analysis Equipment

Permeate composition measurement equipment (shown in Fig. 2) consists of a multi-port valve containing an accessory loop that can be switched out of the flow of permeate to allow the carrier gas to take a sample of permeate to a Varian Aerograph Series 1400 thermal conductivity gas chromatograph. The chromatograph is coupled to a Sargent Model SR chart recorder. The column used in the chromatograph is a 1/8" × 6.5' stainless steel tubing packed with 5A molecular sieve. The following operating conditions are used:

Column Temperature — 24°C (ambient)

Detector Temperature — 130°C

Detector Current — 150 Milliampères

Experimental Procedure

There are two major steps to test membrane selectivity.

1. Membrane manufacture using polyvinylidene fluoride as the base resin.
2. Test run the membranes.

(For commercial membranes see Table 1.)

Table 1. List of Commercial Membranes.

Run #	Membrane Composition	Brand Name	Manufacturer
1	Polysulfone	P-1700	Union Carbide
2	Polyester made from polyethylene terephthalate	Mylar Type-S [®]	DuPont
3	Silicone	MEM-213	General Electric
4	Cellophane-regenerated cellulose	PD-150	DuPont
5	Polystyrene-oriented	Trycite-1000 [®]	Dow Chemical
6	Polyethylene + 2.5% Vinyl Acetate	--	Union Carbide
7	Polyethylene	Type-A	DuPont
8	Cellulose Triacetate and Pyridine 5 gms. CTA/100 ml Pyr.	--	--
9	Ethyl Cellulose	--	Dow Chemical
10	Nylon-6	Zytel [®]	DuPont
11	Nylon-6 made from experimental caprolactam	Capran 77C [®]	Allied Chemical

Membrane Manufacture

Membranes are manufactured using the following procedure:

A pyrex vial is carefully cleaned and weighed on a Mettler balance having a sensitivity of 1×10^{-2} gr. The appropriate amount of membrane modifier is weighed into the vial. The corresponding amount of vinylidene fluoride resin is then added to the vial. Six point five cu. cm. of solvent/gm. of vinylidene fluoride resin is added to the vial and the mixture is stirred. The vial is then covered and placed in an oven at approximately 100°C for 24 hours to facilitate complete dissolution. When complete dissolution has been achieved, the open vial is placed in a vacuum chamber for 30 minutes to allow degassing of the mixture. The films are formed by pouring the solution on a 9.5" x 5" x 3/4" glass plate with taped raised edges to give the desired thickness. The tape used is common duct tape with 3 layers giving a 2 mil thick membrane upon drying. The solution is distributed evenly by drawing a glass rod down the length of the plate. The plate is then placed in a ventilated electric oven set at approximately 110°C for 30 minutes for complete drying of the membrane. Due to

membrane shrinkage while cooling, the membrane is cooled to room temperature before using. Membranes, modifiers and solvents used are listed in Table 2.

Table 2. List of Modifiers Used in Modified Membranes. **

Run #	Modifier	Manufacturer	Solvent
12	5-ring PMPE (Poly-m-phenyl ether)	Varian Aerograph	DMFA
13	3-Methyl Sulfone	Phillips Petroleum Co.	DMFA
14	L-Menthol	K&K Laboratories	DMFA
15	Bis-hydroxymethyl terephthalate	---	DMFA
16	Diphenyl Amine	---	DMFA
17	N-isopropyl benzyl Amine	J. T. Baker Chemical Co.	DMFA
18	Tetra-Hydro-3-Thiophene Amine 1,1-Dioxide	Aldrich Chemical Co.	DMFA
19	Monoethanol Amine	Union Carbide	DMFA
20	Diethanol Amine	Dow Chemical Co.	DMFA
21	Triethanol Amine	Aldrich Chemical Co.	DMFA
22	Diisopropyl Ethanol Amine	Union Carbide	DMFA
23	Propylene Glycol	Union Carbide	DMFA
24	Tripropylene Glycol	Union Carbide	DMFA
25	50% Dipropylene; 50% Diethylene Glycol	Kalama Chemical Co.	DMFA
26	Diethylene Glycol	Union Carbide	DMFA
27	Triethylene Glycol	Union Carbide	DMFA
28	Tetraethylene Glycol	Union Carbide	DMFA
29	1,4-Butylene Glycol	Celanese Chemical Co.	DMFA
30	Pentamethylene Glycol	Union Carbide	DMFA
31	Dipropylene Glycol Dibenzoate	Kalama Chemical Co.	DMFA
32	Ethylene Glycol Methyl Ether	Dow Chemical Co.	DMFA
33	Propylene Glycol Methyl Ether	Dow Chemical Co.	DMFA
34	Propylene Glycol Dimethyl Ether	Dow Chemical Co.	DMFA
35	Diopropylene Glycol Dimethyl Ether	Dow Chemical Co.	DMFA
36	Diphenyl Ether	Dow Chemical Co.	DMFA
37	None	---	DMFA (Wet)
38	None	---	DMFA (Dry)
39	None	---	DMSO (Wet)

**Note: Base resin used in membrane manufacture was polyvinylidene fluoride: Trade name Kylar manufactured by Penwalt Corp. All membranes contained 10% (wt) modifier.

Membrane Test Run Procedure

The dried membrane is cut to size by using one of the permeation cell's flanges as a template. The flanges are lightly greased along the outside rim using high vacuum grease to prevent gas from flowing around the outside edge of the membrane. Next, a filter paper is

placed on the pressed-metal membrane support and the membrane is placed on the filter paper. The other flange is placed on the membrane and the two flanges are secured by threading the securing nut over both. Care must be taken to make sure a tight seal is obtained to insure accurate data. The assembled membrane cell is placed in the constant temperature enclosure on the cell support and all inlet and outlet lines are attached. The test cell is brought up to pressure by slowly bleeding in the feed gas until a slow and steady stream is achieved at the outlet. After the system is brought up to pressure, it is checked for leaks using a low viscosity liquid soap. When this has been accomplished, the permeate side of the membrane must be completely purged of all air by sweeping with hydrogen or helium. To check for complete purge, a sample is run through the chromatograph. While doing this the enclosure and membrane cell can be brought up to required run temperature. After the purge, the flux monitoring oil is drawn up into the calibrated teflon tube by inserting a hypodermic into the in-line septum and withdrawing purge gas until the required amount of oil is in place. The test run is now ready to start. The permeation rate of gas is measured by timing the rate of oil flow out of the teflon line. The measurements are used to calculate the flux values. After the flux has been measured, the sample valve is turned and a sample of the permeate is sent to the gas chromatograph for composition analysis.

RESULTS

Commercial Films

The separation indexes at various temperatures are reported in Table 3 and on Figures 4 and 5.

Of the commercial films tested polystyrene gave the highest separation index; 4.01 at 50° C. Cellophane gave the lowest index; .83 at 100° C. Cellophane was the only membrane to give separation indexes below 1.00. This indicates that nitrogen is preferentially permeated over oxygen. Polyester, silicone and cellophane were the only membranes to show relatively steady separation indexes over the entire temperature range. Most commercial membranes show a maximum separation index between 40° C to 70° C. Comparing membrane 6 versus membrane 7 shows that the addition of a small amount of vinyl acetate to polyethylene only affects the separation at the lower temperatures.

Miscellaneous Modified Membranes

Of the miscellaneous modified membranes L-menthol gave the highest separation value; 2.82 at 50° C (see Fig. 6 and Table 4). However, at higher temperatures the separation drops sharply. Of all membranes tested 5-ring poly-m-phenyl ether (PMPE) was the only one to show an increase in the separation index across the entire temperature range. 3-Methyl sulfone showed an initial increase in the separation index up to 1.26 then leveled out above 58° C. Membrane 38 on Figure 6 is nonmodified polyvinylidene fluoride (PVF). This membrane was used as a standard for the comparison of the effect the modifiers had on the membrane separation characteristics. Comparing this membrane to the modified membranes shows that adding a modifier definitely effects the separation characteristics.

Table 3. Summary of Test Results for Commercially Available Films.

Run #*	Membrane	Temperature (°C)	Flux** (m ³ (STP)/ m ² -hr)	% Oxygen in Permeate	Separation Factor
1	Polysulfone	23	---	28.6	1.51
		40	---	47.4	3.39
		50	---	51.6	4.01
		60	---	49.4	3.67
		69	---	48.8	3.59
		79	---	49.2	3.64
		90	---	45.1	3.09
		100	---	38.9	2.40
2	Polyester	70	---	24.2	1.21
		79	---	24.7	1.24
		89	1.57×10^{-4}	24.4	1.22
		100	4.17×10^{-4}	24.4	1.22
3	Silicone (unbacked)	24	2.03×10^{-1}	31.8	1.76
		40	2.16×10^{-1}	29.2	1.56
		50	2.60×10^{-1}	28.4	1.50
		60	2.90×10^{-1}	27.5	1.44
4	Cellophane	40	1.92×10^{-4}	18.8	0.88
		60	2.26×10^{-4}	19.8	0.93
		100	2.83×10^{-4}	17.9	0.83
5	Polystyrene	22	1.62×10^{-3}	51.3	3.99
		40	2.72×10^{-3}	53.1	4.29
		50	1.77×10^{-3}	51.4	4.00
		59	3.96×10^{-3}	52.1	4.12
		70	3.44×10^{-3}	46.5	3.23
		80	4.83×10^{-3}	48.1	3.51
		89	3.50×10^{-2}	26.0	1.33
6	Polyethylene + 2.5% Vinyl Acetate	23	2.76×10^{-3}	25.5	1.30
		40	5.14×10^{-3}	36.4	2.17
		50	9.55×10^{-3}	38.9	2.41
		60	2.45×10^{-2}	35.2	2.06
		70	3.14×10^{-2}	34.6	2.00
		80	3.86×10^{-2}	33.3	1.89
		90	5.02×10^{-2}	32.1	1.79
		100	6.69×10^{-2}	31.3	1.72
7	Polyethylene	24	1.95×10^{-3}	34.0	1.95
		40	3.51×10^{-3}	38.6	2.38
		50	6.88×10^{-3}	37.2	2.24
		60	9.38×10^{-3}	35.6	2.09
		70	1.61×10^{-2}	35.4	2.07
		78	2.24×10^{-2}	34.4	1.98

Table 3 (continued).

Run #**	Membrane	Temperature (°C)	Flux** (m ³ (STP)/ m ² -hr)	% Oxygen in Permeate	Separation Factor
8	Cellulose Triacetate + Pyridine	50	4.70×10^{-4}	42.4	2.79
		60	1.32×10^{-3}	46.0	3.22
		70	1.76×10^{-3}	48.4	3.55
		80	2.51×10^{-3}	47.9	3.48
		90	3.32×10^{-3}	45.8	3.20
		100	3.95×10^{-3}	45.4	3.04
9	Ethyl Cellulose	40	7.24×10^{-4}	42.0	2.74
		49	1.51×10^{-3}	43.9	2.96
		59	2.64×10^{-3}	43.7	2.94
		69	3.75×10^{-3}	40.0	2.52
		80	5.62×10^{-3}	37.8	2.30
		90	7.54×10^{-3}	38.4	2.36
		100	9.79×10^{-3}	37.2	2.24
10	Nylon-6		No diffusion at all temperatures		
11	Nylon-6 (made from experimental caprolactam)		No diffusion at all temperatures		

*Note: Run designations used are the same as those used on the figures.

**Note: All flux values are based on membranes having a thickness of 1 mil.

***Note: Where there are no recorded separation indexes the permeation was too low to allow measurement.

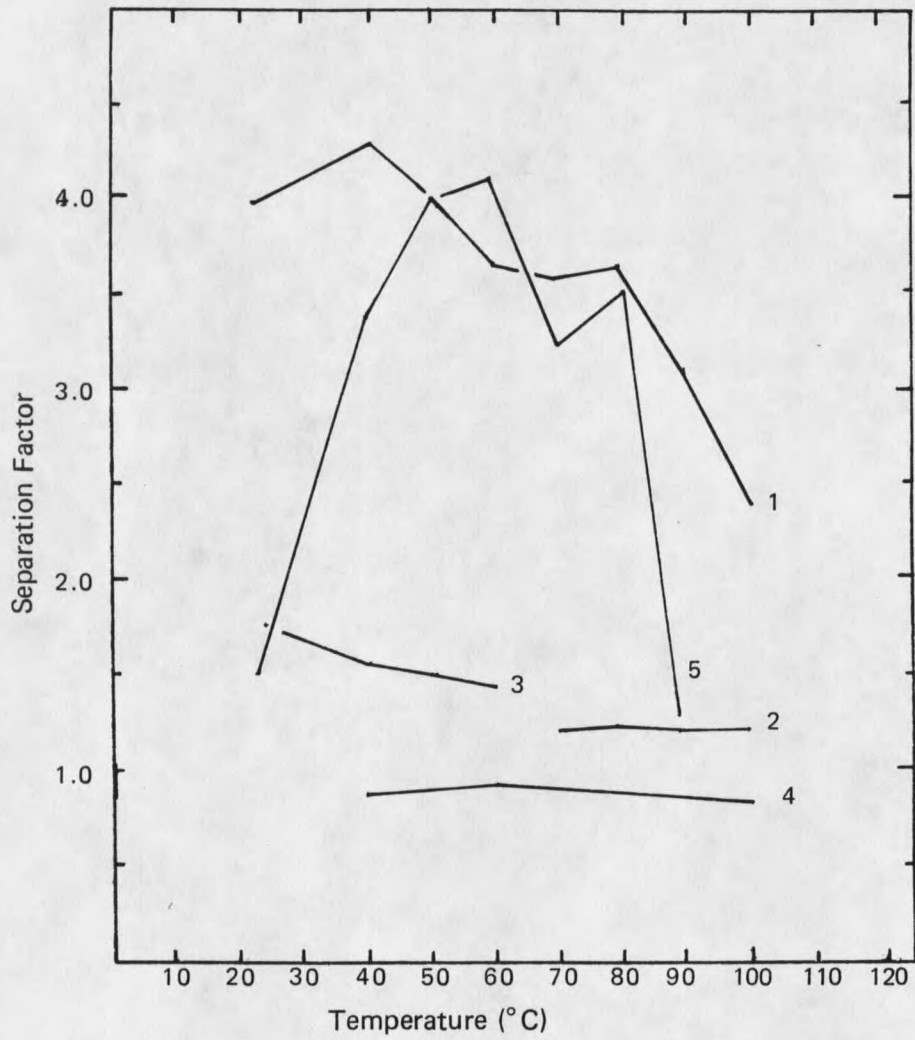


Figure 4. Separation factor vs. temperature for commercially available films. Note: For film identification see Table 3.

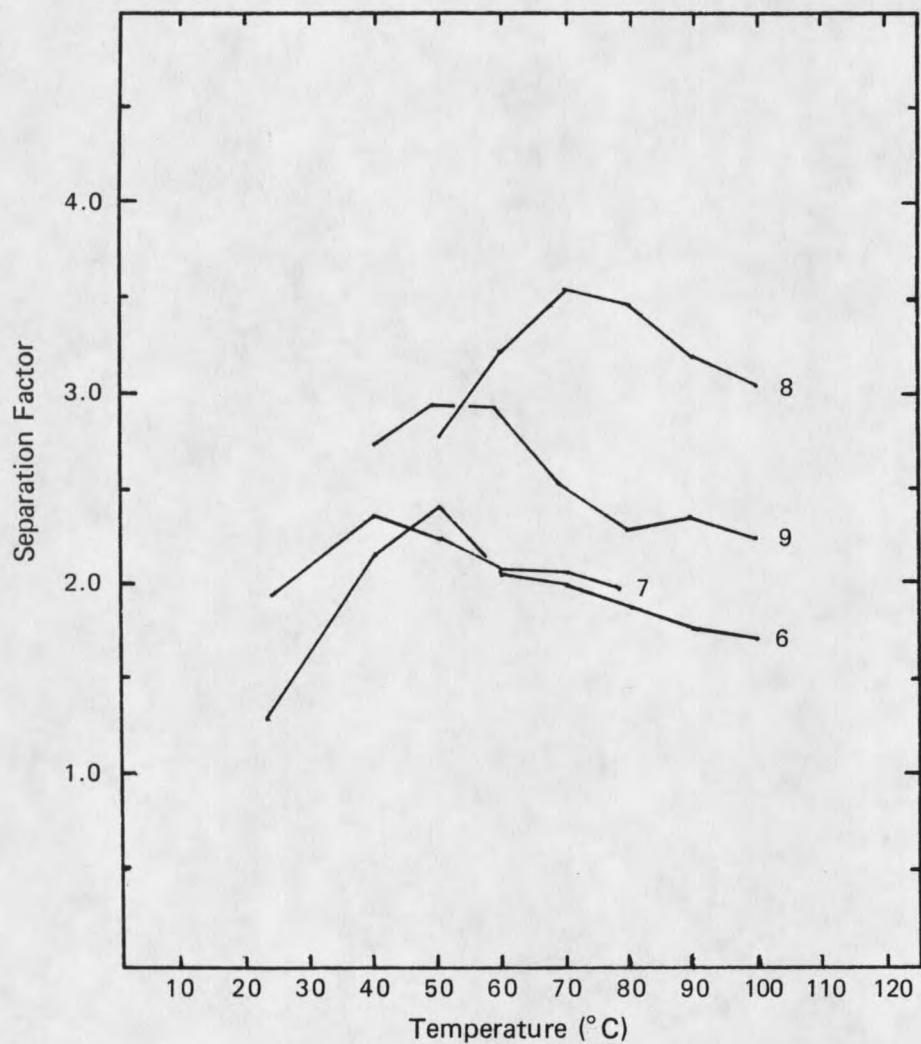


Figure 5. Separation factor vs. temperature for commercially available films. Note: For film identification see Table 3.

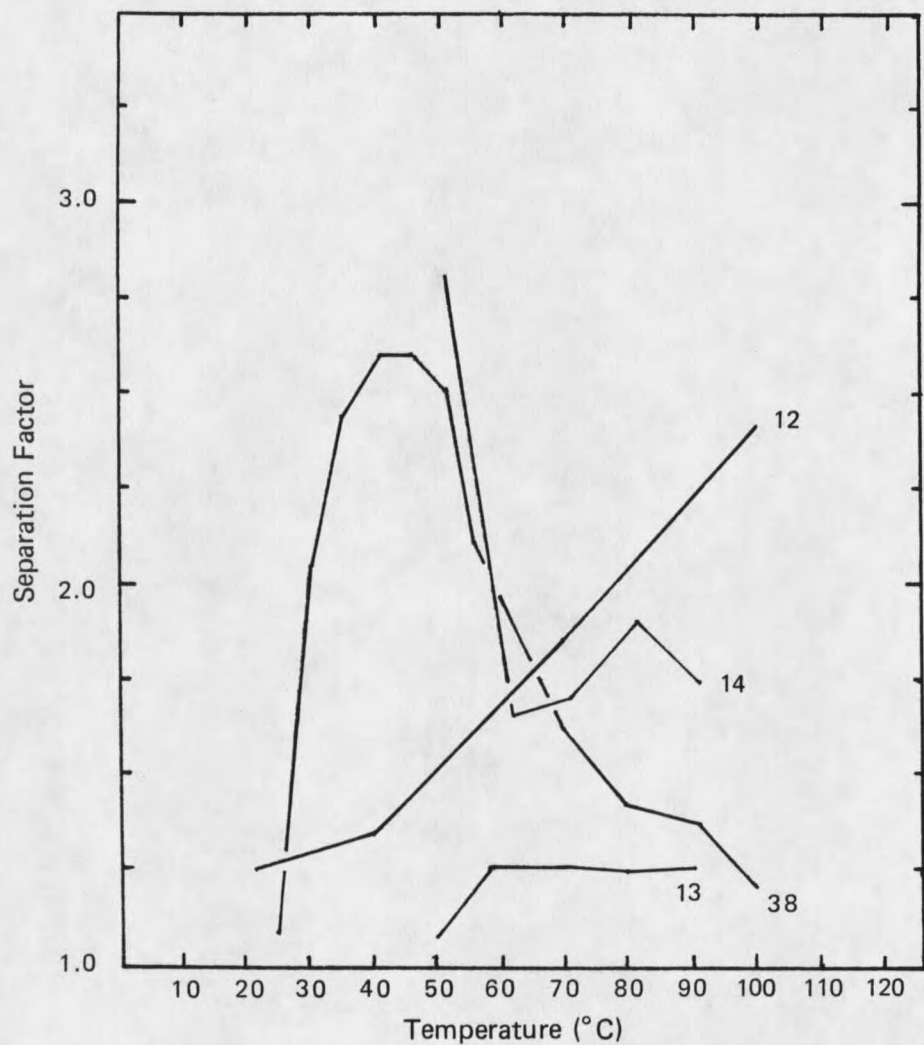


Figure 6. Separation factor vs. temperature for modified polyvinylidene fluoride films.
Note: For film identification see Table 4.

Table 4. Summary of Test Results for Miscellaneous Modified Polyvinylidene Fluoride Films.

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/m ² -hr)	% Oxygen in Permeate	Separation Factor
12	5-Ring PMPE	22	3.81×10^{-4}	25.1	1.26
		40	5.16×10^{-4}	26.4	1.35
		70	1.30×10^{-3}	33.1	1.86
		100	3.22×10^{-3}	39.1	2.42
13	3-Methyl Sulfone	50	3.97×10^{-4}	22.2	1.08
		58	6.86×10^{-4}	25.0	1.26
		70	1.06×10^{-3}	25.0	1.26
		80	1.96×10^{-3}	24.9	1.25
		90	3.84×10^{-3}	25.0	1.26
14	L-Menthol	51	1.45×10^{-4}	42.8	2.82
		62	7.11×10^{-4}	30.6	1.66
		71	1.76×10^{-3}	31.3	1.71
		81	1.95×10^{-3}	33.7	1.91
		91	3.19×10^{-3}	31.7	1.75
15	Bis-hydroxymethyl terephthalate	92	5.90×10^{-4}	35.5	2.07
38	Polyvinylidene Fluoride Film No solvent present	25	---	22.5	1.09
		30	---	35.3	2.05
		35	---	39.4	2.45
		41	---	41.0	2.61
		46	---	41.0	2.61
		51	---	40.1	2.52
		55	---	36.0	2.12
		70	---	30.2	1.63
		80	---	27.5	1.43
		91	---	26.8	1.38
		100	---	24.5	1.22

*Note: Run designations used are the same as those used on the figures.

**Note: All flux values are based on membranes having a thickness of 1 mil.

***Note: Where there are no recorded separation indexes the permeation was too low to allow measurement.

The effect will depend on the modifier used and temperature as indicated in the theory section of this thesis.

Modified Membranes Using Amines

Membranes 15 through 22 were modified using different amines (see Table 5 and Fig. 7).

Table 5. Summary of Test Results for Amine-Modified Polyvinylidene Fluoride Films.

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/m ² -hr)	% Oxygen in Permeate	Separation Factor
16	Diphenyl Amine	23	---	36.0	2.12
		36	---	47.7	3.43
		40	---	49.3	3.66
		49	---	48.1	3.48
		58	---	41.3	2.65
		70	---	35.0	2.03
		80	---	34.6	1.99
		91	---	33.1	1.86
		101	---	30.2	1.63
17	N-isopropyl Benzyl Amine	23	1.56×10 ⁻⁴	32.7	1.83
		40	1.78×10 ⁻⁴	23.3	1.14
		51	5.87×10 ⁻⁴	39.2	2.43
		61	7.35×10 ⁻⁴	35.6	2.08
		71	1.74×10 ⁻³	34.9	2.02
		82	5.21×10 ⁻³	33.4	1.89
		92	1.18×10 ⁻²	25.7	1.30
18	Tetra-hydro-3-thiophene Amine 1,1-Dioxide	61	2.90×10 ⁻⁴	34.1	1.95
		71	4.87×10 ⁻⁴	30.2	1.63
		81	1.17×10 ⁻³	29.0	1.54
		92	2.39×10 ⁻³	28.6	
19	Monoethanol Amine	102	8.71×10 ⁻⁴	37.3	2.24
20	Diethanol Amine	91	1.41×10 ⁻³	39.2	2.43
		101	2.36×10 ⁻³	40.4	2.55
21	Triethanol Amine	91	1.01×10 ⁻³	42.6	2.79
		100	1.52×10 ⁻³	40.9	2.60
22	Diisopropyl Ethanol Amine	81	3.74×10 ⁻⁴	32.4	1.80
		93	1.14×10 ⁻³	38.4	2.35
		100	1.91×10 ⁻³	36.6	2.17

Table 5 (continued).

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/ m ² -hr)	% Oxygen in Permeate	Separation Factor
38	Polyvinylidene Fluoride Film No Solvent present	25	---	22.5	1.09
		30	---	35.3	2.05
		35	---	39.4	2.45
		41	---	41.0	2.61
		46	---	41.0	2.61
		51	---	40.1	2.52
		55	---	36.0	2.12
		70	---	30.2	1.63
		80	---	27.5	1.43
		91	---	26.8	1.38
		100	---	24.5	1.22

*Note: Run designations used are the same as those used on the figures.

**Note: All flux values are based on membranes having a thickness of 1 mil.

***Note: Where there are no recorded separation indexes the permeation was too low to allow measurement.

Of the amines the use of diphenyl amine as the modifier gave the highest separation index; 3.66 at 40°C. Only two of the amine-modified membranes gave measurable separation indexes over the entire temperature range. Of these, only diphenyl amine gave consistently higher separation indexes than those of the nonmodified PVF. Diphenyl amine also shows behavior similar to that of nonmodified PVF over the entire temperature range. Replacing one of the phenyl groups (membrane 16) with a propyl group (membrane 17) lowers the separation index substantially. None of the ethanol amines gave results below 80°C due to the permeation rate being too low to be measured. However, among the amine-modified membranes the ethanol amines gave the highest separation indexes, 2.17 to 2.79, above 90°C.

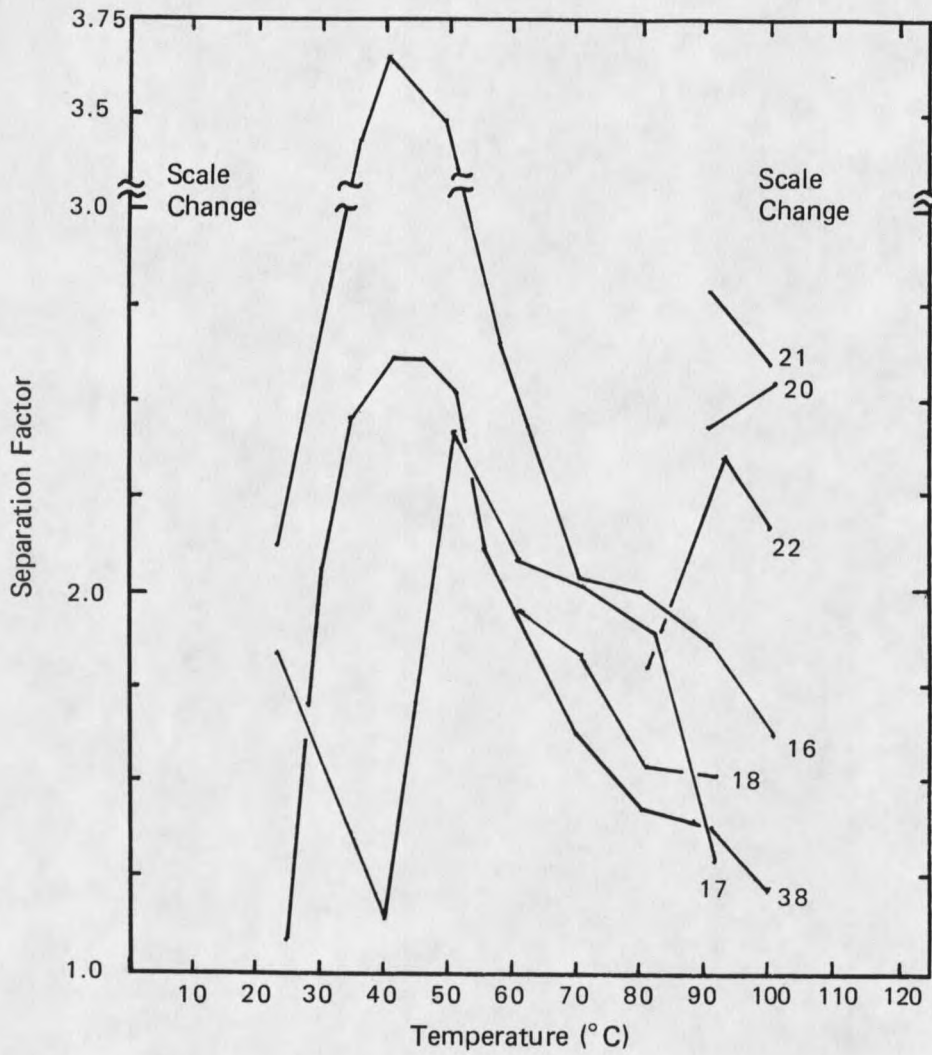


Figure 7. Separation factor vs. temperature for amine-modified polyvinylidene fluoride films. Note: For film identification see Table 5.

Modified Membranes Using Glycols

Membranes 23 through 31 were modified using various glycols. The results are reported in Table 6 and on Figures 8, 9, and 10. The best separation index was 3.27 at 42°C. This was obtained from using diethylene glycol as the modifier. Looking at the results obtained from diethylene, triethylene and tetraethylene glycol (see Fig. 6) it can be seen that the addition of ethylene groups to the glycol molecule decreases the separation at temperatures above approximately 55°C. Adding additional propylene groups also decreases the separation as shown in Figure 8, membranes 23 and 24. Above approximately 70°C the glycols show similar separation characteristics. In general the use of glycols as modifiers increases the separation index of PVF at temperatures above approximately 60°C.

Modified Membranes Using Ethers

Membranes 32 through 36 were modified using various ethers. The results are reported on Figure 11 and Table 7. The maximum separation index observed was 2.54 at 60°C using diphenyl ether as the modifier. All the membranes except membrane 35 (Modifier-dipropylene glycol dimethyl ether) show very similar separation characteristics over the entire temperature range. Increasing the size of the glycol group on the methyl ether group decreases the separation above 60°C. This same result occurs when increasing the size of the glycol group on dimethyl ether. However, this does not occur when adding a methyl to the methyl ether having the same glycol. In general the use of ethers as modifiers increases separation at temperatures above approximately 60°C as compared to the separation of nonmodified PVF.

Table 6. Summary of Test Results for Glycol-Modified Polyvinylidene Fluoride Films.

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/ m ² ·hr)	% Oxygen in Permeate	Separation Factor
23	Propylene Glycol	25	---	24.9	1.25
		41	---	38.9	2.40
		52	---	44.9	3.07
		62	---	45.5	3.13
		71	---	42.1	2.73
		80	---	40.7	2.58
		91	3.37×10^{-4}	38.1	2.32
		102	4.50×10^{-4}	34.3	1.96
24	Tripropylene Glycol	27	---	28.5	1.50
		42	---	30.9	1.68
		55	---	40.5	2.56
		62	---	38.8	2.38
		72	---	40.6	2.57
		80	3.89×10^{-4}	37.6	2.27
		90	1.74×10^{-3}	34.9	2.02
		101	3.39×10^{-3}	34.3	1.96
25	50% Dipropylene 50% Diethylene Glycol	27	---	24.2	1.20
		42	---	32.6	1.82
		51	---	37.3	2.24
		61	---	41.2	2.64
		70	5.13×10^{-4}	40.2	2.53
		80	1.85×10^{-3}	39.7	2.48
		90	4.08×10^{-3}	36.8	2.19
		101	7.21×10^{-3}	35.2	2.04
26	Diethylene Glycol	25	---	27.4	1.42
		42	---	46.5	3.27
		52	---	35.8	2.10
		62	---	40.2	2.53
		70	---	39.1	2.42
		80	4.91×10^{-4}	35.7	2.09
		91	1.79×10^{-3}	32.8	1.84
		100	3.35×10^{-3}	34.2	1.96
27	Triethylene Glycol	26	---	24.0	1.19
		41	---	32.0	1.77
		51	---	39.3	2.44
		58	---	30.5	1.65
		70	---	40.9	2.60
		81	---	36.5	2.16
		92	1.24×10^{-3}	35.2	2.04
		101	2.85×10^{-3}	33.1	1.86

Table 6 (continued).

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/ m ² ·hr)	% Oxygen in Permeate	Separation Factor
28	Tetraethylene Glycol	27	---	29.2	1.55
		43	---	36.0	2.12
		52	---	39.9	2.50
		62	---	39.9	2.50
		72	---	38.8	2.39
		80	5.43×10^{-4}	37.8	2.29
		90	1.91×10^{-3}	35.7	2.09
		100	3.56×10^{-3}	35.2	2.04
29	1,4-Butylene Glycol	22	---	21.7	1.04
		41	---	30.4	1.64
		51	---	36.9	2.20
		59	---	37.8	2.29
		69	---	40.8	2.59
		80	---	39.1	2.42
		90	3.92×10^{-4}	37.3	2.24
		100	2.15×10^{-3}	36.5	2.16
30	Pentamethylene Glycol	23	---	23.4	1.15
		40	---	24.6	1.23
		51	---	36.5	2.16
		60	---	38.7	2.37
		70	---	41.2	2.64
		79	---	39.1	2.42
		91	7.69×10^{-4}	38.9	2.40
		100	2.78×10^{-3}	35.8	2.10
31	Dipropylene Glycol Dibenzoate	27	---	25.2	1.27
		42	---	30.5	1.65
		51	---	33.1	1.86
		61	---	38.2	2.33
		70	4.50×10^{-4}	37.4	2.25
		80	1.53×10^{-3}	38.3	2.34
		90	3.50×10^{-3}	37.0	2.21
		100	6.57×10^{-3}	34.8	2.01
38	Polyvinylidene Fluoride Film No solvent present	25	---	22.5	1.09
		30	---	35.3	2.05
		35	---	39.4	2.45
		41	---	41.0	2.61
		46	---	41.0	2.61
		51	---	40.1	2.52
		55	---	36.0	2.12

Table 6 (continued).

Run #*	Membrane	Pressure = 290 psia		Feed = 21% Oxygen in Air	
		Temperature (°C)	Flux** (m ³ (STP)/ m ² -hr)	% Oxygen in Permeate	Separation Factor
38	Polyvinylidene	70	---	30.2	1.63
(cont.)	Fluoride Film	80	---	27.5	1.43
	No solvent present	91	---	26.8	1.38
	(cont.)	100	---	24.5	1.22

*Note: Run designations used are the same as those used on the figures.

**Note: All flux values are based on membranes having a thickness of 1 mil.

***Note: Where there are no recorded separation indexes the permeation was too low to allow measurement.

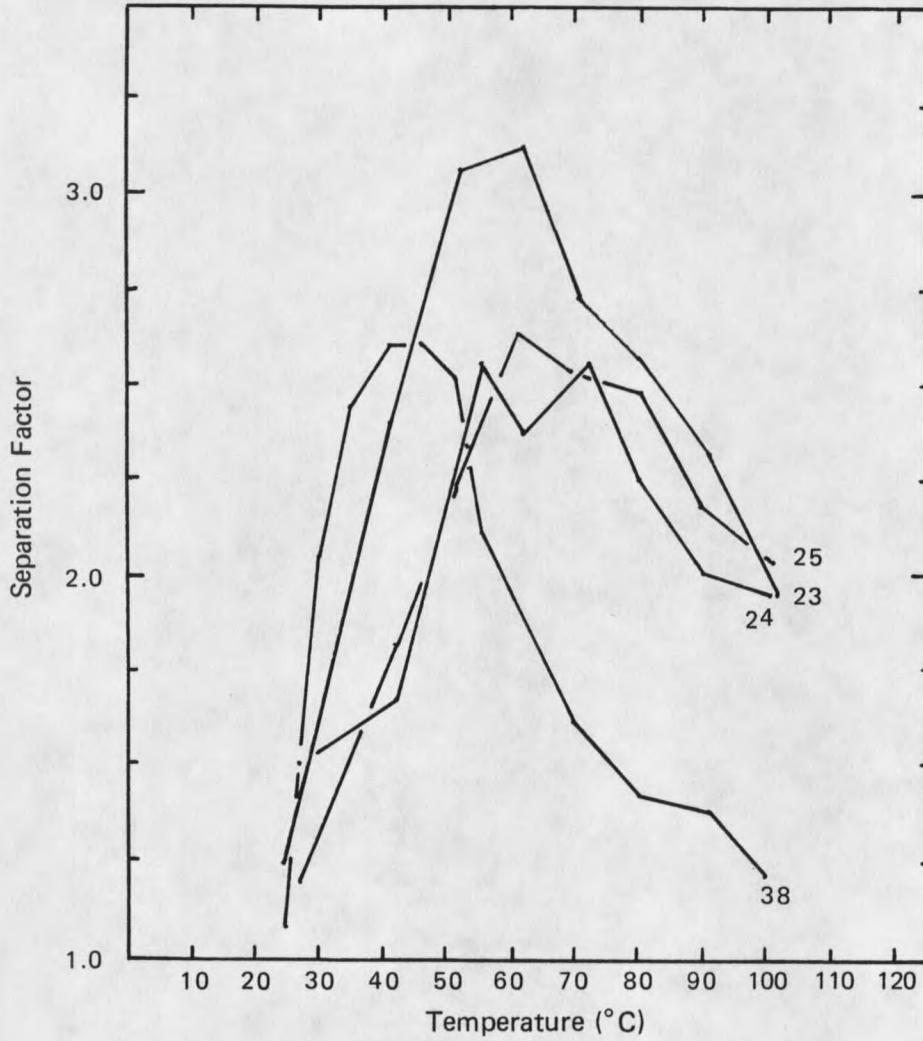


Figure 8. Separation factor vs. temperature for glycol-modified polyvinylidene fluoride films. Note: For film identification see Table 6.

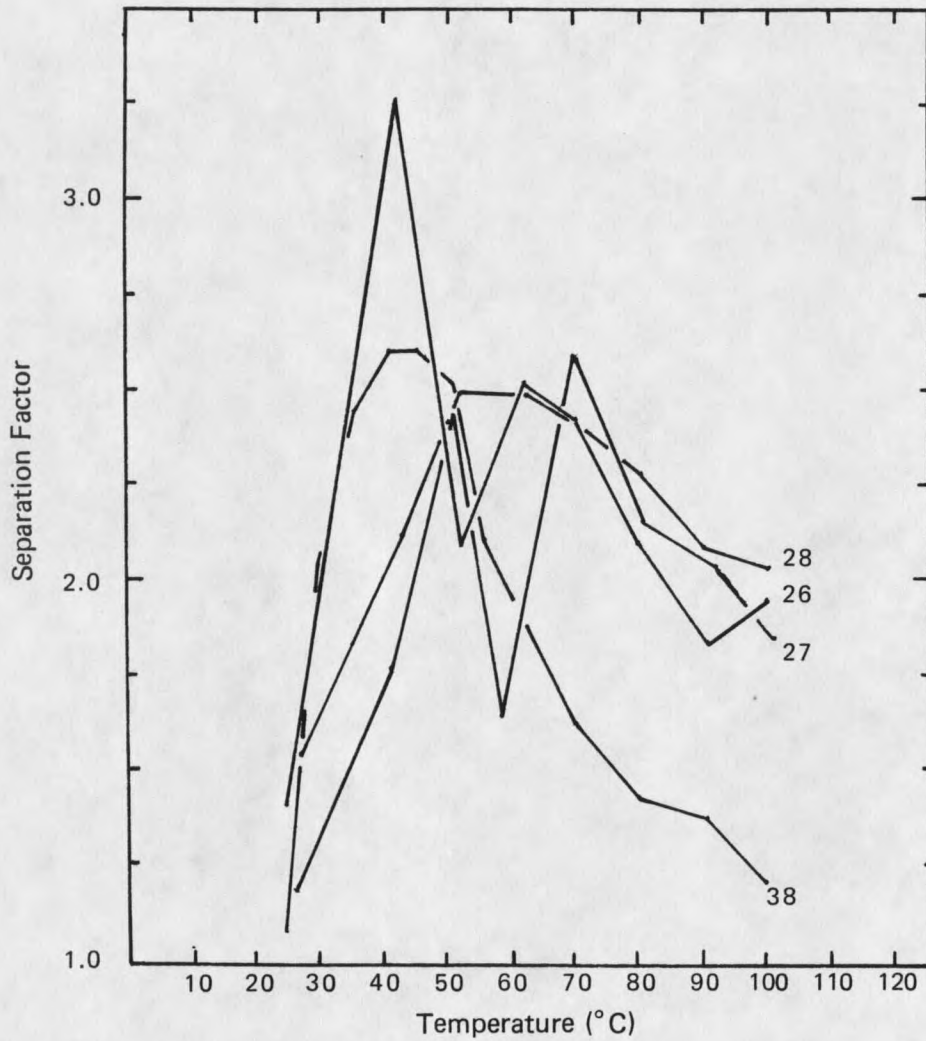


Figure 9. Separation factor vs. temperature for glycol-modified polyvinylidene fluoride films. Note: For film identification see Table 6.

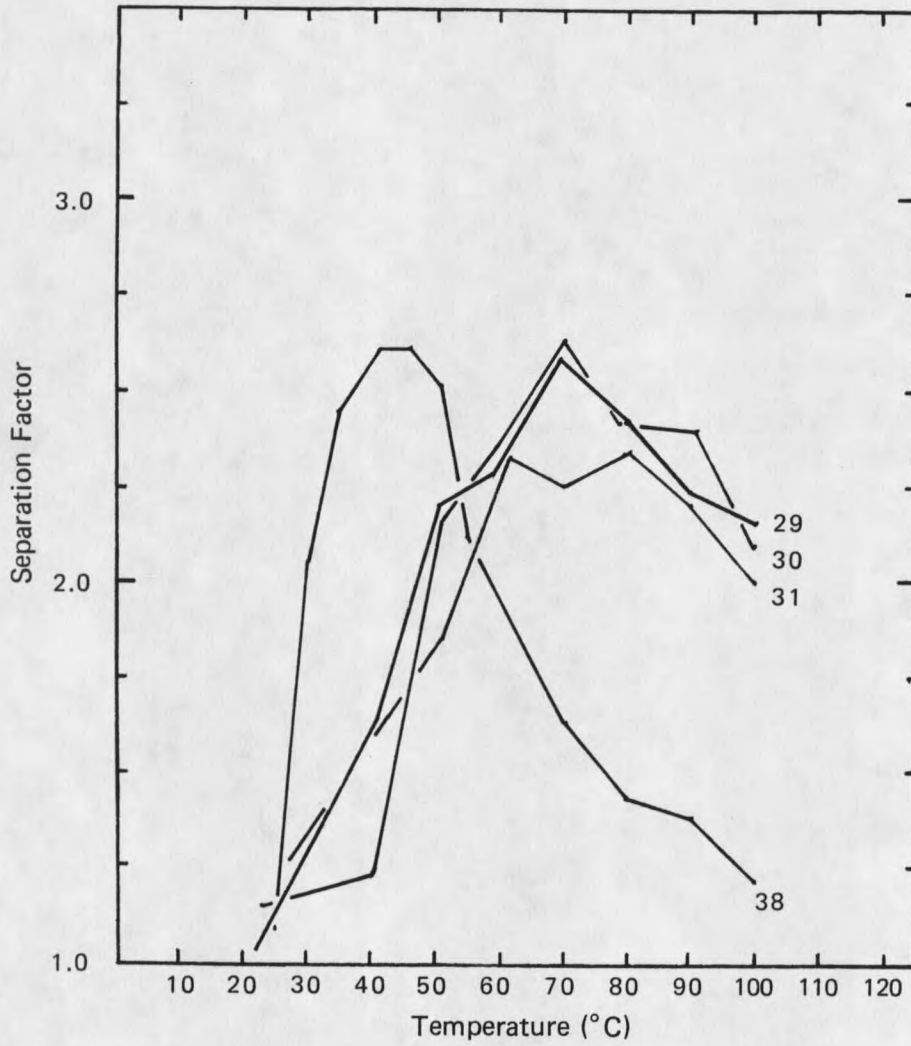


Figure 10. Separation factor vs. temperature for glycol-modified polyvinylidene fluoride films. Note: For film identification see Table 6.

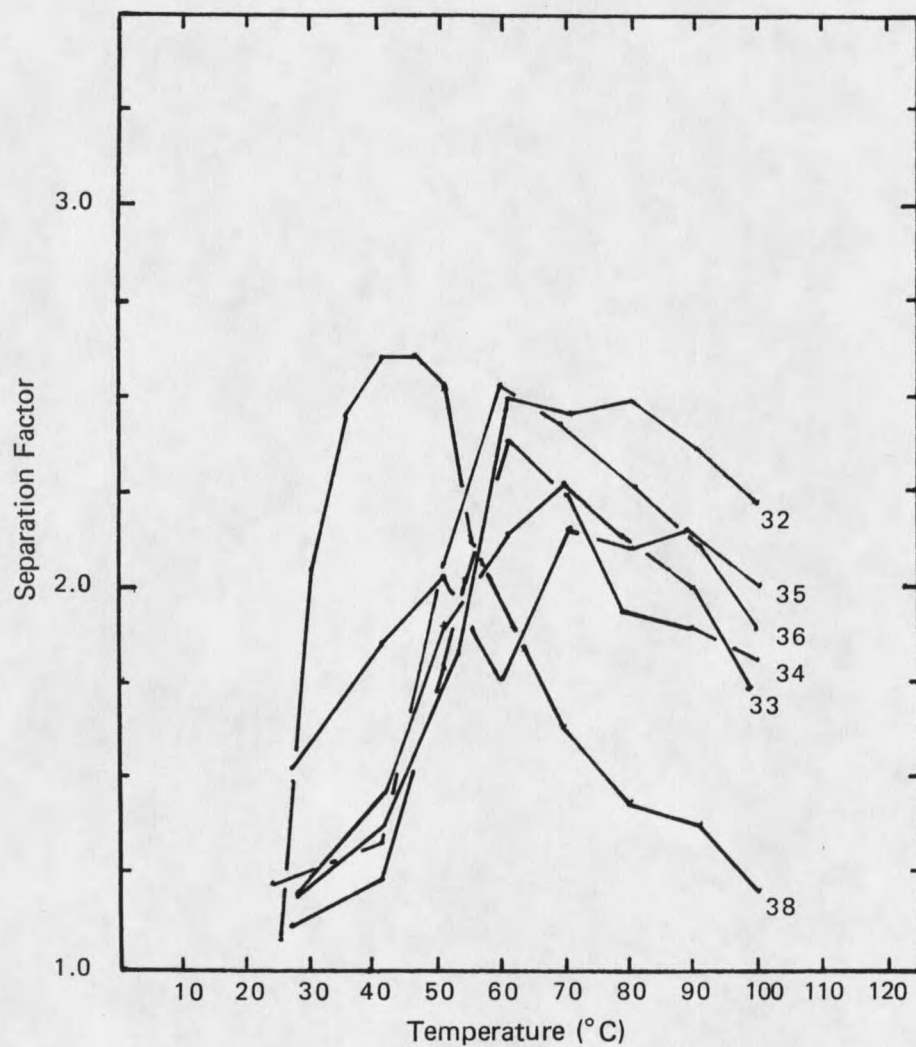


Figure 11. Separation factor vs. temperature for ether-modified polyvinylidene fluoride films. Note: For film identification see Table 7.

Table 7. Summary of Test Results for Ether-Modified Polyvinylidene Fluoride Films.

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/ m ² -hr)	% Oxygen in Permeate	Separation Factor
32	Ethylene Glycol Methyl Ether	28	---	24.0	1.19
		42	---	26.8	1.38
		53	---	32.7	1.83
		61	---	39.9	2.50
		71	---	39.5	2.46
		80	---	39.8	2.49
		91	5.10×10^{-4}	38.7	2.37
		100	2.49×10^{-3}	37.2	2.23
33	Propylene Glycol Methyl Ether	28	---	24.0	1.19
		42	---	28.0	1.46
		51	---	33.6	1.90
		61	---	36.3	2.14
		70	---	37.7	2.28
		79	---	36.3	2.14
		90	---	34.7	2.00
		99	1.05×10^{-3}	31.6	1.74
34	Propylene Glycol Dimethyl Ether	27	---	22.9	1.12
		41	---	24.8	1.24
		51	---	32.2	1.79
		60	---	38.9	2.40
		70	---	37.4	2.25
		79	---	34.0	1.94
		90	5.37×10^{-4}	33.4	1.89
		100	1.66×10^{-3}	32.6	1.82
35	Dipropylene Glycol Dimethyl Ether	27	---	28.8	1.52
		41	---	33.1	1.86
		51	---	35.0	2.03
		60	---	31.9	1.76
		70	---	36.5	2.16
		80	---	35.9	2.11
		89	3.34×10^{-4}	36.5	2.16
		100	2.12×10^{-3}	34.8	2.01
36	Diphenyl Ether	24	---	24.5	1.22
		41	---	26.3	1.34
		51	---	35.4	2.06
		60	---	40.3	2.54
		69	---	39.2	2.43
		81	---	37.6	2.27
		91	2.49×10^{-4}	36.0	2.12
		100	1.70×10^{-3}	33.6	1.90

Table 7 (continued).

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/ m ² -hr)	% Oxygen in Permeate	Separation Factor
38	Polyvinylidene Fluoride Film No solvent present	25	---	22.5	1.09
		30	---	35.3	2.05
		35	---	39.4	2.45
		41	---	41.0	2.61
		46	---	41.0	2.61
		51	---	40.1	2.52
		55	---	36.0	2.12
		70	---	30.2	1.63
		80	---	27.5	1.43
		91	---	26.8	1.38
		100	---	24.5	1.22

*Note: Run designations used are the same as those used on the figures.

**Note: All flux values are based on membranes having a thickness of 1 mil.

***Note: Where there are no recorded separation indexes the permeation was too low to allow measurement.

Nonmodified PVF Using Different Solvents

Three nonmodified PVF membranes were tested (see Table 8 and Fig. 12). Membrane 38 was manufactured using dimethyl formamide (DMFA) as the solvent with all the solvent driven off in the drying stage. This membrane was used to establish baseline results to compare the effect of modifiers. Membrane 37 contained DMFA while the test was run and membrane 39 contained dimethyl sulfoxide (DMSO) as the solvent. The presence of solvent was checked by using a gas chromatograph. The solvent would show up as a third peak much later than the oxygen and nitrogen peaks. All three membranes showed the same separation results, with a maximum separation index of approximately 2.6 at 40°C to 50°C. This could be an indication of the similarity of the effect that the two solvents have on separation.

Table 8. Summary of Test Results for Nonmodified Polyvinylidene Fluoride Films.

Run #*	Membrane	Pressure = 290 psia Feed = 21% Oxygen in Air			
		Temperature (°C)	Flux** (m ³ (STP)/m ² -hr)	% Oxygen in Permeate	Separation Factor
37	Polyvinylidene Fluoride Film Saturated with DMFA	25	---	22.1	1.07
		32	---	35.0	2.03
		35	---	39.0	2.41
		39	---	41.0	2.61
		43	---	40.9	2.60
		48	---	40.1	2.52
		55	---	32.7	1.83
		70	---	30.1	1.62
		80	---	27.1	1.40
		91	---	27.0	1.39
		100	---	25.2	1.27
38	Polyvinylidene Fluoride Film No solvent present	25	---	22.5	1.09
		30	---	35.3	2.05
		35	---	39.4	2.45
		41	---	41.0	2.61
		46	---	41.0	2.61
		51	---	40.1	2.52
		55	---	36.0	2.12
		70	---	30.2	1.63
		80	---	27.5	1.43
		91	---	26.8	1.38
		100	---	24.5	1.22
39	Polyvinylidene Fluoride Film Saturated with DMSO	25	---	23.1	1.13
		31	---	35.3	2.05
		35	---	40.6	2.57
		40	---	41.6	2.68
		45	---	41.5	2.67
		51	---	40.9	2.60
		55	---	34.0	1.94
		70	---	31.5	1.73
		81	---	27.3	1.41
		89	---	27.0	1.39
		99	---	23.7	1.17

*Note: Run designations used are the same as those used on the figures.

**Note: All flux values are based on membranes having a thickness of 1 mil.

***Note: Where there are no recorded separation indexes the permeation was too low to allow measurement.

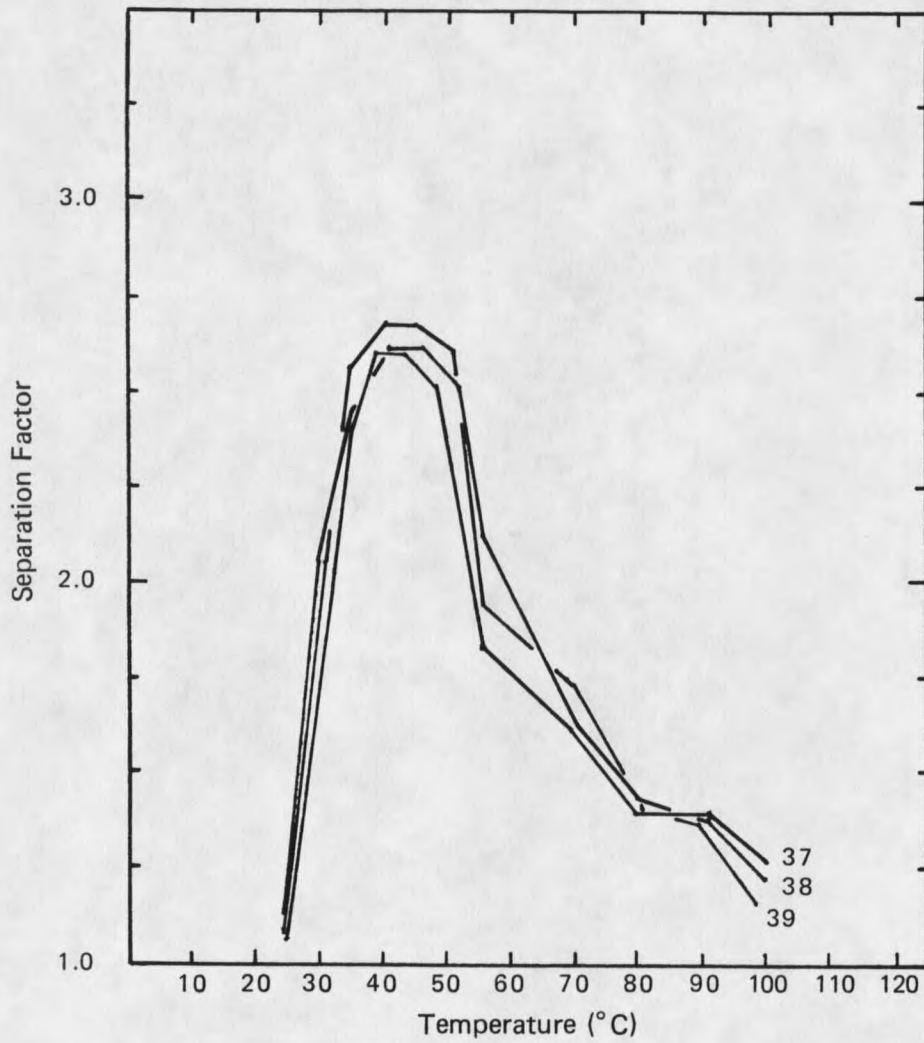


Figure 12. Separation factor vs. temperature for nonmodified polyvinylidene fluoride films. Note: For film identification see Table 8.

DISCUSSION

One possible reason for the preferential selectivity of the membranes for oxygen versus nitrogen could be that oxygen tends to be more soluble than nitrogen in the modifiers. Another possible reason is that the oxygen molecule has a smaller diameter than nitrogen. This difference in size would give oxygen a higher diffusivity than nitrogen.

From the separation results obtained, it can be seen that almost all membranes tested gave separation factors above 1.00. Only cellophane decreased the oxygen content of the permeate below that of the feed.

The unmodified PVF gave high separation indexes from 35°C ($\alpha = 2.45$) to 51°C ($\alpha = 2.52$). Above 51°C the separation dropped off rapidly (Fig. 12). The cause of this could be that at the higher temperatures the difference in solubility of oxygen and nitrogen becomes less until the solubility of nitrogen exceeds that of oxygen. This would negate the effect of higher diffusivity and solubility of oxygen versus nitrogen in the membrane. Most of the modifiers added to PVF decreased the separation index of the membrane below the 50°C to 60°C temperature range. Above this temperature range the modifiers increased the separation index of PVF. The individual solubilities and diffusivities of oxygen and nitrogen become the controlling factor in determining the selectivity of the membrane. The individual separation characteristics are then determined by the modifier used.

Of the modifiers used two did not show this behavior. 3-Methyl sulfone did not give enough permeate, below 50°C, to enable measurement of the separation index. Above 50°C, 3-methyl sulfone gave separation indexes lower than those of unmodified PVF. Diphenyl amine was the only membrane modifier to give separation indexes greater than those of unmodified PVF over the entire temperature range. In this case it appears the

modifier increased the solubility of oxygen versus nitrogen in the membrane. This increase in solubility becomes the controlling factor in the separation of oxygen from the feed.

Three membranes showed little change in the separation index as the temperature was increased. These membranes were modified by the use of polyester, silicone, and 3-methyl sulfone. Cellophane also showed constant separation over the temperature range. However, these separation indexes were obtained only at 40°C, 60°C, and 100°C. To confirm the results the membrane should be tested at other temperatures. One possible reason for the constant separation indexes is the degree of crystallinity and crystallite size. If the degree of crystallinity is high and the crystallite size is large, temperature increase has less effect on the separation process [9, p. 412].

The maximum separation indexes obtained among each chemical group and from the commercial membranes are: polystyrene, $\alpha = 4.29$; diphenyl amine, $\alpha = 3.66$; diethylene glycol, $\alpha = 3.27$; diphenyl ether, $\alpha = 2.54$. Of these only the glycol has no phenyl group. From the limited data obtained it appears that phenyl groups tend to increase the separation index of a membrane more than aliphatic groups do. For instance, among the commercial membranes, adding a phenyl group to the ethylene units in polyethylene to form polystyrene increases the maximum separation index from 2.38 to 4.29. Looking at the amine-modified membranes it can be seen that removing the n-isopropyl group from n-isopropyl benzyl amine and replacing it with a phenyl group (diphenyl amine) increases the maximum separation index from 2.43 to 3.66. Further tests need to be made in order to confirm this observation.

Of the membranes tested, polystyrene and ethyl cellulose have oxygen-nitrogen separation indexes reported in the literature [3]. Polystyrene has a reported separation index of 3.1 and ethyl cellulose has a separation index of 3.3. In comparison, the maximum separation indexes obtained in this study for polystyrene and ethyl cellulose were 4.29 at 40°C

and 2.96 at 49°C, respectively. One reason for this difference between reported and present experimental separation factors could be different operating temperatures. No operating conditions were given in the literature report [3].

The largest separation indexes reported in the literature are obtained by using facilitated transport membranes [3]. The maximum reported separation index is 30 (approximately 88% oxygen) which is almost seven-fold better than the best index achieved in this study (polystyrene, $\alpha = 4.29$).

CONCLUSIONS

1. Most commercial membranes tested can be used to enrich the oxygen content of air.
2. Nonmodified polyvinylidene fluoride substantially enriches the oxygen content of air between 30°C to 50°C.
3. The most promising amine-modified PVF membrane was diphenyl amine which more than doubled the oxygen content in the permeate between 36°C and 50°C. Of the ethers, diphenyl ether was the most promising modifier. Of the commercial membranes tested, polystyrene was the most promising. It appears that the addition of phenyl groups versus aliphatic chains increases the coefficient of permeability of oxygen in the membranes.
5. In general the addition of a glycol or ether as a modifier increased the separation characteristics of nonmodified PVF above 60°C.
6. In general above the midrange temperatures the solubility and diffusivity of nitrogen is affected more than that of oxygen as evidenced by the decrease in the separation characteristics of the modified membranes.

RECOMMENDATIONS FOR FURTHER STUDY

1. Further study using phenyl groups on the modifier compounds is recommended. Specific compounds to try are phenyl-amine, phenol, benzyl phenol, diphenyl ethane, etc. The use of these compounds as modifiers, along with the data presented in this thesis, would help show the effect that the phenyl groups have on preferential oxygen selectivity of membranes.
2. Tests should be made on the effect of modifiers on crystallinity of the membrane to determine how much effect the crystallinity has on separation characteristics.

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