# TEFLON AF MEMBRANE TRANSPORT OF ORGANIC SOLUTES

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Submitted to the Graduate Faculty of

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of the requirements for the degree of

Master in Sciences

University of Pittsburgh

2006

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February 3, 2006

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Teflon AF 2400 membranes containing various weight percent FC-70 were cast from FC-72 solution. The membrane surface is hydrophobic as shown by contact angle measurement.

Free volume in Teflon membranes was calculated by measuring the membrane density using the hydrostatic method. Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were conducted to study the thermal transitions of Teflon AF membranes. The glass transition temperature of Teflon membranes is -63 °C at 5 wt% FC-70 in comparison with 240 °C at 0 wt% FC-70.

The permeability of Teflon membranes was investigated by transport experiments. The four probe solutes were toluene, α,α,α-trifluorotoluene, nitrobenzene and pentafluoronitrobenzene. The permeability coefficients of the probe solutes are found to be very sensitive to the FC-70 content and the temperature. The permeability coefficients of all solutes change with FC-70 in a similar way. They decrease initially as FC-70 content increases at low FC-70 concentration with reversal of this trend at higher FC-70 concentration, and decrease again and finally level off. Teflon AF membranes with less than 10 wt% FC-70 could be associated with the polymer's anti-plasticization, an effect indicated by a reduction in the free volume, a decrease in the glass transition temperature and a reduction in the partition ratio and permeability coefficient. Teflon AF membranes with 10wt% FC-70 or more could be plasticized, resulting in lower glass transition temperature, higher free volume and higher permeability coefficient.

Selectivity of the membranes was investigated for the pair α,α,α-trifluorotoluene/toluene and for the pair pentafluoronitrobenzene/nitrobenzene. It reaches a maximum at 10 wt% FC-70 for both pairs at 20 $^{o}$C. 10 wt% FC-70 is likely a turning point of plasticization, which is quite interesting since it is also related to the highest selectivity.

Teflon AF membranes could also be plasticized by the organic liquid with which it is in contact. Chloroform seems to plasticize the membranes (they get pliable) and change the properties of the membranes to a less ‘fluorous’ environment. The concentration of FC-70 may change during transport experiments. We thus need to find a means to plasticize the films while keeping them fluorous.

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# ACKNOWLEDGMENTS

I would like to thank, first and foremost, my advisor, Dr. Stephen Weber, for his guidance, remarkable patience and caring support throughout the two years in the United States. His impressive knowledge and creative thinking have been the source of inspiration for me throughout this work. I am also extremely grateful to the members of my committee, Dr. Dennis Curran, Dr. Adrian Michael, for their excellent comments and suggestions which helped me to improve my work.

My thanks also go to my colleagues in Dr. Weber's group, especially Hong Zhao, Yanhong Yang, Yifat Guy, Kristi O'Neal, Hui Fang. Their support and friendship have made the process enjoyable. I would like to thank Dr. Abul Hussam for his nice HSGC work. Special thanks to Marie Urick for her $T_g$ measurement.

I would like to thank the National Science Foundation for financial support through Grant CHE-0315188 and CHE-0078520.

Finally, I would like to express my profound thanks to my beloved parents and husband for their support, encouragements and love throughout my studies over the years.

# 1.0 INTRODUCTION

## 1.1 MOTIVATION AND OBJECTIVES

Molecular recognition is one of the most fundamental processes in chemistry, physics and biology. The recognition process is largely driven by non-covalent forces such as hydrogen bond interactions, electrostatic interactions, van der Waals forces, π-π interactions, and conformational energy.[1] Those non-covalent forces can apply to both inter- and intra-molecular processes.[2] Specific examples of molecular recognition include protein-based catalysis in biological systems as well as hydrogen bond-mediated construction of receptors. Artificial receptor-based molecular recognition can enhance the selectivity of extraction while minimizing the consumption of solvents.[3] There are a large number of factors (energetic, entropic and kinetic, etc) which have to be taken into account for the theoretical description of molecular recognition.[4] Recently developed models such as the induced fit models, the proofreading models and the lock-and-key models have revealed the importance of complementarity in size, shape, and functional groups in molecular recognition.[5] The lock-and-key models, proposed by Emil Fischer over 100 years ago, are still the most up-to-date principles in molecular recognition. The complementarity between the receptor and the substrate is very similar to the "lock-and-key" function, with the lock being the receptor such as a protein or enzyme and the key being the substrate such as a drug, which is recognized by the receptor to give a well defined receptor-substrate complex.[1, 6, 7] Based on molecular recognition mechanisms, numerous types of receptors have been designed and investigated for the binding of complementary substrates of chemical or biological significance.

The membrane separation based on molecular recognition has received much attention in various fields because of its high selectivity for target molecules.[8-13] A membrane can be viewed as a barrier, which separates two phases and restricts the motion of molecules passing through it so that some molecules transfer more quickly than others and separation can thus be achieved. A large number of mechanisms are available for this restriction; for example, size variability of the molecules, affinity for the membrane material and permeation driving forces, typically concentration or pressure gradient. The molecular recognition mechanism is widely used to facilitate the membrane-based separation. For example, Yanagioka et al developed a molecular recognition polymer membrane with high selectivity.[14] They use a thermosensitive polymer poly(N-isopropylacrylamide) [P(NIPAM)] to control the molecular recognition ability and a receptor β-cyclodextrin (CD) to recognize the specific guest molecule. Artificial receptors can act as carriers for the selective transport of various types of substrates through artificial or biological membranes. Ideal receptors should possess steric and electronic features complementary to those of the substrate to be bound, together with a rigidity-flexibility balance suitable for the function to be performed. How well things fit together often depends on their predisposition, or preorganization. The molecular recognition based on well-defined interaction patterns can thus be used to explore information at the molecular level in membrane separation processes.

Teflon AF is a novel, potentially useful material for separation. Teflon AF is a copolymer of tetrafluoroethylene (TFE) and 2,2-bistrifluoromethyl-4,5-difluoro-1,3 dioxole (PDD) (Fig. 1).

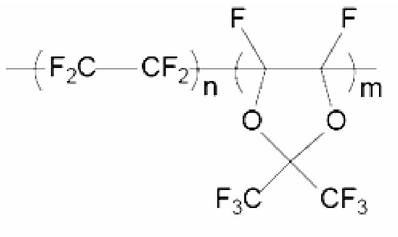
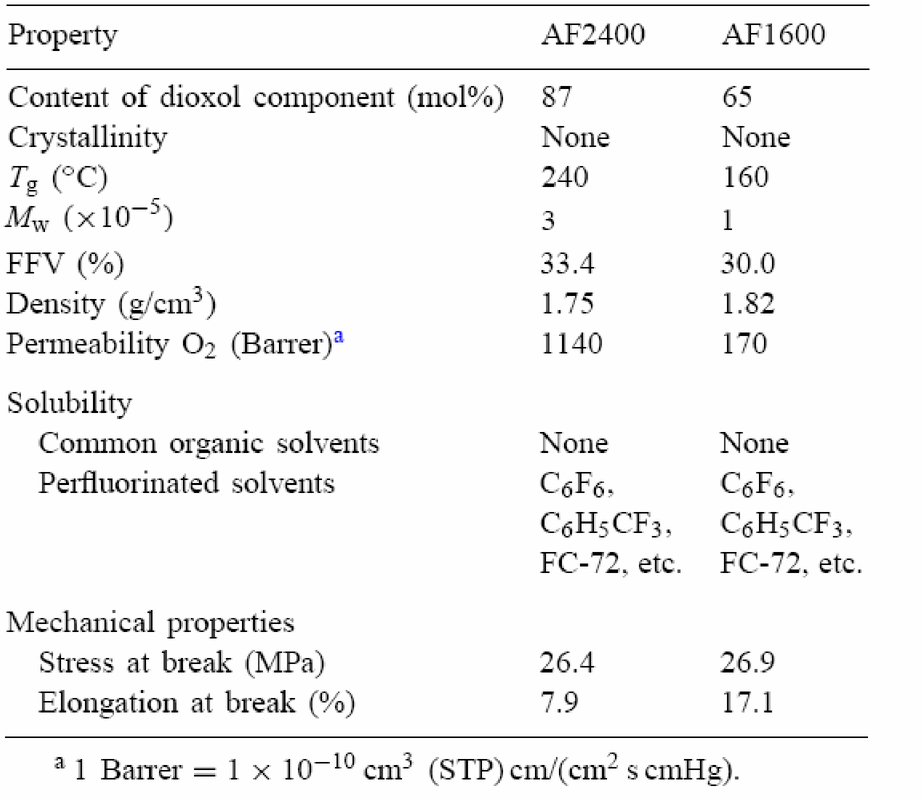


**Figure 1.** Teflon AF

It is commercially available in two polymeric grades, namely Teflon AF 1600 (65% mol PDD, Tg 160 ºC) and Teflon AF 2400 (87 mol% PDD, Tg 240 ºC). Some physical parameters of the two Teflon AF polymers are presented in Table 1.

**Table 1.** Properties of Teflon AF[15, 16]



| Property | AF2400 | AF1600 |
|---|---|---|
| Content of dioxol component (mol%) | 87 | 65 |
| Crystallinity | None | None |
| $T_g$ (°C) | 240 | 160 |
| $M_w$ ($\times 10^{-5}$) | 3 | 1 |
| FFV (%) | 33.4 | 30.0 |
| Density (g/cm$^3$) | 1.75 | 1.82 |
| Permeability $O_2$ (Barrer)[a] | 1140 | 170 |
| Solubility | | |
| Common organic solvents | None | None |
| Perfluorinated solvents | $C_6F_6$,<br>$C_6H_5CF_3$,<br>FC-72, etc. | $C_6F_6$,<br>$C_6H_5CF_3$,<br>FC-72, etc. |
| Mechanical properties | | |
| Stress at break (MPa) | 26.4 | 26.9 |
| Elongation at break (%) | 7.9 | 17.1 |

[a] 1 Barrer = $1 \times 10^{-10}$ cm$^3$ (STP) cm/(cm$^2$ s cmHg).

Teflon AF exhibits high thermal, chemical, mechanical, and electrical stability and shows limited solubility in selected perfluorinated solvents, thus it can be cast into dimensionally stable membranes. Teflon AF membranes have been studied in gas separation[17-21] and pervaporation.[15, [16, 22] In membrane-based gas separation, Teflon AF membranes show high permeability coefficients, which are only secondary to poly(trimethylsilyl propyne) (PTMSP), the most permeable polymer ever known.[17, 20] The high gas permeability may be related to the large free volume since the average radii of free volume elements in Teflon AF are about 5-6Å, which is much larger than those in other polymers. Both Teflon AF membranes reveal high liquid permeation rates and similar selectivity for some mixtures in pervaporation, while Teflon AF 2400 with a larger fractional free volume (FFV) displays higher permeation rate[15, 16, 20]. In the case of membrane separation, attractive materials must meet several requirements: a combination of good permeability and selectivity, stability in contact with the penetrants to be separated, thermal stability as well as time stability. Besides high permeability, Teflon AF membranes show stable transport and mechanical characteristics over time[16] and moderate selectivity to a variety of gases and organic vapors.[15, 17, 20] Moreover, our group investigated Teflon AF membrane transport of organic liquids and suggested the selectivity for the pair trifluorotoluene /toluene and for the pair pentafluorobenzoic acid /benzoic acid.[23, 24] However, more work still needs to be done to improve the selectivity of these membranes.

Emphasis is usually placed on improving both the permeability and selectivity of membranes although there always exists a trade-off between them. The development of supported liquid membranes gives rise to the possibilities of increasing membrane selectivity. Supported liquid membrane (SLM) is a microporous membrane filled with a carrier liquid. The carrier liquid can extract one or more chemical species from a feed liquid. The membrane with the carrier liquid serves as a selective barrier between two phases immiscible with the liquid. Supported liquid membranes have been studied extensively in recent years for separation of metals, organic acids and organic pollutants etc, from dilute aqueous solutions.[25-28] For instance, Ata investigated different types of supported liquid membranes (kerosene/Teflon; n-heptane/Teflon; n-octane/Teflon; and kerosene/Durapore) and demonstrated the high selectivity for the transport of $Cu^{2+}$ across the membranes from an aqueous solution containing $Cd^{2+}$, $Zn^{2+}$, $Co^{2+}$, and $Ni^{2+}$ ions.[29] Our strategy is motivated by the combination of the high selectivity of supported liquid membranes and the large permeability of Teflon AF polymers. Would it result in better separation medium? What kind of carrier liquids could work in our system?

Fluorous liquids are selective solvents for fluorous compounds. Among many commercially available perfluorinated solvents, FC-70, primarily perfluorotripentyl amine, has the highest boiling point of 201~221$^0$C, considerable stability and solvophobicity. FC-70 is thus chosen to aid the selective solvation of fluorous compounds into Teflon membranes. What can we anticipate from the addition of FC-70 into the membranes? Can FC-70 accelerate the transport of some organic solutes while maintaining the high permeability of the membranes? The objective of my research is to explore the possibility of optimizing Teflon AF membranes by addition of FC-70. Our strategy has implications in separation science as well as in organic synthesis since the unique nature of fluorous solvents makes them significant in fluorous biphasic synthesis and fluorous biphasic catalysis.[30-34]

## 1.2 BACKGROUND

We and others are working on developing Teflon AF polymers as dimensionally stable separation medium.[15-18, 20, 22-24, 35, 36] Emphasis is usually placed on developing this novel material for gas or organic vapor separation.[15-22] The permeation process in membrane-based separation is describe by many models (the solution-diffusion model, the pore-flow model, etc), among which the solution-diffusion model is the most widely accepted model of transport in gas permeation, pervaporation, dialysis and reverse osmosis etc. [37] The penetrant transport through a glassy polymeric membrane occurs in three steps:[37-39]

1. partition of penetrant from the source phase into the glassy polymeric membrane;
2. diffusion of the penetrant through the membrane;
3. release of the penetrant at the receiving phase.

According to this model, the permeability coefficient (P) is the product of the diffusion coefficient (D) and the partition ratio of the penetrant from the source phase to the membrane ($K_D$).

$$P = D \cdot K_D \qquad (1\text{-}1)$$

Transport process can thus be categorized in terms of diffusivity- or partition-controlled mass transfer. The diffusion coefficient depends on the amount of energy necessary for the penetrant to execute a diffusive jump through the polymer membrane. Therefore, it is determined by the packing and motion of the polymer segments and by the size and shape of the penetrant molecules. The partition ratio is a measure of the polymer-penetrant interaction and the amount of free volume existing in the polymer membrane. Hence, it is directly relevant to the nature of the penetrant as well as the polymer. In general, permeability decreases with the size of the penetrant for diffusion- controlled mass transfer. In the case of partition-controlled mass transfer, both permeability and partition ratio increase with the size and mass of the penetrant.

The selectivity of the membrane can be defined as:[17]

$$\alpha_{A,B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right)\left(\frac{K_{DA}}{K_{DB}}\right) \qquad (1\text{-}2)$$

The first term, ($D_A/D_B$), is often called the diffusivity selectivity. This term reflects the size of the penetrants relative to the inter- and intra-molecular chain spacing of the polymer. The second term, ($K_{DA}/K_{DB}$), is called the partition or solubility selectivity. It reflects the relative sorption of the penetrants.

Several models (the dual-mode sorption model, the partial immobilization model, etc) have been presented in the literature to explain the sorption behavior of glassy polymeric membranes.[37, 40-46] Transport properties (sorption, diffusion and permeation) might be explained in terms of the structures of the membranes. A glassy polymeric membrane structure is composed of two parts: microvoids (frozen free volume or extra hole free volume) and the polymer matrix as shown in Fig. 2.[44, 47]

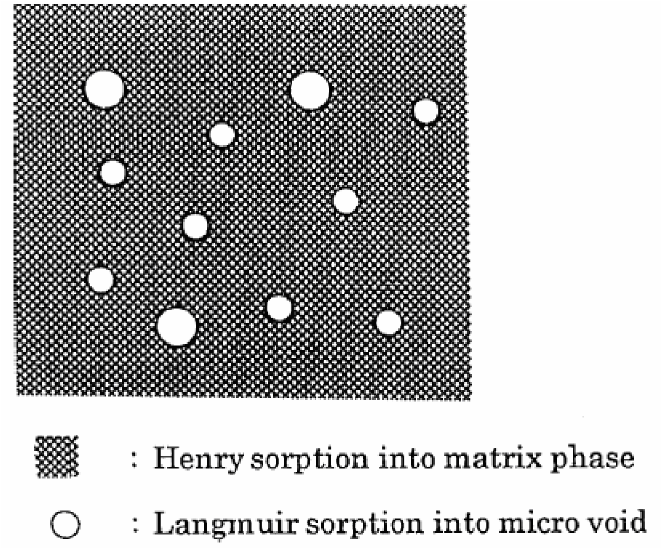
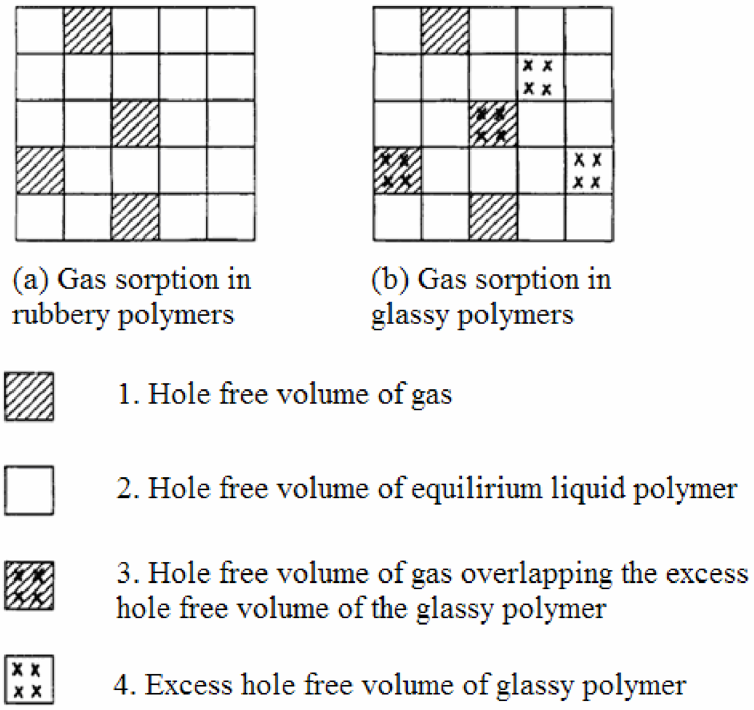


**Figure 2.** Schematic representation of polymeric glassy state depicting the matrix and microvoids

Gas sorption into the glassy membrane can be regarded as sorption into the matrix phase and the microvoid region. According to the dual-mode sorption model, Henry sorption dominates sorption into the matrix phase while Langmuir sorption dominates sorption into the microvoid region. The total sorption is thus equal to the sum of Henry sorption and Langmuir sorption.

Compared to the glassy polymer, the rubbery polymer does not have extra hole free volume as shown in Fig. 3. The lattice sites in Fig. 3(a) represent the hole free volumes associated with the gas and the equilibrium liquid polymer respectively, while the lattice sites in Fig. 3(b) also include the extra hole free volume due to the nonequilibrium state of the glassy polymer. Consequently, the gas sorption in rubbery polymers can be well described at low sorption levels by Henry's law instead of the dual mode sorption model.



(a) Gas sorption in rubbery polymers

(b) Gas sorption in glassy polymers

**Figure 3.** Schematic representation of the free volume based lattice. (a) represents gas sorption in rubbery polymers where two distinct sites can be identified. (b) represents gas sorption in glassy polymers where four distinct sites can be identified.[48]

The free volume theory was proposed to interpret the transport behavior of membranes on a microscopic level. Gas transport through amorphous glassy polymeric membranes is now commonly explained in view of the free volume concept.[48-50] Kanig suggested the definition of specific free volume as:[51]

$$\hat{V}_F = \hat{V} - \hat{V}_0 \qquad (1\text{-}3)$$

where $\hat{V}_F$ is the specific free volume (cm$^3$/g), $\hat{V} = 1/\rho$ is the experimentally determined specific volume (cm$^3$/g), $\hat{V}_0$ is an estimate of the specific volume (cm$^3$/g) at the absolute zero of temperature. The fractional free volume is defined as: [51]

$$FFV(\%) = \frac{\hat{V}_F}{\hat{V}} \qquad (1\text{-}4)$$

The value of $\hat{V}_0$ can be estimated as suggested by Bondi.[52, 53]

$$\hat{V}_0 = 1.3\hat{V}_w \qquad (1\text{-}5)$$

where $\hat{V}_w$ is the van der Waals specific volume of the repeat unit of the polymer. $\hat{V}_w$ can be calculated using the group contribution methods.

The free volume theory gives precise explanation on plasticization. On the macroscopic scale, plasticization shows an increase in softness and ductility, and a decrease in glass transition temperature $T_g$, while on the microscopic level, it reflects a reduction in the interaction between adjacent segments of neighbouring polymer chains and consequently an enhancement in penetrant permeability and diffusivity. In terms of the free volume theory, the addition of a plasticizer of lower molecular weight would increase the free volume of the polymer by increasing the chance of its main chain movement, thus lowering its glass transition temperature. Consequently, a plasticizer with lower $T_g$ is more efficient in reducing the $T_g$ of the whole system. A branched plasticizer is more effective than a linear one with the same molecular weight, since more free volume can result from the branched plasticizer.

Hong Zhao et al explored the separation of organic liquids by Teflon AF membranes.[23, 24] The concentration independence of the permeability of benzene and pyrazine is consistent with the solution-diffusion transport mode. FTIR showed high solvent uptake into Teflon AF membrane, the sorption isotherm of which agrees with the dual-mode sorption model. Teflon AF membrane was demonstrated to have high Langmuir sorption capacity and Henry constants compared to other glassy polymers. The reduction in permeability of Teflon AF membrane doped with Krytox FSH was explained in terms of the free volume theory. Krytox FSH occupies free volume and restricts solute diffusion significantly even as it plasticizes Teflon AF membrane by increasing its chain mobility. With the addition of Krytox FSH, the environment within the free volume becomes more viscous in comparison to the solvent-saturated membrane. The decrease in permeability with the addition of Krytox FSH is thus associated with antiplasticization,[54] i.e., a reduction in glass transition temperature and in permeability.

## 1.3 PROPOSALS

Specifically, here are the questions that I try to answer in this research work in order to understand this novel material and maximize its selectivity and permeability.

1. What is the effect of temperature on transport?

The diffusion and partition of organic liquids in Teflon membranes are obviously thermally activated process. In the case of membrane separation of organic liquids, variation in permeability and selectivity with increasing temperature is thus related to the diffusivity and partitioning of penetrants. The temperature dependence of penetrant permeation through polymers without any thermal transitions is given by the Arrhenius relationship:[16]

$$P = P_0 \exp\left(\frac{-\Delta G_P}{RT}\right) \tag{1-6}$$

where $P_0$ is a pre-exponential factor, $\Delta G_P$ is the activation energy of permeation, R is the gas constant and T is the gas temperature. The van't Hoff equation can be used to describe the temperature dependence of partition ratio:[16]

$$K_D = K_{D0} \exp\left(\frac{-\Delta H_K}{RT}\right) \tag{1-7}$$

where $\Delta H_K$ is the enthalpy change due to the partition of penetrant from the source phase to the polymer. The temperature dependence of diffusion coefficient is defined by the Arrhenius equation:[16]

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \tag{1-8}$$

where $E_D$ is the activation energy for diffusion.

The effects of temperature on the gas transport properties have been reported extensively in the literature.[15, 16, 55-58] Temperature could change the physical state of a polymer, for instance, from a glassy to a rubbery state. An increase in temperature is often accompanied by an increase in the polymer free volume, which suggests changes in the structure and morphology of the polymer matrix itself. Many models show the relationship between various transport parameters and the temperature.[59, 60] The gas transport parameter D was generally observed to increase with temperature, while $K_D$ and P are related to the temperature in a complex way. Up till now, most of the published work focused on the temperature influence on transport properties of gas or organic vapor. The aim of my study is to investigate the trend for organic liquids. Determining how the ratio of permeability coefficients of two organic liquids, i.e. the selectivity, is affected by the temperature is important in selective extraction, since one solute is always desired and others are not.

2. What is the effect of film composition on transport?

FC-70 could function as a plasticizer to Teflon membranes. Preliminary results show that the transport parameters of my membranes are very sensitive to the concentration of FC-70. It is therefore necessary to understand the role FC-70 plays in the membranes. FC-70 could help fluorous liquids partition into the membrane, while restricting their diffusion by occupation of free volume, which would be taken by the solutes otherwise. $T_g$ measurement is necessary in order to understand the physical properties of Teflon AF membranes doped with FC-70.[54, 60-65]

3. What is the effect of free volume on the transport properties of Teflon AF membranes?

The transport of organic liquids through glassy polymers is believed to be facilitated by the presence of free volume in the polymer. One would expect that the greater the amount of free volume, the more permeable the membrane, and the lower the activation energies. Nevertheless this trend is commonly observed for the transport of gas molecules through various glassy polymers, we need to confirm it for the transport process of organic liquids through Teflon AF membranes. Although diffusion coefficient is a measure of the polymer chain mobility, it is often related to the free volume content of the material. The two parameters, however, may not be directly correlated. Therefore, probing the free volume of Teflon AF membranes with different contents of FC-70 can at least help us understand qualitatively the effect of film composition on the permeability and selectivity of membranes.

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# 2.0 EXPERIMENTAL SECTION

## 2.1 REAGENTS

Teflon AF 2400 was purchased from Dupont (Wilmington, DE). FC-72 (perfluorotriethyl amine) and FC-70 (perfluorotripentyl amine) were obtained from 3M (Minneapolis, MN). Acid red 37, Reichardt's dye and spectrophotometric grade chloroform were purchased from Aldrich (Milwaukee, WI). The analytes used in transport experiments, benzene, hexafluorobenzene, toluene, α,α,α-trifluorotoluene, nitrobenzene, pentafluoronitrobenzene were used as received. Deionized water were produced from a Milli-Q A10 system (Millipore, Bedford, MA). Other chemicals not specified were reagent grade from Aldrich.

## 2.2 APPARATUS

UV spectra were acquired with an Agilent 8453E spectrophotometer (Palo Alto, CA). Quartz cuvettes with path lengths of 0.1 cm and 1.0 cm were purchased from Starna Cells (Atascadero, CA). IR spectra were obtained on an Excalibur FTS 3000 Spectrometer (DigiLab, Randolph, MA). Contact angles were obtained using VCA 2000 Video Contact Angle system (Advanced Surface Technology, INC). Transport experiments were carried out on an eight-position multicell transport device. The homemade glass transport cuvette (1 × 1 × 4 cm) had well-polished walls and a hole of 0.5 cm id on the wall in contact with the film. Film thicknesses were measured by a Starrett micrometer (Athol, MA) with an accuracy of ±1 μm.

## 2.3 MEMBRANE PREPARATION

Teflon AF membranes were cast from a 1 wt% solution of Teflon AF2400 polymer in FC-72. A defined amount of solution was transferred into a flat-bottomed glass Petri dish with the i.d. of 7.5 cm. The solution was capped by a piece of weighing paper and a glass cover. The solvent FC-72 was allowed to evaporate overnight or longer at room temperature until constant weight of the membranes was reached. The membranes were then stripped from the bottom of Petri dish and cut into small pieces (about 1 × 1 cm) with scissors for transport experiments. Small amount of water was added to help peal off the membranes if necessary. The membranes were dried in an oven at 60 °C for 2 hours, and stored in a container at room temperature.

To prepare membranes doped with FC-70, the dopant was weighed and mixed with the 1 wt% solution of Teflon AF2400 polymer in FC-72 in the desired proportions. All doped membranes were prepared under the same conditions as described above, and were pealed off with a scalpel readily without the water-soaking procedure. The membranes were then placed in a covered container with air saturated by FC-70.

Hence, two types of membranes were investigated, pure Teflon AF2400 membranes and membranes doped with FC-70 in the desired ratios.

## 2.4 TRANSPORT OF SOLUTES THROUGH MEMBRANES

Transport of solutes was conducted with a home-made, three-phase transport device (Fig. 4)[1] at three different temperatures, 20°C, 25°C and 30°C. The subject membrane was sandwiched between two pieces of viton rubber with holes of a diameter of 0.5 cm (an area of 0.196 $cm^2$) to define the transport area. The rubber-secured membrane was then clamped between two transport cuvettes. The eight-position multicell transport cell holder holds eight cells in a rack, which is kept at a constant temperature by water circulated from a thermostatic water bath. Three parallel transport experiments can therefore be conducted simultaneously with one transport experiment being the control. The stirring module for the multicell transport can control the stirring speed, which was kept the same throughout my experiments.

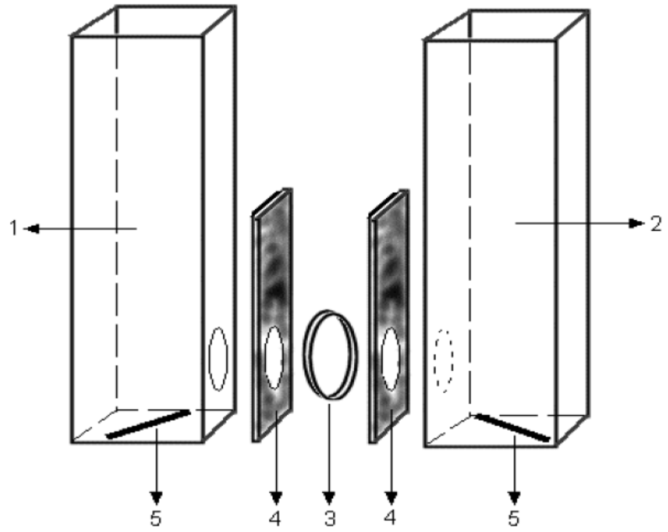

**Figure 4.** Schematic diagram of the transport apparatus.[1]
1, cuvette for the source phase; 2, cuvette for the receiving phase;

3, membrane; 4, Vition ruber; 5, stirring bars.

The source phase contained 3 mL analyte solution at a defined concentration, while the receiving phase contained 3 mL pure solvent at the beginning of the experiments. Transport of analytes in chloroform through the membranes was carried out in a three-phase transport apparatus. The solute concentration in the receiving phase was monitored by a UV spectrophotometer.

The steady-state flux, $J$, of a solute through a membrane is obtained from Eq 2-1,[2]

$$J = (dC_r/dt)(V/A) \quad (\mathrm{mol{\cdot}s^{-1}{\cdot}cm^{-2}}) \qquad (2\text{-}1)$$

where $A$ is the effective membrane area, $V$ is the volume of the receiving phase, and $dC_r/dt$ is the accumulation rate of the solute in the receiving phase. The permeability coefficient, $P$, is deduced from the flux.

$$P = J{\cdot}l \,/\, (C_s - C_r) \approx J{\cdot}l \,/\, C_{s0} \quad (\mathrm{cm^{2}{\cdot}s^{-1}}) \qquad (2\text{-}2)$$

where $l$ is the thickness of the membrane. $C_s$ and $C_r$ are the concentrations of the solute in the source phase and the receiving phase, respectively. Since $C_r$ is negligible at the beginning period of transport, $C_s$–$C_r$ is taken as the initial concentration of the solute in the source phase, $C_{s0}$. The permeability coefficient depends on the nature of the solute, the properties of membranes and the temperature.

## 2.5 DETERMINATION OF DIFFUSION COEFFICIENTS AND PARTITION RATIOS OF ANALYTES

The time-lag method[3-5] is widely used in experimental determination of diffusion coefficients. The time-lag is a transient period at the beginning of membrane transport during which an analyte diffuses across the membrane and reaches a steady state flux. The basis of the time-lag method is that the permeation rate of the analyte will become constant with time. This means that the concentration of the analyte in the receiving phase will increase linearly with time after a certain short period. Diffusion coefficient is calculated by testing the time lag during transport experiments.

$$D = l^2 / 6t_{lag} \tag{2-3}$$

Nonlinear fit of diffusion curves by Mathcad can also be applied to obtain diffusion coefficients. The accumulation of a substance in the receiving phase can be described by Eq. 2-4.

$$Q_t = C_1 l(\frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_1^{\infty}\frac{(-1)^n}{n^2}\exp(-Dn^2\pi^2 t/l^2)) \tag{2-4}$$

$Q_t$ denotes the total amount of diffusing substance that has passed through the membrane in time $t$; $D$ is the diffusion coefficient of the diffusing substance; $l$ is the membrane thickness; $C_1$ is the concentration of the diffusing substance at the membrane interface contacting the source phase. Although this equation is an infinite series, n in the third term of Eq.2-4 can be satisfactorily taken as 10. For a diffusing substance with concentration $C_s$ in the source phase, $C_1$ can be deduced through the following equation.

$$C_1 = C_s . K_D \tag{2-5}$$

where $K_D$ is the partition ratio of the substance from the source phase to the membrane. The diffusion equation is then changed to:[6]

$$Q_t = K_D C_s l(\frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_1^{\infty}\frac{(-1)^n}{n^2}\exp(-Dn^2\pi^2 t/l^2)) \tag{2-6}$$

Transport experiments were carried out with a transport device. A quartz cuvette was employed as the receiving phase to realize continuous UV measurements of the receiving phase. By monitoring the concentration of diffusing substance in the receiving phase, we can get the values of partition ratio and diffusion coefficient by nonlinear curve fit. Membranes with various thicknesses were chosen to study the effect of membrane thickness on permeability.

## 2.6 FC-70 CONTENT MEASUREMENT BY FTIR

The IR absorbance of Teflon AF2400 membranes with and without FC-70 was monitored by a FTIR spectrometer. To determine the content of FC-70 in Teflon membranes, membranes with thickness of 20μm were used for IR measurements. The control experiments were carried out under the same conditions with pure Teflon membranes. The content of FC-70 in membranes can be calculated according to the IR absorbance.

## 2.7 DENSITY MEASUREMENTS

The regular weighing method and the hydrostatic weighing method were used for the determination of membrane densities. In the regular weighing method, membrane density is obtained by dividing the mass of a membrane by its volume, which is just the product of the membrane area and thickness. In the hydrostatic weighing method, membranes were hung on the hook of a suspension system, which is kept immersing into a liquid with known density. The mass change of the suspension system with and without the sample was recorded. Silicone oil was chosen due to its relatively high boiling point. It also allows for the neglect of the effects of absorption and swelling on density measurement. The density was calculated using the following equation,[7, 8]

$$d_{meas} = \frac{m}{(W - W_0)/d_W} + d_A \qquad (2\text{-}7)$$

where $d_{meas}$ is the density of the sample, m is the mass of dry sample in air, $W - W_0$ is the mass difference of the suspension system with and without the sample, $d_w$ is the density of silicone oil at the temperature of measurement and $d_A$ is a correction for the density of air ($d_A$=0.00129g/cm$^3$).

## 2.8 CONTACT ANGLE MEASUREMENTS

Contact angle measurements were carried out using a VCA 2000 Video Contact Angle Camera under ambient conditions. The probed liquid used was deionized water. Water droplet was deposited on the membrane surface and the contact angle was measured immediately upon needle removal. Three advancing angles and receding angles were measured. Contact angle measurements were used to determine the surface properties of membranes since it is highly surface sensitive.

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# 3.0 RESULTS AND DISCUSSION

## 3.1 MEMBRANE PROPERTIES

### 3.1.1 MEMBRANE MORPHOLOGY

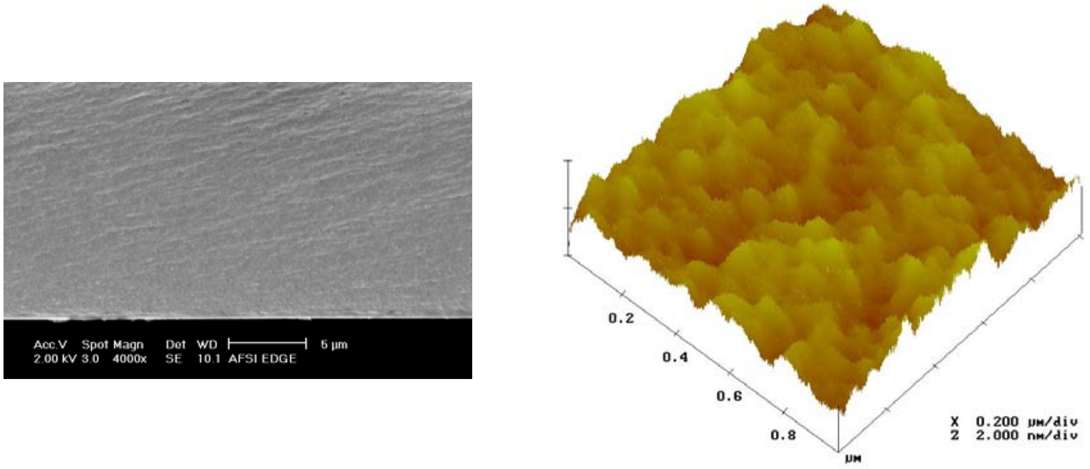


**Figure 5.** SEM image of the cross section of Teflon AF membrane (left); AFM image of the topography of Teflon AF membrane (right)[1]

Hong Zhao et al.[1] used SEM and AFM to image the topography of Teflon AF membranes (Fig. 5). SEM image shows the relative homogeneity through the cross section, while AFM image indicates the smoothness of the membrane surface, with RMS roughness of 0.4 nm over a 10µm scan range. Neither of these two images shows obvious pinholes or cracks in Teflon AF membranes. The smooth surface of the membranes cast from Teflon AF allows for the preparation of thin stable membranes with minimal defects.

Transport experiments were conducted in order to check the integrity of Teflon AF membranes. Acid red 37 and Reichardt's dye were chosen due to their high molecular weight and extremely strong UV absorbance. Figure 6 shows their structures. An aqueous solution of acid red 37 and a chloroform solution of Reichardt's dye were used as the source phases, while the same amount of pure water and chloroform was employed as the receiving phase accordingly. UV absorbance has been measured every half hour for 3 days. In terms of the detection sensitivity, the permeability coefficients are estimated to be no more than $1.1\times 10^{-12}$ $cm^2.s^{-1}$ for acid red 37 and no more than $1.2\times 10^{-12}$ $cm^2.s^{-1}$ for Reichardt's dye. The results proved that the membranes did not contain defects that allowed significant passage of polar molecules of ~500 Da.

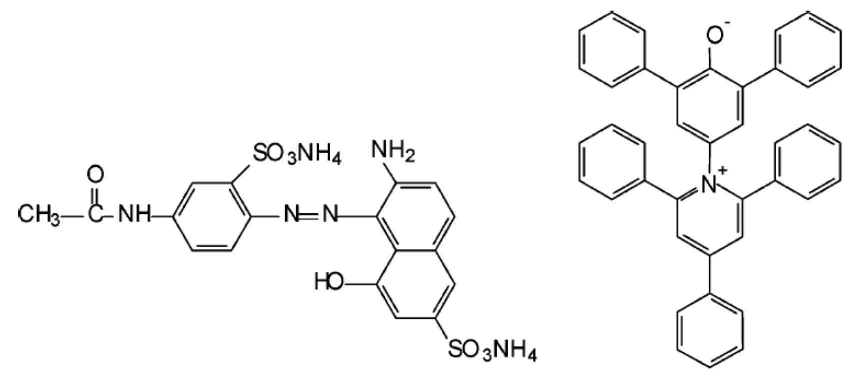


**Figure 6.** Acid red 37 (left) and Reichardt's dye (right).

Membranes made from Teflon AF polymer were prepared on slices to conduct contact angle measurement. Contact angle values are around $115^0$ for all the Teflon AF membranes measured. The result confirms the hydrophobic character of the membranes.

### 3.1.2 MEMBRANE DENSITIES

Transport properties of membranes can be interpreted in terms of free volume, as probed by density measurement. The densities of Teflon AF membranes were determined by both the regular weighing method and the hydrostatic weighing method. The results are shown in Table 2.

**Table 2.** Teflon AF membrane densities measured by the regular weighing method and the hydrostatic weighing method

| Membranes [a] | Membrane density ($g/cm^3$) (±SEM, number of measurement, number of batches) | |
|---|---|---|
| | The regular weighing method [b] | The hydrostatic weighing method [b] |
| 100% Teflon AF | 1.76±0.03 (5,5) | 1.81±0.02 (12,3) |
| 50% Teflon AF/ Krytox FSH7500 | 1.93±0.05 (4,4) | 1.94±0.02 (11,3) |

[a] Teflon AF membranes were cast by a perfluorinated solvent FC-72.

[b] All the measurements were conducted at ambient temperature.

The density of pure Teflon AF membrane was reported to range from 1.74 $g/cm^3$ to 1.77±0.01 $g/cm^3$[32]. These values are in good agreement with my own considering that all these membranes were processed under different conditions such as casting solution and evaporation conditions, and determined by different measurement methods. In the case of more volatile casting solvent, the polymer chains have less time to relax into a dense packing and the density of membrane formed would be lower. Even as the boiling points of the casting solutions are the same, other factors such as evaporation conditions during membrane formation could also have a considerable influence on the density of membranes. Moreover, I determined the membrane density by immersing membranes in silicone oil because silicone oil was found to absorb negligible amount of solutes by weighing the membranes before and after the immersion.

Statistical tests are used to evaluate the data given by the two methods. T tests show no statistically significant difference at the 0.05 significance level between the density values measured by the two methods. F tests show no significant difference at the 0.05 significance level between their variances. Both of these methods can therefore be applied to evaluate the membrane density.

Table 3 shows the densities of pure Teflon AF membranes obtained by the two methods. It can be found that the densities in general increase with increasing thickness. The more the amount of the casting solution, the slower the solvent evaporates, the denser the membrane structure and the higher the membrane density. However, the membrane densities obtained by the regular weighing method were found not only noticeably lower than those by the hydrostatic weighing method, but showed slight deviation from the trend. This is mainly due to the difference in preparation procedures. A piece of weighing paper with an inverted Petri dish on it was applied to cover Teflon AF polymer solution to form membranes used in the latter method, whereas membranes used in the former method were formed by covering the polymer solution only by an inverted Petri dish. Although all the membranes were cast from the same FC-72 solution, weighing paper could significantly slow down the evaporation process, resulting in membranes with higher density and homogeneity.

**Table 3.** Densities of 100% Teflon AF membranes with different thickness

| Membrane thickness (μm) | Membrane density (g/cm$^3$)<br>(±SEM, number of measurement, number of batches) | |
|---|---|---|
| | The regular weighing method | The hydrostatic weighing method |
| 8 | 1.61±0.10 (2,2)[1] | 1.71±0.01 (9,3) |
| 12 | 1.65±0.06 (2,2)[1] | 1.76±0.01 (7,3) |
| 20 | 1.76±0.03 (5,4) | 1.81±0.02 (12,3) |
| 38 | 1.74±0.07 (9,3)[1] | 1.84±0.02 (7,3) |

Since the membrane density was found to be influenced by the thickness, Teflon AF membranes of the thickness of 20μm were consequently used to investigate the effect of FC-70 content on the membrane density. Table 4 shows the dependence of membrane density on the content of FC-70.

**Table 4.** Densities of Teflon AF membranes with different content of FC-70

| $C_{FC\text{-}70}$ (wt%) | Membrane density [a] (g/cm$^3$) (±SEM, number of measurement, number of batches) |
|---|---|
| 0 | 1.81±0.02 (12,3) |
| 5 | 1.90±0.03 (6,2) |
| 7 | 1.92±0.02 (7,2) |
| 10 | 1.86±0.01 (6,2) |

[a] The membrane density was measured by the hydrostatic weighing method.

The interaction between FC-70 and Teflon AF leads to an increase in membrane density at low FC-70 content and then a decrease at higher FC-70 content. The slight increase in the density can be attributed to the better packing of the polymer chains, accompanied by a decrease in free volume, and vice versa.

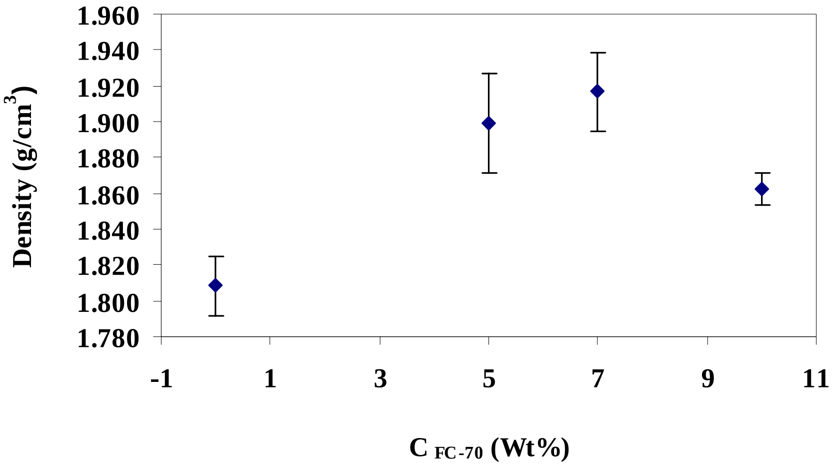


**Figure 7.** Dependence of membrane density on the concentration of FC-70

### 3.1.3 FREE VOLUME

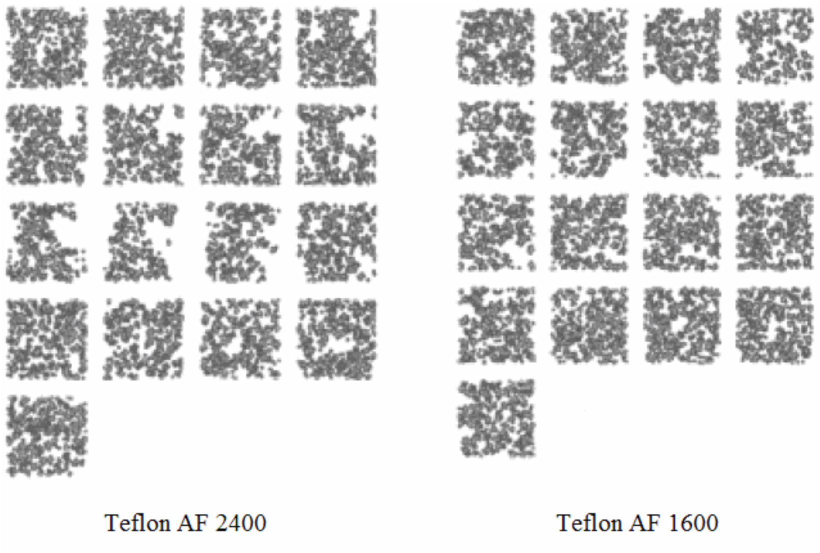
The amount and distribution of free volume in amorphous polymers are of great importance to their transport properties. Permeability coefficients of gases were demonstrated to correlate well with the size of free volume in different polymers.[3-7] A similar correlation also holds for diffusion coefficients.[3, 8-11] Free volume is characterized by several experimental methods such as $^{129}$Xe-NMR spectroscopy[12], inverse gas chromatography (IGC)[13, 14], positron annihilation lifetime spectroscopy (PALS)[8, 14, 15], as well as computer molecular modeling[16]. The results of various experimental techniques and computer modeling are generally in agreement. Radii of free volume elements of Teflons AF based on different methods are presented in Table 5.

**Table 5.** Radii of free volume elements (Å) based on various methods

| Polymer | $^{129}$Xe-NMR | | PALS | | IGC |
|---|---|---|---|---|---|
| | $R_{sp}$ | $R_c$ | $R_{sp}$ | $R_c$ | |
| Teflon AF 2400 | 8.04[a12]<br>7.83[b12] | 5.12[a12]<br>5.02[b12] | 5.95[17]<br>6.0[8] | 6.33[12] | 6.4[13] |
| Teflon AF 1600 | 6.66[12] | 4.43[12] | 4.89[17]<br>5.2[8] | 5.43[12] | 5.8[12]<br>5.5[13] |

$R_{sp}$ Assuming holes with spherical geometry; $R_c$ Assuming holes with cylindrical geometry; a Powder; b Film.

Teflon AF polymers reveal large free volume according to all the experimental methods above. Computer modeling not only shows high free volume of Teflons AF, but provides a more detailed insight into free volume distribution. Figure 8 shows a qualitative impression of the free volume distributions for typical packing models of Teflon AF polymers.



Teflon AF 2400

Teflon AF 1600

**Figure 8.** Qualitative "visual" impression of the free volume distributions for typical packing models of Teflons AF. The figures present a series of approximately monatomic layers cut perpendicular to the respective z-axis with the distance between successive slices of about 3Å.[16]

The Figure above implies that an assumption that free volume elements have the shape of spheres and cylinders is rather rough. Free volume elements in highly permeable polymers can instead be represented as a system of interpenetrating pores surrounded by densely packed matrix. Specifically, in the case of ultrahigh free volume polymers like Teflons AF, they are distinguished by the presence of two qualitatively different regions for penetrants. One region has high segmental packing density, where the free volume distribution resembles that in conventional glassy polymers. The other region is comprised of large voids, which have a tendency to form a partially continuous hole with lateral void widths in the range of 5-20Å. We would expect that the presence of such free volume clusters allows the transport of small penetrants without overcoming considerable energy barriers. In the cases of less permeable polymers such as poly[vinyltrimethylsilane]PVTMS, poly[1-phenyl-2-[*p*-(triisopropylsilyl)phenyl] acetylene]PPrSiDPA, and poly[1-phenyl-2-[*p*-(triphenylsilyl)phenyl] acetylene]PPhSiDPA, the free volume distribution comprises only microvoids, with no indication of a contionuous hole phase.[16]

Figures 9~10 present the accessible free volume distributions of Teflons AF for probes with different size. The character of free volume size distribution does not change much as the size of the probe used in the modeling increases from 1.1 Å to 1.7 Å. Both figures reveal bimodal hole size distributions with a distinct gap between the two modes. Teflon AF 2400 is shown to have higher peaks at the high radii range in comparison to Teflon AF 1600. The position of peaks is in principle related to the permeabilities in these polymers. With this respect Teflon AF 2400 is more attractive than Teflon AF 1600 since it should display higher permeability. In this work, I investigate the transport properties of Teflon AF 2400.

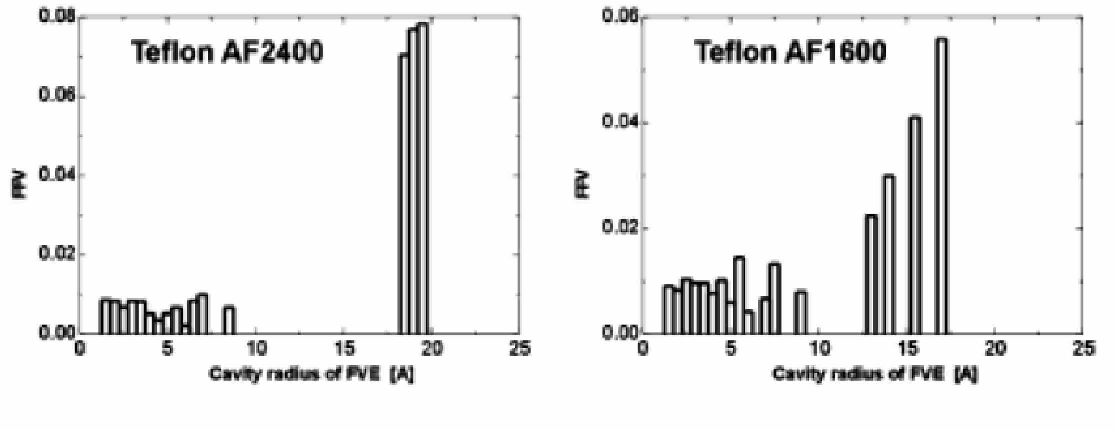


**Figure 9.** V_connect accessible free volume distributions for the positronium probe molecule (R=1.1Å).[16]

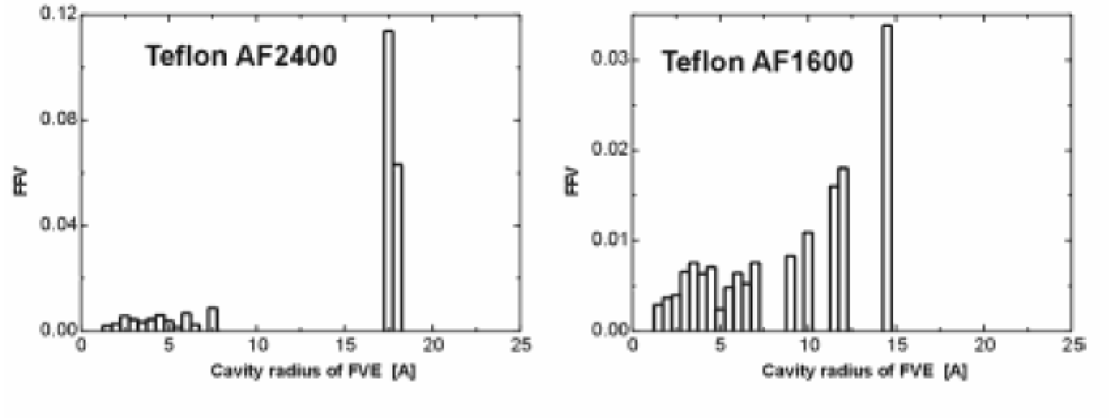


**Figure 10.** V_connect accessible free volume distributions for the oxygen probe molecule (R=1.73Å).[16]

## 3.2 DATA VALIDATION

### 3.2.1 THE CONTENT OF FC-70 IN TEFLON AF MEMBRANE MEASURED BY FTIR

According to Beer's law, the absorbance displays a simple dependence on the cell path length and the sample concentration. I use the law to estimate the concentration of FC-70 in Teflon AF membranes. Beer's law is often written in the form of this equation,

$$A_T = \varepsilon_T \cdot C_T \cdot l_T \tag{3-1}$$

where $A_T$ is the absorbance of pure Teflon AF membrane at the given wavenumber, $\varepsilon_T$ is the absorptivity of pure Teflon AF, $C_T$ is the concentration of pure Teflon AF membrane and $l_T$ is the thickness of the membrane. $C_T$ is taken as the weight percentage of Teflon AF for the convenience of calculation, so $C_T$ of 100% Teflon AF is taken as 1. $A_{FC}$ can be defined in the same way as below,

$$A_{FC} = \varepsilon_{FC} \cdot C_{FC} \cdot l_{FC} \tag{3-2}$$

where $A_{FC}$ is the absorbance of pure FC-70 at the given wavenumber, $\varepsilon_{FC}$ is the absorptivity of pure FC-70, $C_{FC}$ is the concentration of pure FC-70 and $l_{FC}$ is the thickness of FC-70. $C_{FC}$ is taken as the weight percentage of FC-70, so the $C_{FC}$ value of 100% FC-70 is 1.

According to the principles of absorption additivity, the absorbance of a mixture is equal to the sum of the absorbance of each colored component.

$$A_a = \sum A_i = \varepsilon_T \cdot C_{Ta} \cdot l_{Ta} + \varepsilon_{FC} \cdot C_{FCa} \cdot l_{FCa} \tag{3-3}$$

where $A_a$ is the absorbance of Teflon AF membrane doped with FC-70 at the given wave-number.

$$l_{Ta} = l_{FCa} = l_T = l_{FC} = 20um \tag{3-4}$$

$$C_{Ta} = 1 - C_{FCa} \tag{3-5}$$

By combining the equations 3-3~3-5, the weight percentage of FC-70 in the membrane can thus be calculated from the following equation:

$$C_{FCa} = \frac{A_a - A_T}{A_{FC} - A_T} \tag{3-6}$$

Figure 11 shows the IR spectra of pure FC-70 and pure Teflon AF membrane. Both FC-70 and Teflon AF absorb strongly over a wide range between 1450 and 500 cm$^{-1}$ due to C-F stretching modes, whereas FC-70 shows distinct peaks at 578 and 891cm$^{-1}$ as indicated by the arrows. This is probably due to the bending modes of tertiary amine in FC-70.

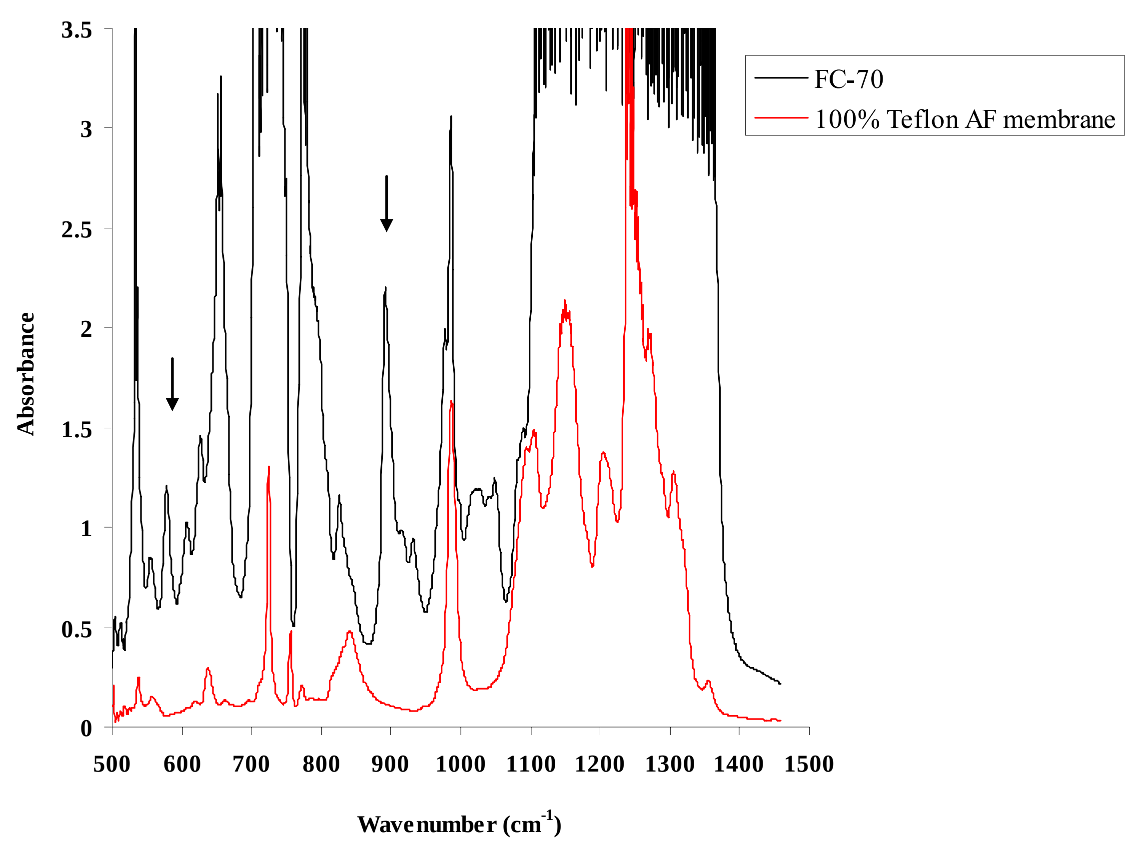


**Figure 11.** IR absorption spectra of 100% Teflon AF membrane and FC-70

Figure 12 shows the IR spectra of two Teflon AF membranes doped with different amount of FC-70, while the spectrum of pure Teflon AF membrane at the same scale is also included for comparison. It is obviously seen that both of these two Teflon AF membranes show peaks at 578 and 891cm$^{-1}$ in comparison to the pure Teflon membrane. This result demonstrated that the membranes do contain FC-70.

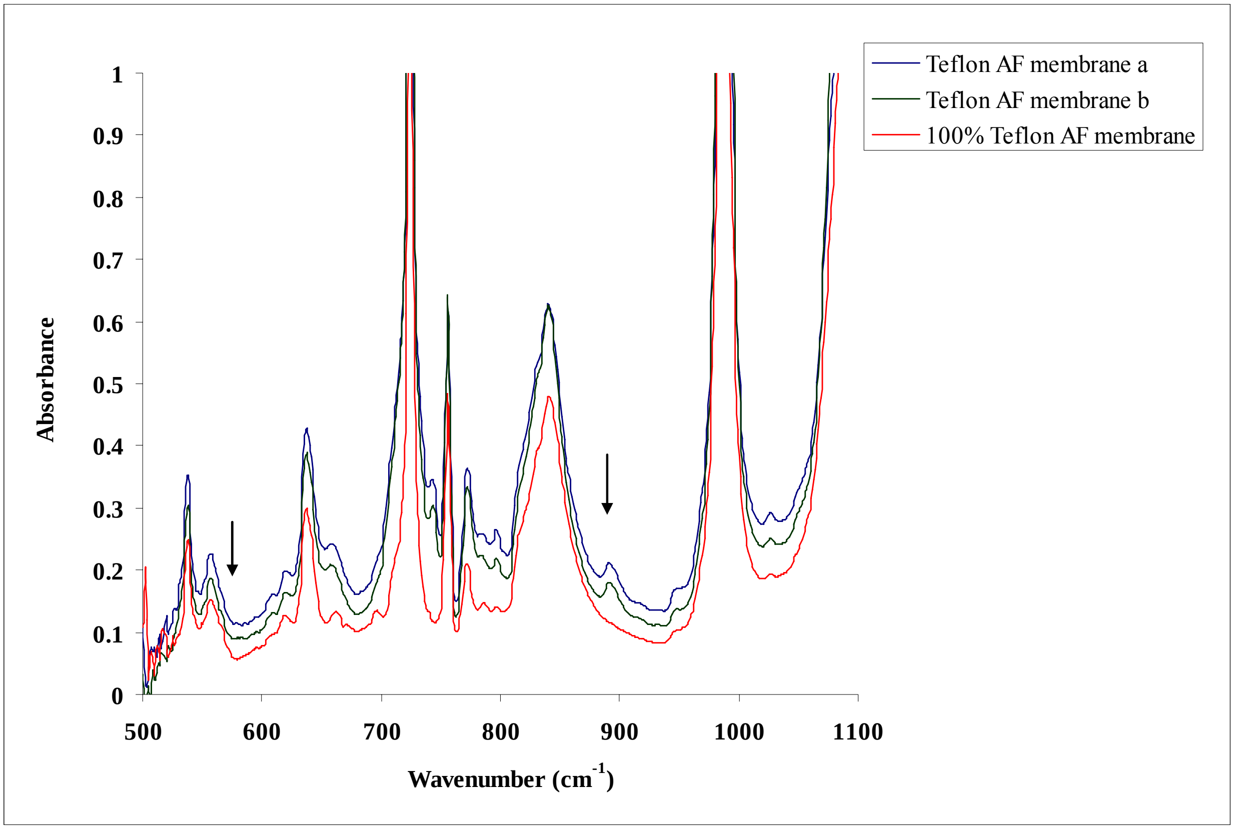


**Figure 12.** IR absorption spectra of Teflon AF membranes with and without FC-70

The content of FC-70 in the membrane can be calculated with the equation 3-6. The absorbance values of the membranes doped with FC-70 were taken at 5 different wave-numbers. The results obtained are shown in Table 6.

**Table 6.** The absorbance values and the content of FC-70 obtained

| Wavenumber ($cm^{-1}$) | 557.4 | 597.4 | 948.5 | 1025.2 | 1388.5 |
|---|---|---|---|---|---|
| $A_T$ | 0.1515 | 0.0740 | 0.1037 | 0.1931 | 0.0567 |
| $A_{FC}$ | 0.8196 | 0.6931 | 0.5835 | 1.1928 | 0.5019 |
| $A_a$ | 0.2252 | 0.1248 | 0.1707 | 0.2914 | 0.0953 |
| $A_b$ | 0.1857 | 0.1000 | 0.1376 | 0.2490 | 0.0764 |

| | | | | | |
|---|---|---|---|---|---|
| $C_{FC-70}$ (wt%) in **a** | 11.0 | 8.2 | 14.0 | 9.8 | 8.7 |
| $C_{FC-70}$ (wt%) in **b** | 5.1 | 4.2 | 7.1 | 5.6 | 4.4 |
| $C_{FC-70}$ (wt%) (±SEM) in **a** | 10.3±1.0 | | | | |
| $C_{FC-70}$ (wt%) (±SEM) in **b** | 5.3±0.5 | | | | |

The contents of FC-70 in membrane **a** and **b** are 10.3±1.0 and 5.3±0.5wt% respectively, which are in good agreement with the values 10±1 and 5±1wt% from a gravimetric method. The method is based on the assumption that the mass of Teflon AF would not change during the membrane preparation process. The mass of FC-70 is obtained by subtracting the initial mass of Teflon AF from the final mass of the membrane. The good agreement between FTIR and the gravimetric method implies that either of the methods can be used to determine the content of FC-70 in the membrane. For simplicity, I used the gravimetric method to calculate FC-70 content for the rest of my membranes.

### 3.2.2 THE INFLUENCE OF MEMBRANE THICKNESS ON PERMEABILITY COEFFICIENTS

The permeation of gases and liquids could depend on membrane thickness. The evaluation of the influence of thickness on permeability is therefore of importance. The permeability of α,α,α-trifluorotoluene was studied for several pure Teflon AF membranes with thickness in the range 14-97μm. It can be found from Table 7 that the permeability coefficients remain unaffected for membranes with thickness less than about 50μm. For very thick membranes (with higher thickness), permeability significantly increases with increasing thickness. Hence, the membranes with thickness less than 50μm were used in all transport experiments since permeability coefficient can not be used to characterize a membrane without demonstration of its independence of membrane thickness.

**Table 7.** Dependence of permeability on membrane thickness

| Film thickness (um) | P ($\times 10^8$) * (cm$^2$/s) (±SD) |
|---|---|
| 14 | 1.06±0.02 |
| 23 | 1.05±0.02 |
| 49 | 1.50±0.08 |
| 58 | 2.25±0.05 |
| 97 | 2.80±0.17 |

* The permeability coefficient was the average of duplicate experiments at 25$^o$C.

### 3.2.3 THE INFLUENCE OF CHLOROFORM EXPOSURE ON PERMEABILITY COEFFICIENTS

Hong found that Teflon AF membranes can imbibe solvent chloroform, the concentration of which in equilibrium with saturated vapor is 1.13±0.04M. Compared with chloroform-free Teflon AF membrane, the sorbed chloroform in the membrane was found to decrease the partition coefficient of benzene. However, the effect of solvent uptake on the permeability coefficient has not been evaluated.

The permeability coefficients of toluene and α,α,α-trifluorotoluene were measured for fresh membranes and the membranes which had been saturated by chloroform. As shown in Fig.13, the permeability coefficients of Teflon AF membranes were influenced by chloroform exposure. The exposure to chloroform makes the membrane more organic-like. The partition and diffusion of fluorocarbons would probably become more difficult due to the decreased free volume and the increased viscosity of the membrane. The partition coefficient of the hydrocarbon analogs may also decrease due to the decreased free volume, whereas the diffusion coefficient may increase because the sorbed chloroform plasticized the membrane by increasing its segmental motion. Hence, the permeability coefficient of toluene does not change much as a result of the counteraction. For comparison, I would therefore use fresh membranes for all the transport experiments.

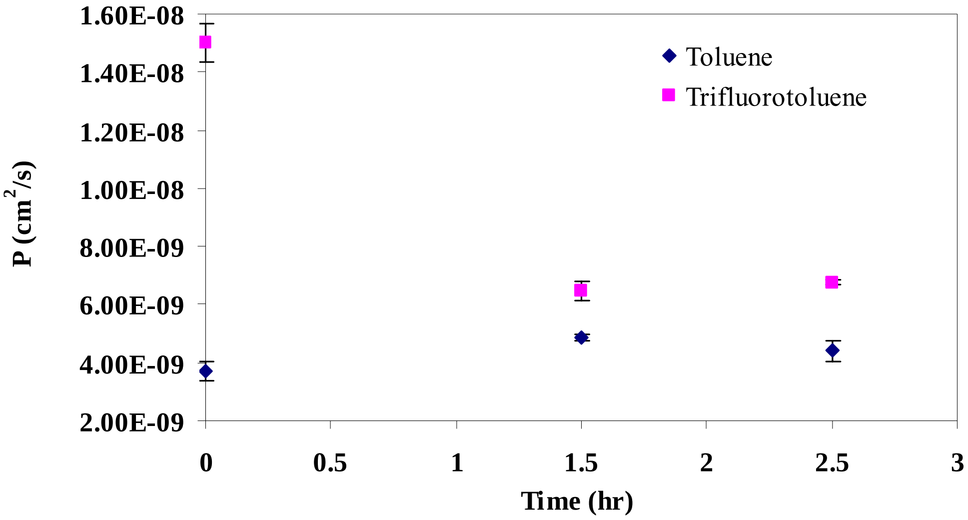


**Figure 13.** The dependence of permeability coefficients on the time of membranes soaking in chloroform

### 3.2.4 THE REUSABILITY OF MEMBRANES

The reusability of membranes deserves serious consideration due to the needs of commercialization. The permeability coefficient of α,α,α-trifluorotoluene was determined for fresh Teflon AF membranes. After the first transport experiment, the membranes were washed by sufficient amount of chloroform several times in order to extract the penetrants remaining in the membranes back into chloroform. The second transport experiment was conducted with the membranes which were dried in oven at 70°C to get rid of the chloroform, whereas the third was conducted with the membranes without drying.

As shown in Table 8, the permeability coefficients obtained by the first two measurements were essentially the same, while that of the third measurement was found to decrease significantly. On the one hand, the results in Table 8 agree with the decrease in permeability of α,α,α-trifluorotoluene shown in Fig. 13. On the other hand, the essentially unchanged permeability coefficients suggest the reusability of Teflon AF membranes. The structure of the membranes can relax back toward an as-cast state over a short time scale after solvent chloroform is removed.

**Table 8.** Permeability coefficients of α,α,α-trifluorotoluene

| Measurement | P ($\times 10^8$) * ($cm^2/s$) (±SD) |
|---|---|
| 1st | 2.64±0.28 |
| 2nd | 2.67±0.13 |
| 3rd | 1.08±0.62 |

## 3.3 DATA ANALYSIS

### 3.3.1 DSC AND TMA RESULTS

Differential Scanning Calorimetry (DSC) and Thermomechanical analysis (TMA) were conducted to study the thermal transitions of Teflon AF membranes. DSC allows the detection of heat capacity changes as the polymer matrix goes from the glassy state to the rubbery state. TMA determines the changes in the coefficient of thermal expansion as the polymer changes from glassy to rubbery state with an associated change in free molecular volume. DSC is thus measuring a heat effect, whereas TMA is measuring a physical effect. The glass transition temperature $T_g$ measured with DSC is often higher than the $T_g$ measured with TMA. The difference is often estimated to be approximately 5-10$^oC$. Taking this into account, these two methods yield $T_g$ values with high correlation.

Surprisingly, no glass transition events were observed for Teflon AF membranes doped with 5wt% FC-70 by DSC. Since the glass transition temperature is just identified as the midpoint in glass transition by DSC, the glass transition probably happens at a temperature range too broad to be detected. The high sensitivity of TMA allows it to detect weak transitions that may not be observed by DSC. If a polymer has a fairly distinct change in thermal expansion coefficient at or around its $T_g$, glass transition can be measured with TMA because TMA is sensitive to dimensional changes. Teflon AF membranes doped with FC-70 were therefore measured with TMA. Table 9 presents the glass transition temperatures of Teflon AF membranes measured with TMA or DSC. The average glass transition temperature was determined from two samples prepared from different batches of membranes. The TMA results are shown in Fig.14~15.

**Table 9.** Dependence of glass transition temperature on the film composition

| Membrane | Teflon AF membrane | Teflon AF membrane doped with 5wt% FC-70 | Teflon AF membrane doped with 10wt% FC-70 | Teflon AF membrane doped with 50wt% Krytox FSH |
|---|---|---|---|---|
| $T_g$ ($^oC$) | 240$^a$ | -63±10$^b$ | -29±2$^b$ | -40$^a$ |

a The glass transition temperature was measured with DSC.

b The glass transition temperature was measured with TMA.

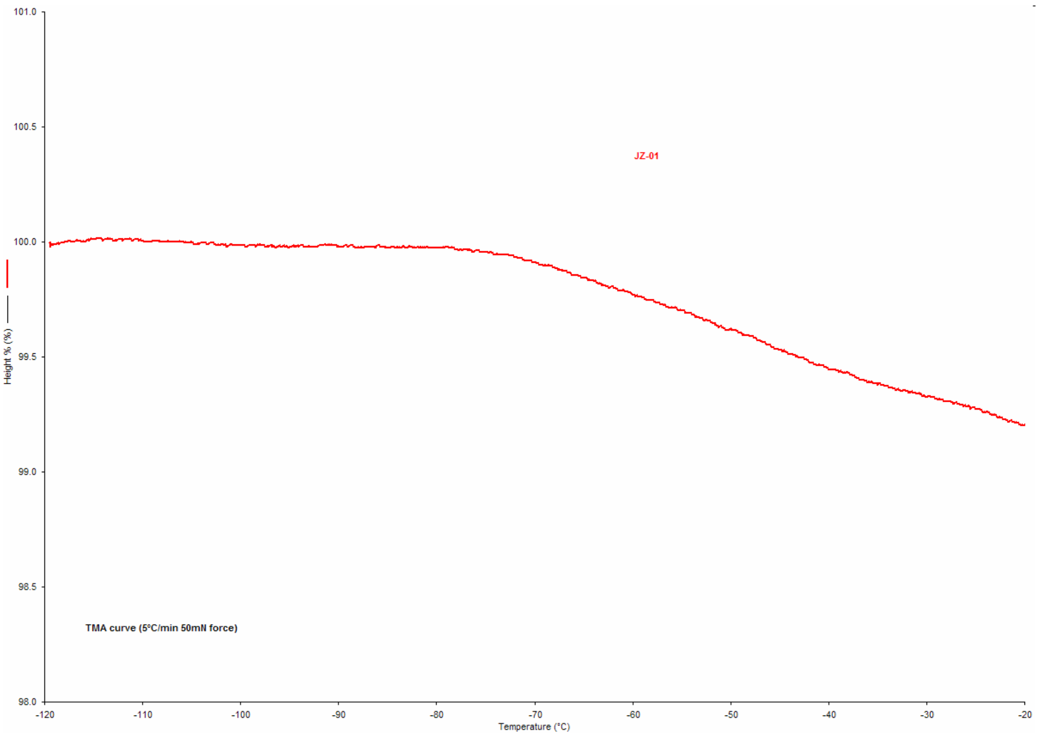


**Figure 14.** Thermal test result on Teflon membrane doped with 5wt% FC-70. (Courtesy of Marie)

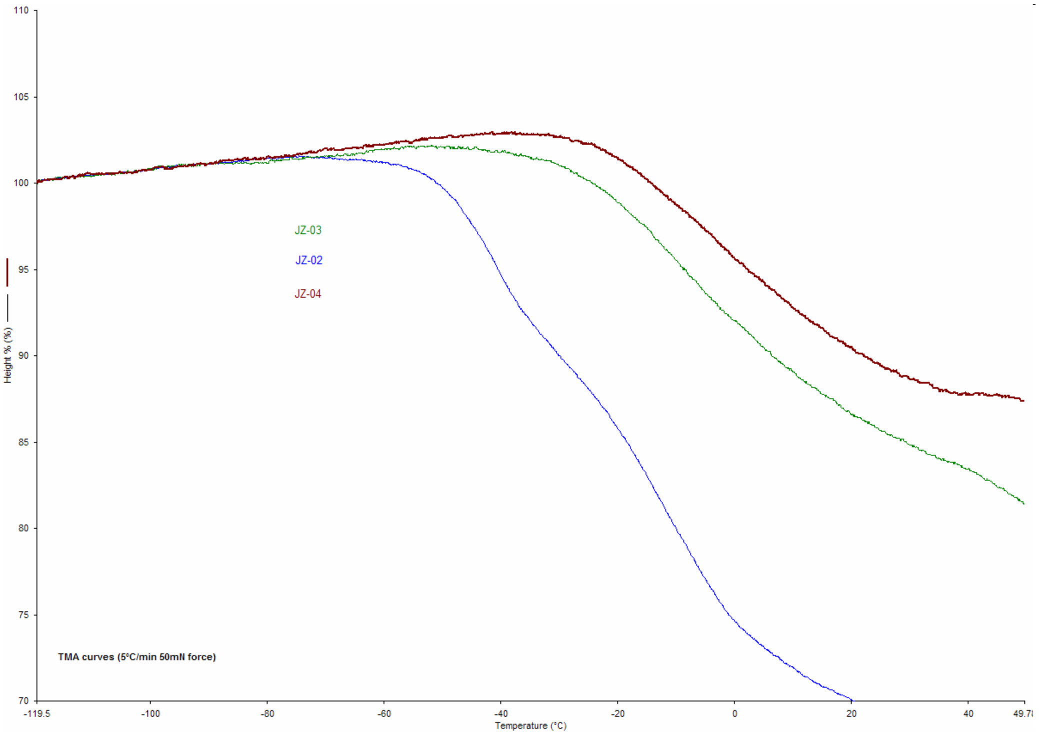
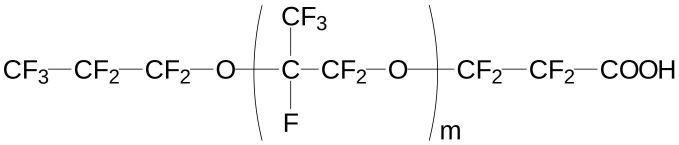


**Figure 15.** Thermal test results on Teflon membranes doped with 5wt% (one) and 10wt% (two) FC-70. (Courtesy of Marie)

All polymers undergo a phase transition from a soft, rubbery state to a hard, glassy state as the temperature is lowered below their glass transition temperature. It is believed that this glass transition arises from the freezing of rotational motions of polymer chain segments. $T_g$ measurement can thus provide valuable information on the physical states of polymers. Pure Teflon AF membranes would be in glassy state at the experimental temperatures, and Teflon AF membranes with FC-70 or Krytox FSH would be in the rubbery state instead. In the rubbery state, the polymer chains are in equilibrium state within the timescale of permeation experiments, whereas the polymer segments in the glassy state do not have adequate mobility to realize the relaxation to their equilibrium configurations. The transport mechanism of the two kinds of polymers is quite different.

A single glass transition temperature of Teflon AF membranes doped with diluents may indicate that the blends contain no separated domains or phases. Based on the single $T_g$ and the optical clarity of the membranes, One may conclude that the homogeneity of Teflon AF membranes was not disturbed by the diluents.

The decrease in glass transition temperature could be related to plasticization or anti-plasticization in terms of free volume theory. Hong Zhao et al. found that the permeability coefficient of benzene through Teflon AF membranes doped with 50wt% Krytox FSH was considerably lower than that through pure Teflon AF membranes. The permeability coefficient ratio of Teflon AF membranes with and without Krytox FSH is about 1/10[1]. The structure of Krytox FSH is shown in Fig. 16. Although the partition ratio of benzene was found to decrease from 0.04 to 0.03, the main reason of reduced permeability was believed to be a reduction in the diffusion of benzene molecules in the polymer matrix[1]. The remarkable reduction in $T_g$, as well as in permeability coefficient and diffusion coefficient suggested that Teflon AF membranes could be anti-plasticized by Krytox FSH[1].



$$CF_3-CF_2-CF_2-O-\left(\overset{CF_3}{\underset{F}{C}}-CF_2-O\right)_m-CF_2-CF_2-COOH$$

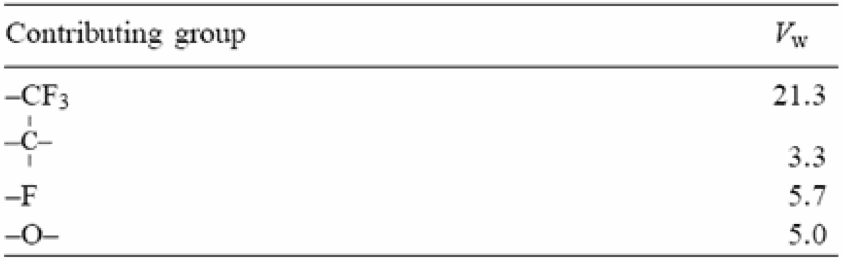
**Figure 16.** Krytox FSH

The magnitude of the decrease in glass transition temperature is often used as an indicator for the plasticization efficiency of an additive. FC-70 could be a better plasticizer than Krytox FSH in view of plasticization efficiency. Both FC-70 and Krytox are perfluorinated compounds, miscible with Teflon AF polymer, but Krytox is a carboxylic acid, the polar nature of which makes it less compatible with the essentially nonpolar polymer.

### 3.3.2 FREE VOLUME CALCULATED BY GROUP CONTRIBUTION METHOD

The fractional free volume of Teflon AF membranes with different FC-70 content is estimated from the difference between the experimentally determined specific volume, which is the reciprocal of measured density, and an estimate of the specific volume at the absolute zero of temperature, which is obtained by simple calculations using the group contribution method.

**Table 10.** Values of Van der Waals molar volume of fluorinated contributing groups[18]



| Contributing group | $V_w$ |
|---|---|
| $-CF_3$ | 21.3 |
| $-\overset{\vert}{\underset{\vert}{C}}-$ | 3.3 |
| $-F$ | 5.7 |
| $-O-$ | 5.0 |

**Table 11.** Fractional free volume of Teflon AF membranes with different FC-70 content

| $C_{FC\text{-}70}$ (wt%) | $\rho^{a}$ (g/cm$^3$) | $\hat{V}$ (cm$^3$/g) | $\hat{V}_0$ (cm$^3$/g) | $\hat{V}_F$ (cm$^3$/g) | FFV (%) |
|---|---|---|---|---|---|
| 0 | 1.808 | 0.5531 | 0.3818 | 0.1713 | 30.96 |
| 5 | 1.899 | 0.5266 | 0.3828 | 0.1439 | 27.32 |
| 7 | 1.917 | 0.5217 | 0.3831 | 0.1387 | 26.58 |
| 10 | 1.863 | 0.5369 | 0.3836 | 0.1533 | 28.55 |

a Density measurements were conducted at ambient temperature.

Based on the membrane densities, it can be concluded that small amount of additive (less than 10wt% FC-70) results in the densification of the polymer matrix, and hence a reduction in free volume. The density increases as more FC-70 is added. The trend of density should be parallel to that of permeability.

Generally speaking, the density would decrease with an increase in temperature. As the temperature increases, the polymer would dilate, the amount of free volume would increase, and thus the density would decrease. The lower the density or the higher the free volume, the higher is the permeability. In this regard, the permeability coefficient and the density have to be measured at the same temperature. However, compared with most other fluoropolymers, Teflon AF shows low thermal expansion coefficient over wide range of use temperatures. Moreover, membrane transport experiments were conducted at 20°C, 25°C or 30°C, all close to ambient temperature at which the densities were taken. It seems unnecessary for us to evaluate the density value at each temperature respectively.

### 3.3.3 THE INFLUENCE OF FILM COMPOSITION ON PERMEABILITY COEFFICIENT

#### 3.3.3.1 PERMEATION RESULTS

Transport experiments were conducted with a home-made, three-phase transport device at three temperatures ($20^0$C, $25^0$C, $30^0$C). The eight-position multicell transport cell holder holds eight cells in a rack which is kept at a constant temperature with water circulated from a thermostatic water bath. Three parallel transport experiments can therefore be conducted simultaneously with one transport experiment being the control. Kinetic mode was applied due to its automatic nature whereas with standard mode all the measurements had to be taken manually. The stirring module for the multicell transport enables us to control the stirring speed. The stirring speed was kept the same throughout my experiments.

Figures 17~20 show the dependence of permeability coefficients of toluene, α,α,α-trifluorotoluene, nitrobenzene, pentafluoronitrobenzene on Teflon AF membrane composition at different temperatures. The permeability coefficient values shown in Fig. 17~20 are the average of two or three parallel experiments. All error bars represent the standard errors of the mean. The permeability coefficients of all these solutes are found to be very sensitive to the FC-70 content and the test temperature. The permeability coefficients of toluene in Fig. 17 decrease initially as FC-70 content increases at low FC-70 concentration with reversal of this trend at higher FC-70 concentration, and decrease again and finally level off. Figures 18~20 display basically the same trend.

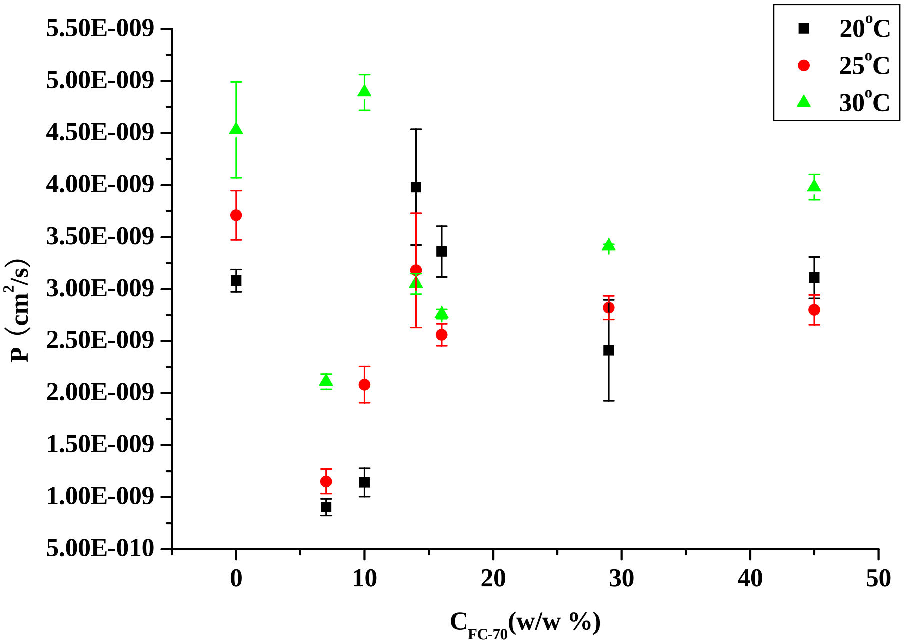


**Figure 17.** Dependence of permeability coefficients of toluene on the film composition

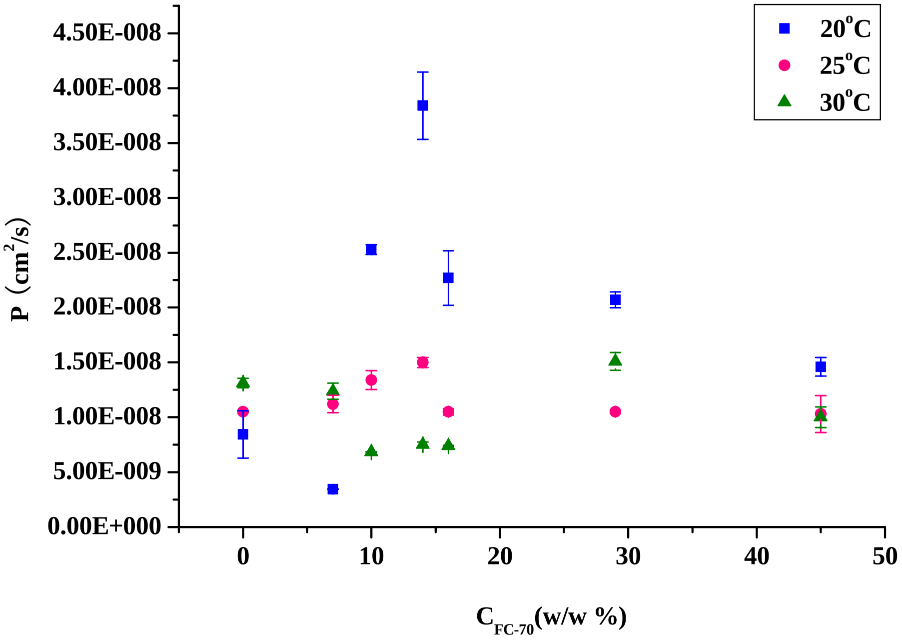


**Figure 18.** Dependence of permeability coefficients of α,α,α-trifluorotoluene on the film composition

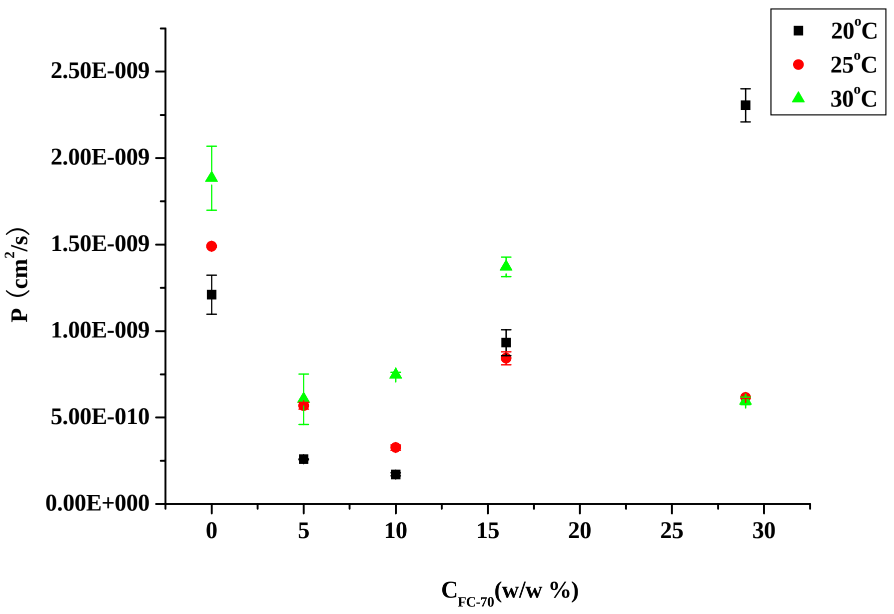


**Figure 19.** Dependence of permeability coefficients of nitrobenzene on the film composition

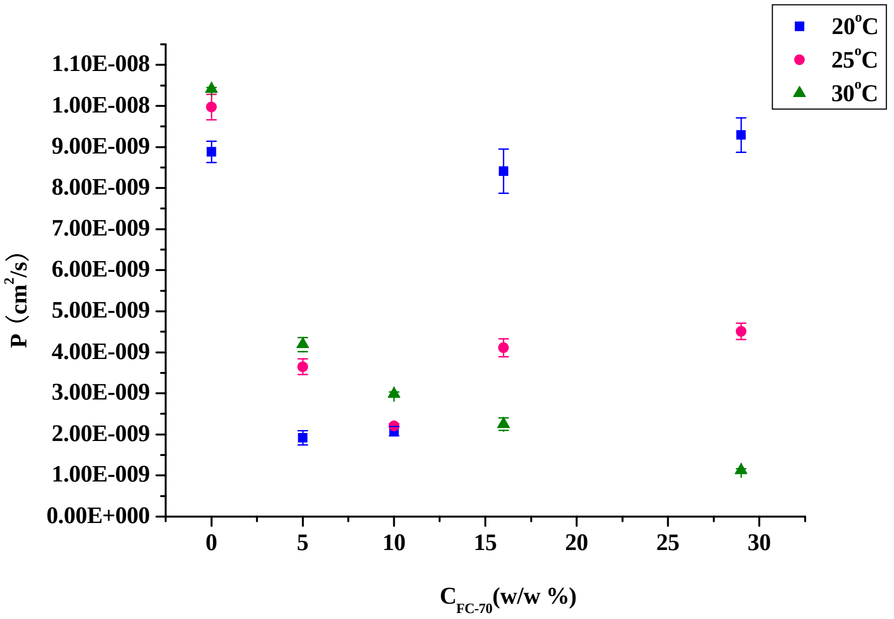


**Figure 20.** Dependence of permeability coefficients of pentafluoronitrobenzene on the film composition

### 3.3.3.2 PLASTICIZATION OR ANTI-PLASTICIZATION

The free volume of a polymer could be increased by the introduction of a miscible compound, which could add more space between the polymer chains and thus increase their segmental motions. When perfluorinated solvent FC-70 was added to fluorous Teflon AF membrane, the additive is supposed to increase the free volume of the membrane in view of its branched structure and relatively large molecular weight, indications of good plasticizers.

However, the free volume is found to decrease with the addition of FC-70 at FC-70 content less than 10wt% with reversal of this trend at higher FC-70 content. I assume that the incorporation of a small quantity of FC-70 would create more room for the redistribution of the polymer configurations. This would result in an increase in order of chain alignments and a decrease in free volume. The addition of a small quantity of FC-70 to Teflon AF polymer could therefore lead to the polymer's anti-plasticization, an effect indicated by a reduction in the free volume, a decrease in the glass transition temperature and a reduction in the partition ratio and permeability coefficient. When a larger quantity of FC-70 was added, the amorphous polymer could be plasticized, resulting in lower glass transition temperature, higher free volume and higher permeability coefficient.

Low molecular weight additives could therefore play a dual role as a plasticizer or an anti-plasticizer. A large number of literature focused on the plasticization/anti-plasticization effect of low molecular weight additives on the thermal and mechanical properties of polymers.[19-23] Water in tapioca starch films was demonstrated to have plasticizing or anti-plasticizing effects in terms of mechanical properties such as tensile strength, toughness and strain-at-break.[24] On the basis of the discussion above, it can be concluded that Teflon AF membranes with FC-70 less than 10wt% could be anti-plasticized, and Teflon AF membranes with 10wt% FC-70 or more could be plasticized.

Teflon AF membranes could also be plasticized by the organic liquid in contact. Hong et al. demonstrated that Teflon AF polymers can imbibe chloroform. The solvent chloroform was demonstrated to plasticize Teflon AF membranes by increasing the average interchain distance and thus weakening the molecular interactions between neighboring polymer chains.[25]

### 3.3.4 THE DEPENDENCE OF PERMEABILITY COEFFICIENTS ON THE TEMPERATURE

The temperature dependence of penetrant permeation through polymers without any thermal transitions is given by the Arrhenius equation:[26, 27]

$$P = P_0 \exp\left(\frac{-\Delta G_P}{RT}\right) \tag{3-7}$$

where $P_0$ is a pre-exponential factor, $\Delta G_P$ is the "activation energy" of permeation, R is the gas constant and T is the gas temperature. The so-called "activation energy" of permeation is just the slope of a plot of Log P versus 1/T. The plot is linear, i.e. P changes exponentially with temperature. $\Delta G_P$ does not have much physical meaning, since the permeation is a function of a kinetic term D and a thermodynamic term K. Numerically, $\Delta G_P$ is just the sum of the activation energy for diffusion $E_D$ and the enthalpy of partition $\Delta H_K$.[8, 27-29]

$$\Delta G_P = E_D + \Delta H_K \tag{3-8}$$

The partition ratio can be expressed in terms of a van't Hoff relationship:[26, 27]

$$K_D = K_{D0} \exp\left(\frac{-\Delta H_K}{RT}\right) \tag{3-9}$$

where $K_{D0}$ is a pre-exponential factor and $\Delta H_K$ is the enthalpy of partition. Partition into polymer membranes could involve both Henry's mode and Langmuir's mode. Henry's mode requires the formation of a site into which penetrants can dissolve, and consequently, it involves an endothermic contribution to the whole process. With Langmuir's mode, the pre-existing site in the polymer matrix makes the partition more exothermic.

The diffusion coefficients also follow an Arrehenius relationship:[26, 27]

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \tag{3-10}$$

Here, $D_0$ is a pre-exponential factor and $E_D$ is the activation energy of diffusion. $E_D$ is thus the energy required to create an opening between polymer chains large enough to allow for the diffusion of penetrant molecules.

### 3.3.4.1 THE INFLUENCE OF PENETRANTS

The permeability coefficients of toluene, α,α,α-trifluorotoluene, nitrobenzene, pentafluoronitrobenzene were measured for pure Teflon AF membranes at different temperatures. Fig. 21 shows the dependence of permeability on temperature. The error bars represent the standard errors of the mean.

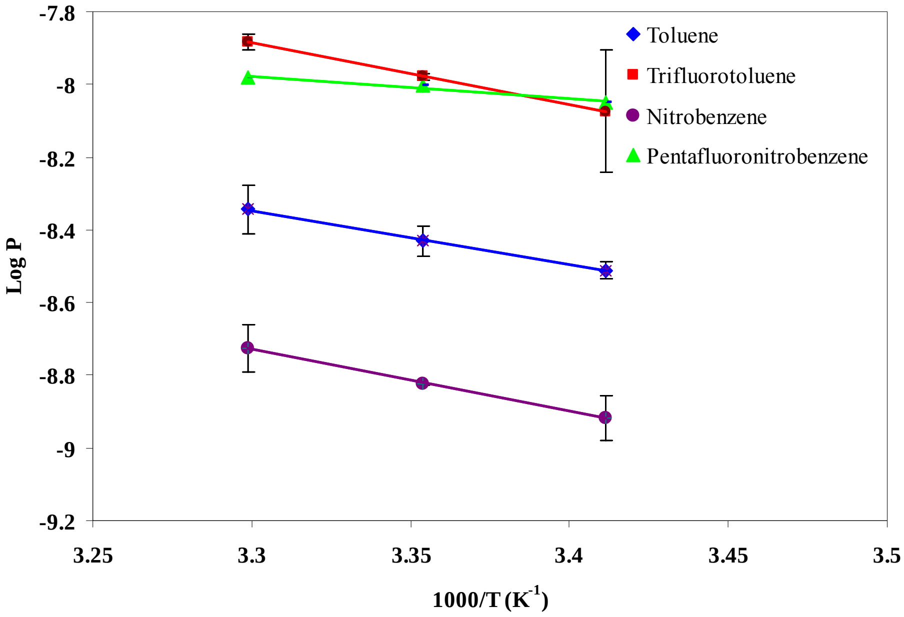


**Figure 21.** Temperature dependence of permeability

The effects of temperature on membrane permeation were analyzed in terms of Equation3.7. This equation holds for permeation of organic liquids in pervaporation process, as well as in membrane transport of organic liquids as Fig. 21 indicates. The results are shown in Table 12.

**Table 12.** $\Delta G_P$ values of some penetrants

| Compound | P (cm$^2$/s) | | | Correlation | $\Delta G_P$ (kJ/mol) |
|---|---|---|---|---|---|
| | 20$^o$C | 25$^o$C | 30$^o$C | | |
| $C_6H_5CH_3$ | 3.08E-09 | 3.71E-09 | 4.53E-09 | -0.9995 | 28.4 |
| $C_6H_5CF_3$ | 8.44E-09 | 1.05E-08 | 1.31E-08 | -0.9999 | 32.6 |
| $C_6H_5NO_2$ | 1.21E-09 | 1.49E-09 | 1.88E-09 | -0.9993 | 32.7 |
| $C_6F_5NO_2$ | 8.88E-09 | 9.97E-09 | 1.04E-08 | -0.9688 | 11.7 |

$\Delta G_P$ is comparable to the values of $E_a$, poorly defined as the activation energy of permeation in pervaporation experiments. $\Delta G_P$ of pure Teflon AF membranes are positive for all four solutes, i.e. the permeability coefficients increase with increasing temperature. This result implies that temperature has a more effect on diffusion than on partition, which is consistent with behaviors reported in most glassy polymers.

**Table 13.** $\Delta H_K$ and $E_D$ values of the penetrants investigated

| Compound | $T_c$ (K) | $V_c$ (cm$^3$/mol) | $\Delta H_S$ (kJ/mol)$^*$ | $\Delta H_K$ (kJ/mol) | $E_D$ (kJ/mol)$^\#$ |
|---|---|---|---|---|---|
| $C_6H_5CH_3$ | 592 | 316 | -29.3 | 4.3 | 24.1 |
| $C_6H_5CF_3$ | 565 | 356 | -44.2 | -11.3 | 43.9 |
| $C_6H_5NO_2$ | 719 | 349 | -31.9 | 12.2 | 20.5 |
| $C_6F_5NO_2$ | 604 | 393 | -47.7 | -9.7 | 21.4 |

[*] $\Delta H_S$ values were obtained by extrapolating the data shown in Merkel's paper, assuming that all penetrants are in gas state.[30]

[#] $E_D$ values were obtained by subtracting $\Delta H_K$ from $\Delta G_P$.

Merkel et al investigated gas sorption into Teflon AF 2400 membranes. They viewed gas sorption into a polymer matrix as a two-step process: (1) condensation from a gas-phase density to a liquid-like density and (2) mixing of condensed penetrant with polymer segments. As a result, the enthalpy of sorption $\Delta H_S$ can be written as the sum of contributions from the two steps:[30]

$$\Delta H_S = \Delta H_{Cond} + \Delta H_{Mix} \tag{3-11}$$

where $\Delta H_{cond}$ and $\Delta H_{mix}$ are the enthalpy changes associated with gas condensation and mixing, respectively. $\Delta H_{cond}$ is always negative, since condensation is an exothermic process. The glassy polymer Teflon AF 2400 has nonequilibrium excess volume, also called Langmuir microvoids or free volume. The presence of pre-existing free volume allows penetrant to be accommodated in the polymer matrix without requiring much energy to create molecular-sized gaps. $\Delta H_{mix}$ is therefore very small. Hence, $\Delta H_S$ is often negative, i.e. organic vapor solubility in glassy polymers decreases with increasing temperature.

My transport experiments deal with liquid sorption and permeation into polymer membranes. So I need to correct Merkel's data for the penetrant condensation process, which involves the enthalpy of condensation plus the integral of the heat capacity from the experimental temperature to the boiling point. The last part is small and can be neglected. As a result, the enthalpy of partition $\Delta H_K$ can be expressed as:

$$\Delta H_K = \Delta H_S - \Delta H_{Cond} \tag{3-12}$$

As shown in Table 13, enthalpies of partition $\Delta H_K$ for fluorous penetrants are negative, while those for their nonfluorous analogs are positive. The result suggests that fluorous penetrants experience a more favorable partition process into fluorinated Teflon polymer than their nonfluorous analogs. Enthalpies of partition for fluorous penetrants increase with increasing penetrant critical volume but fall on a separate trend from the nonfluorous penetrants. The dependence of $\Delta H_K$ on $V_c$ agrees with Harogoppad's data[27], which showed that the estimated enthalpies of partition for four organic liquids increase with increasing penetrant size. Teflon AF polymer is distinguished by its high fractional free volume. The more free volume, the more sorption sites are available for accommodating penetrant molecules. The presence of non-equilibrium microvoids in Teflon AF allows penetrant molecules to be accommodated into these pre-existing voids, which requires no or little energy. As penetrant size increases, $\Delta H_{mix}$ becomes more positive since the penetrant size could be larger than the average free volume in the polymer matrix and thus more energy is needed to create larger gap.

Activation energy of diffusion is related to the size and shape of penetrant molecule. The exceptional low $E_D$ value of pentafluoronitrobenzene is probably due to the relatively even distribution of fluorine atoms in pentafluoronitrobenzene compared to α,α,α-trifluorotoluene. The fluorine atoms in pentafluoronitrobenzene have more chance to interact with Teflon AF membranes than those in α,α,α-trifluorotoluene. As a result, pentafluoronitrobenzene experiences less restriction than α,α,α-trifluorotoluene and hence is associated with lower activation energy of diffusion, although it is larger than α,α,α-trifluorotoluene in view of critical volume. Taking the polarity and size into account, $E_D$ value of nitrobenzene is rather small. This problem is worthy of further consideration.

**Table 14.** Transport properties of some penetrants

| Compound | Dipole moment | P ($cm^2/s$) | $K^*$ | $D^\#(cm^2/s)$ |
|---|---|---|---|---|
| $C_6H_5CH_3$ | 0.36 | 3.71E-09 | 0.35 | 1.05E-08 |
| $C_6H_5CF_3$ | 2.86 | 1.05E-08 | 5.56 | 1.89E-09 |
| $C_6H_5NO_2$ | 4.22 | 1.49E-09 | 0.58 | 2.55E-09 |
| $C_6F_5NO_2$ | 2.52 | 9.97E-09 | 25.9 | 3.86E-10 |

[*] Partition ratios were calculated by dividing permeability coefficients by diffusion coefficients.

[#] Diffusion coefficients of the penetrants investigated can be extrapolated from a pervaporation study[26].

As shown in Table 14, fluorous penetrants display higher permeability than their nonfluorous analogs since they experience more favorable interactions with perfluorinated Teflon AF polymers. For fluorous penetrants with similar polarity, the permeability is also dependent upon the size of the penetrant. $C_6H_5CF_3$ reveals higher permeability than $C_6F_5NO_2$ due to its smaller size. For nonfluorous penetrants, $C_6H_5CH_3$ displays higher permeability than $C_6H_5NO_2$, which can be attributed to its smaller size and much lower polarity considering the basically nonpolar nature of the polymer membrane.

As illustrated in Table 13, enthalpies of partition of fluorous penetrants are more negative than those of their nonfluorous analogues. Partition of nonfluorous penetrants such as toluene and nitrobenzene into perfluorinated Teflon AF polymer is therefore an unfavorable process in terms of hydrocarbon-fluorocarbon interactions. Consequently, partition ratios of nonfluorous penetrants are significantly lower than those of their fluorous analogues as indicated in Table 14.

The permeability of toluene is three times less than that of α,α,α-trifluorotoluene, although the size of toluene is smaller than that of its fluorocarbon analogue. Similarly, the permeability of nitrobenzene is six times less than that of pentafluoronitrobenzene. These results suggest that Teflon AF polymer does not have much size-sieving effect as reported for many other glassy polymers.

To sum up, $\Delta G_P$ of $C_6H_5CF_3$ is slightly higher than that of its hydrocarbon analog whereas $\Delta G_P$ of $C_6F_5NO_2$ is much lower than that of non-fluorine analog. This can be attributed partly to the fluorous nature of the penetrants as well as Teflon AF membranes. The fluorous membranes favor sorption of the fluorous penetrants. In comparison with $C_6H_5CH_3$, the slightly higher $\Delta G_P$ value of $C_6H_5CF_3$ results from the counteraction of its size and fluorous nature. The larger size of $C_6H_5CF_3$ makes it harder to diffuse in the membranes, while the fluorous nature of the membranes makes partition easier. Although activation energy of diffusion for $C_6F_5NO_2$ should be larger in terms of its larger size, $C_6F_5NO_2$ reveals much lower $\Delta G_P$ than $C_6H_5NO_2$ because the high polarity of nitrobenzene makes it difficult to partition into the essentially nonpolar membranes.

#### 3.3.4.2 THE EFFECT OF FC-70 CONTENT

In pervaporation, the enthalpies of sorption are similar in Teflon AF 2400 and Teflon AF 1600, but the activation energies of permeation $E_a$ are markedly larger in Teflon AF 1600 than in Teflon AF 2400. These indicate that sorption is not much influenced by free volume, whereas diffusion is, since polymers with lower free volume are likely related to higher energy barriers for diffusion.

Figures 22~25 present the dependence of the permeability coefficients of toluene, α,α,α-trifluorotoluene, nitrobenzene, pentafluoronitrobenzene on temperature at different FC-70 content in Teflon AF membranes, respectively. All error bars shown in Fig. 22~25 represent the standard errors of the mean.

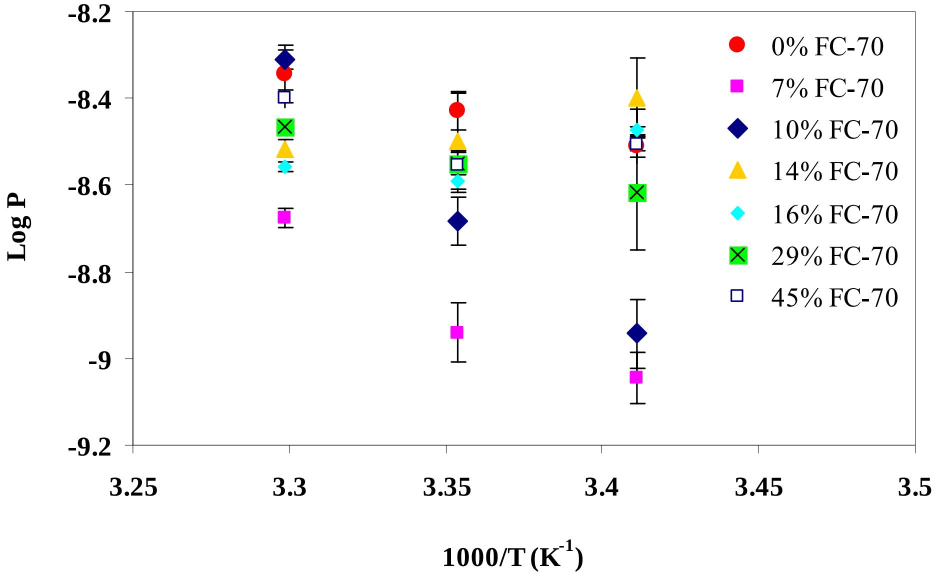


**Figure 22.** Temperature dependence of permeability of toluene

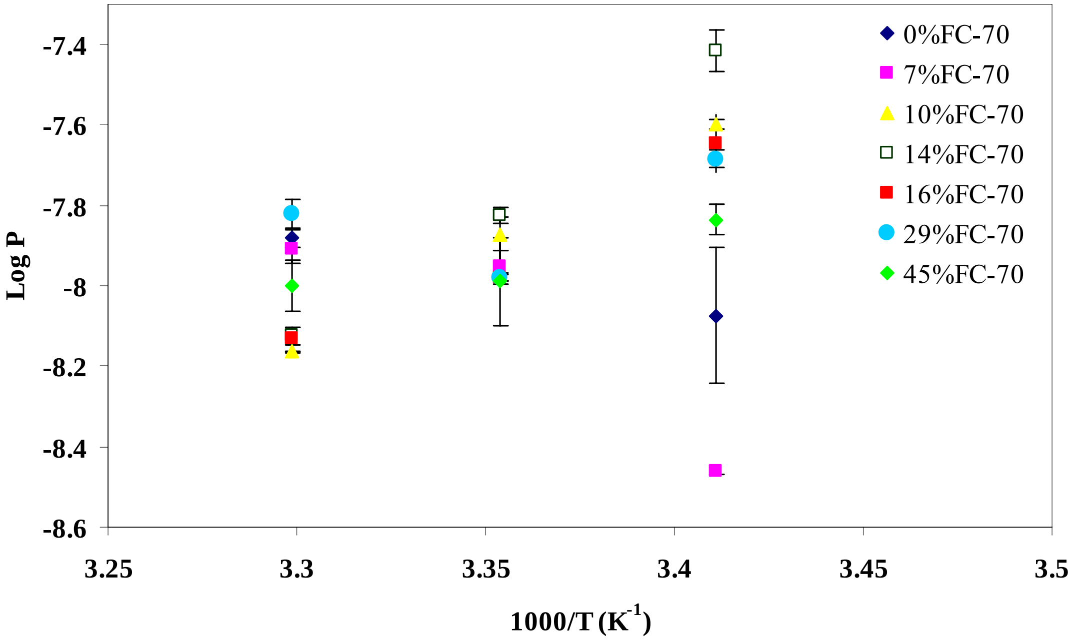


**Figure 23.** Temperature dependence of permeability of α,α,α-trifluorotoluene

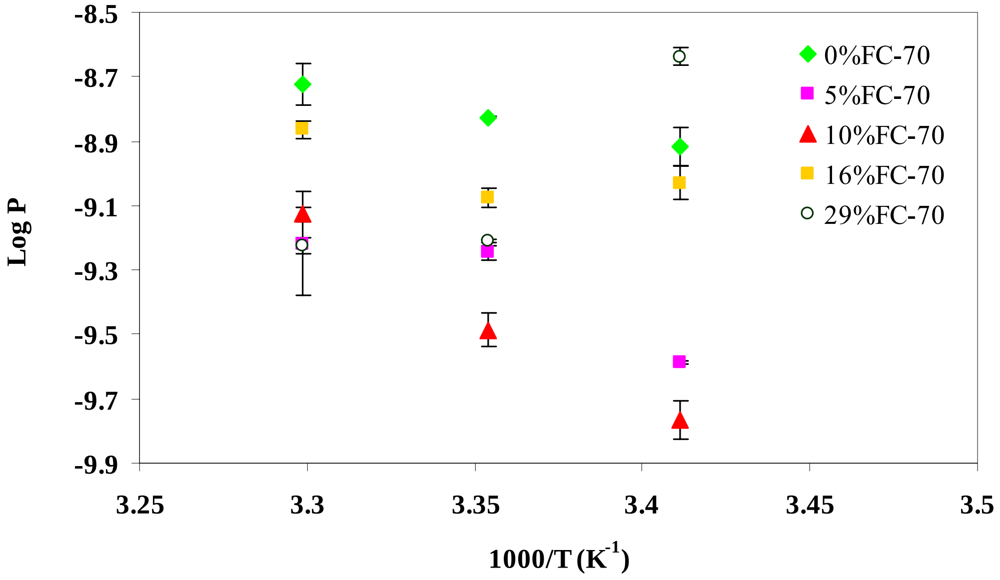


**Figure 24.** Temperature dependence of permeability of nitrobenzene

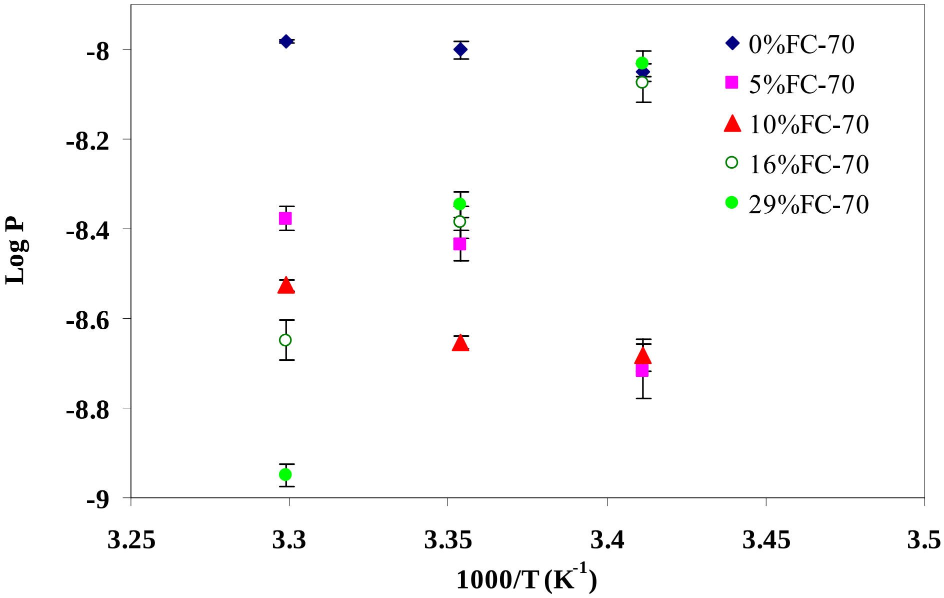


**Figure 25.** Temperature dependence of permeability of pentafluoronitrobenzene

Activation energy of permeation can be extrapolated from the figures above. The results are shown in Table 15.

**Table 15.** $\Delta G_P$ values of membranes with different FC-70 content

| Compound | $\Delta G_P$ (kJ/mol) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0wt% FC-70 | 5wt% FC-70 | 7wt% FC-70 | 10wt% FC-70 | 14wt% FC-70 | 16wt% FC-70 | 29wt% FC-70 | 45wt% FC-70 |
| $C_6H_5CH_3$ | 28.4 | - | 62.6 | 107.5 | -19.8 | -14.7 | 25.7 | 18.0 |
| $C_6H_5CF_3$ | 32.6 | - | 94.8 | -96.6 | -120.6 | -83.1 | -23.9 | -28.0 |
| $C_6H_5NO_2$ | 32.7 | 63.2 | - | 108.6 | - | 28.2 | -100.5 | - |
| $C_6F_5NO_2$ | 11.7 | 57.9 | - | 26.4 | - | -97.6 | -155.9 | - |

A comparison of $\Delta G_P$ values in Table 15 shows that $\Delta G_P$ of all the penetrants changes in a similar way. $\Delta G_P$ values increase initially as FC-70 content increases at low FC-70 concentration with reversal of this trend at higher FC-70 concentration. At low FC-70 content, enthalpies of partition are assumed to remain the same because sorption is not much influenced by free volume, while activation energies of diffusion are supposed to increase with increasing FC-70 content at low FC-70 content since polymers with lower free volume should display higher energy barriers for diffusion. Consequently, $\Delta G_P$ values increase with increasing FC-70 content. The negative activation energies of permeation at higher FC-70 content can be attributed to the negative enthalpies of partition since mixing of FC-70 with penetrant is probably a quite exothermic process. An analysis of permeation behaviors of pentafluoronitrobenzene will be helpful to understand further the trend of $\Delta G_P$.

Figures 26~27 present partition ratios and diffusion coefficients of pentafluoronitrobenzene as a function of temperature at different FC-70 content, respectively. All error bars represent the standard errors of the mean.

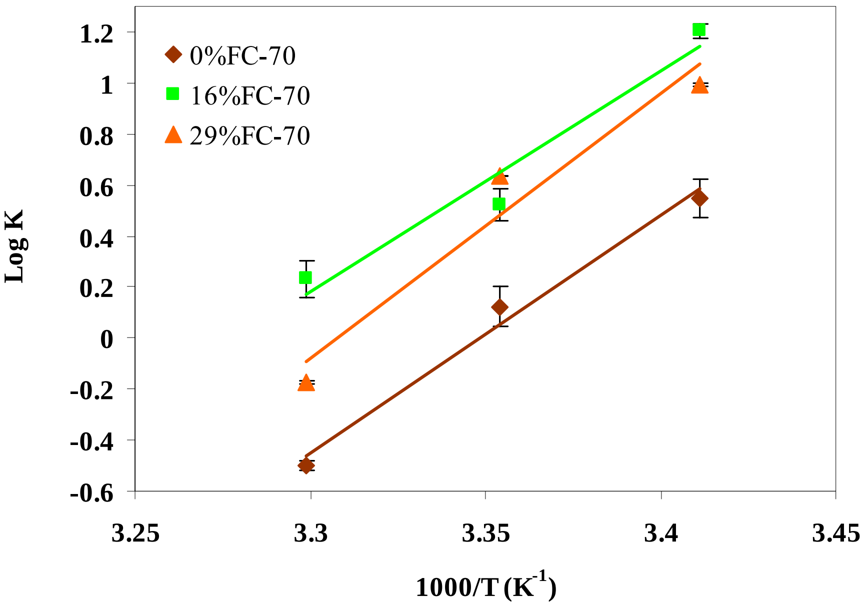


**Figure 26.** Temperature dependence of partition ratios

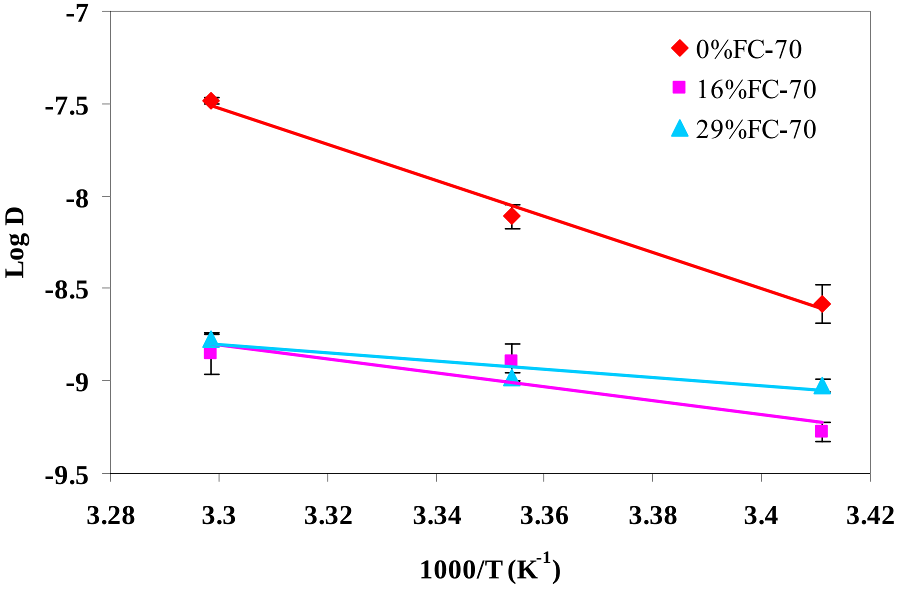


**Figure 27.** Temperature dependence of diffusion coefficients

According to Figure 26, enthalpies of partition of pentafluoronitrobenzene are almost unchanged for the membranes with and without FC-70 since the slope is almost the same. The result may imply that sorption is not much influenced by free volume. I speculate that activation energies of diffusion increase with increasing FC-70 content in membranes because the addition of FC-70 leads to a reduction in free volume of Teflon AF membranes, which would display higher energy barriers for diffusion. The observed decrease in $E_D$ with addition of plasticizer is probably associated with plasticization, which would enhance penetrant diffusion even as FC-70 occupies free volume.

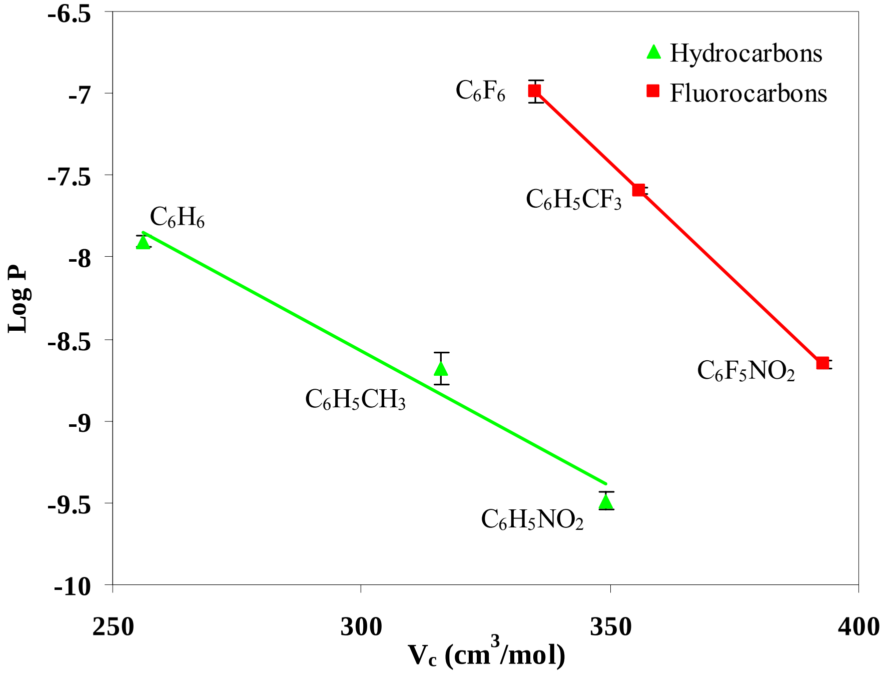


**Figure 28.** Dependence of permeability on critical volume

Fig. 28 presents permeability coefficients of fluorous compounds and their nonfluorous analogs as a function of their critical volume for Teflon AF membranes doped with 10wt% FC-70. It indicates that permeability coefficients decrease with increasing penetrant size. Such behavior was reported for glassy polymers and rubbery polymers in much literature.[31-35] LogP values of fluorous compounds fall on a separate trend from those of their nonfluorous analogs. The fluorous penetrants are more soluble in Teflon AF polymer matrix than their nonfluorous analogs, hence, permeability coefficients of fluorous penetrants are higher than those of their nonfluorous analogues.

Permeation through a rubbery polymer membrane is controlled by molecular diffusion, with partition equilibrium established very rapidly between the penetrant in the source phase and the membrane interface. Since Teflon AF membranes doped with FC-70 are in rubbery states in all test temperatures, permeation through the membranes is controlled by molecular diffusion. Diffusion through polymer membrane is influenced by penetrant size, which displays good correlations with permeation as shown in Fig. 29.

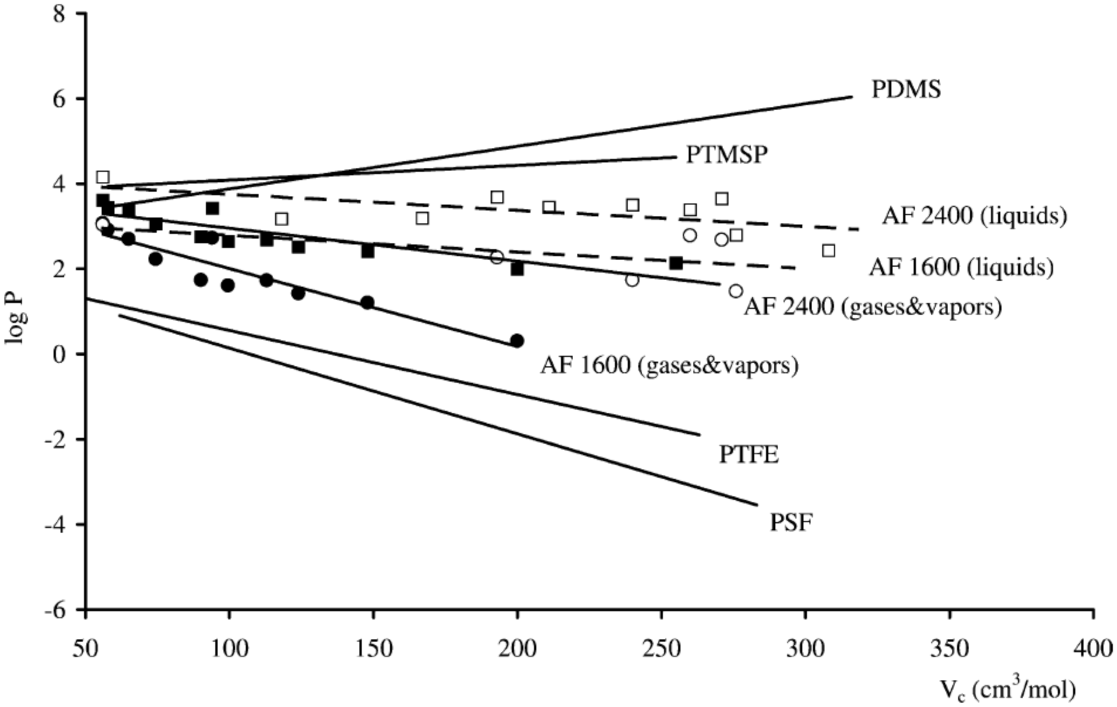


**Figure 29.** Dependence of permeability coefficient P (Barrer) on critical volume (PDMS-40°C; PTMSP-23°C; PTFE-25°C; PSF-23°C). [26]

Fig. 29 presents the correlations of permeability coefficients of gases, vapors and liquids with the critical volume of penetrants. Permeability coefficients of penetrants decrease with increasing penetrant size. It can be found that permeability coefficients of liquids are higher than those of gases and vapors at comparable critical volumes of penetrants. The dependence of permeability on penetrant size is weaker for liquids than for gases. This result is consistent with my previous conclusion, i.e. Teflon AF membranes do not have much size-sieving effect, typical for glassy polymers.

### 3.3.5 THE SELECTIVITY OF TEFLON AF MEMBRANES

Selectivity of Teflon AF membranes was investigated for the pair $C_6H_5CF_3$/ $C_6H_5CH_3$ and for the pair $C_6F_5NO_2$/ $C_6H_5NO_2$. The error bars represent the standard errors of the mean.

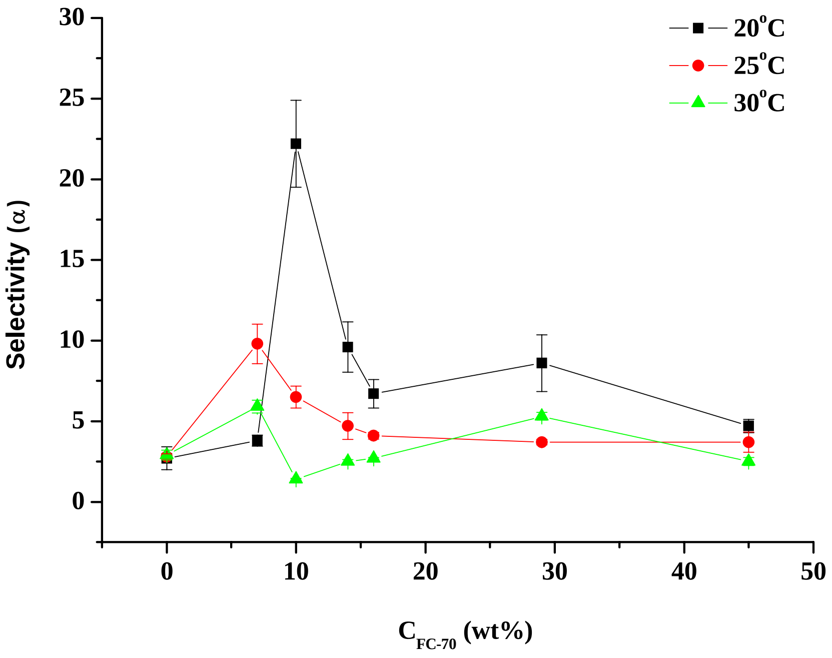


**Figure 30.** Dependence of selectivity for the pair $C_6H_5CF_3$/ $C_6H_5CH_3$ on the FC-70 content

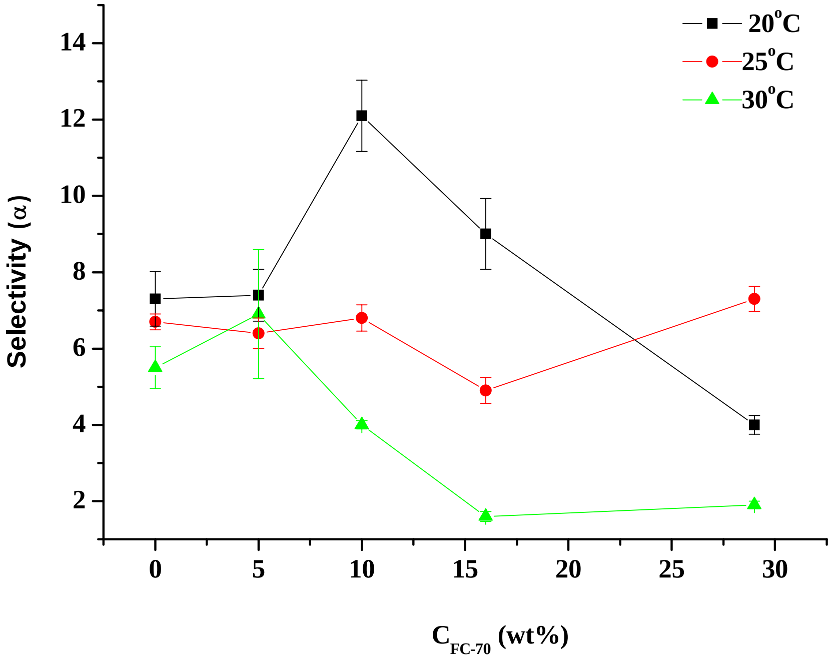


**Figure 31.** Dependence of selectivity for the pair $C_6F_5NO_2$/ $C_6H_5NO_2$ on the FC-70 content

Figures 30~31 present the dependence of selectivity on the FC-70 content in Teflon AF membranes. Selectivity generally decreases as temperature increases. Both figures show that selectivity reaches maximum at 10wt% FC-70 at 20°C. As shown earlier, Teflon AF membranes with FC-70 less than 10wt% could be anti-plasticized, and Teflon AF membranes with 10wt% FC-70 or more could be plasticized. To sum up, 10wt% FC-70 is likely a turning point of plasticization, which is quite interesting since it is also related to the highest selectivity.

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# 4.0 FUTURE PLANS

Teflon AF is very promising as a platform for selective extractions. However, plasticized Teflon AF is quite complex as we have shown. We need to understand the basis of fluorophilicity and fluidity in films. The following is the problems we need to solve in the future.

## 4.1 HOW FLUOROUS?

Solute partitioning and forming complexes in Teflon membranes is quite different from that in fluorous solvents. Thus, it is quite informative to determine infinite dilution activity coefficients and partition coefficients for substituted benzenes in fluorous solvents. HSGC will be used to create data for organic solutes partitioning into fluorous phases.

We need to measure two parameters to gain more insight. One is how much does the Teflon film prefer a fluorinated compound over a nonfluorinated analog. The other is how soluble is an organic solute, and then what is the association constant between this solute and a well-chosen host? It is rather to choose a set of probe compounds and use them across many different films. The probe solutes will be the same as what we are using, trifluorotoluene and toluene, nitrobenzene and pentafluoronitrobenzene. We can also gain some information from studying the films themselves. Hong et al has found that chloroform is imbibed into films, which become less fluorous than expected. We will thus determine solvent uptake by simple weighing where appropriate. We will also use FTIR to monitor the concentration change of FC-70.[1, 2]

## 4.2 HOW LIQUIDS?

We will use our 96-well microtiter plate procedure to determine the partition ratios of organic solutes in fluorous/organic system. Diffusion coefficient is determined from permeability measurements in conjunction with known partition ratios.

Again, we can also gain insight from studying the films. We will determine polymer free volume, which can be calculated from film density using the hydrostatic method[3, 4]. There are a lot of experimental techniques available to study films, such as thermogravimetry (TG) [5, 6], differential scanning calorimetry (DSC)[7-13] and dynamic mechanical analysis (DMA)[5, 10-12, 14]. TG exposes the loss of imbibed solvent. DSC determines glass transition temperatures. Most importantly, DMA gives very clear information on polymer chain mobility, and can confirm $T_g$ measurements. We will use them to characterize the films.

## 4.3 WHAT FILMS?

Our initial hypothesis was that the film would act as a supported liquid membrane[15-20]. However, the preliminary data from transport measurements show that this hypothesis may be too naïve. There is compelling evidence that the polymer itself influences transport. The changes of selectivity with temperature are dramatic. They lead us to postulate that there is some sort of transition near room temperature and the exact temperature depends on the composition of the film. The ‘transition’ could be, or could relate to the imbibed solvent.

We will use several potential plasticizers, namely FC-70, perfluoroperhydrophenanthrene, the perfluorodecalins. We hypothesis that plasticization is caused by a fluorous diluent instead of organic solvent in order to permit rapid diffusion within the films. Another hypothesis is that transport selectivity is highest when the film is the least influenced by the solvent. More generally, we will find out what dominates transport behavior -- diffusion or partition?

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