DEVELOPMENT OF PERVAPORATION MEMBRANE FOR VOLATILE ORGANIC CHEMICAL REMOVAL

by

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A thesis
submitted under the supervision of
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in partial fulfillment of the
requirements for the degree of
Master of Applied Science
in
Environmental Engineering

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Ottawa, Canada
K1N 6N5

February, 1996

ISBN 0-612-15740-7

Canada

UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

ACKNOWLEDGMENTS

I wish to express my sincere appreciation and gratitude to my supervisor Professor Roberto M. Narbaitz for his invaluable guidance, constructive criticism and continued encouragement throughout the course of this study and in the preparation of the thesis. I am grateful to the support, guidance and suggestions of Professors T. Matsuura and J. P. Santerre throughout this research. My sincere thanks are due to Dr. B. A. Morrow, Dr. C. Kazakoff, Department of Chemistry, University of Ottawa and Dr. K. C. Khulbe, Department of Chemical Engineering, University of Ottawa for their help in analysis. Special thanks are extended to Mr. V. A. Pham, Mr. Y. Fang and Mr. J. Mineery, for their cooperation during this study, Mr. L. Tremblay and F. Ziroldo, for their help in assembling the experimental setup, Mr. F. S. Aposaga, for his assistance in maintaining analytical equipment.

I also would like to thank other individuals who have helped me directly or indirectly in the course of this study.

I am specially grateful to my wife and my daughters, who had missed me and helped me in all respects during the course of this research.

Finally, I wish to thank the National Science and Engineering Research Council for the financial support.

ABSTRACT

Pervaporation is a membrane based process which overcomes many of the deficiencies of current technologies for the removal/recovery of volatile organic chemicals (VOCs) from aqueous streams. In this process, VOCs from a liquid stream are driven across a permselective membrane and exit as a vapor due to the vacuum maintained in the downstream side of the membrane. Proven hydrophobic membranes used for pervaporation today suffer from limitations of mechanical stability, while membranes with superior mechanical characteristics do not possess sufficient selectivity to be useful for these applications. To overcome these limitations surface modifying macromolecules (SMMs) have been used as additives in the preparation of polyethersulfone (PES) membranes, which inherently have good mechanical characteristics but are intrinsically hydrophilic. This approach produced membranes with high hydrophobicity (based on contact angles), which were expected to be permselective to VOCs, like chloroform. This thesis investigates the impact of PES/SMM membrane preparation parameters on the reported separation of chloroform from aqueous solutions via pervaporation. These parameters include polyvinylpyrrolidone (PVP) addition levels, solution mixing period, solution age and membrane age. A chemical analysis of the permeate revealed that the permeate contained ethanol but virtually no chloroform. Permeate ethanol concentrations were higher with fresh membranes and decreased both with membrane age and period of use. This indicates that ethanol, which was used during the solvent exchange drying step of membrane preparation, was being leached from the membrane. It was concluded that there was in fact no enrichment of chloroform in the permeate as reported earlier and that the surface hydrophobicity introduced was insufficient to dominate over the intrinsic bulk hydrophilic characteristics of the PES membranes. These findings indicate a need to reevaluate the levels of SMM addition and the process parameters to develop a sufficiently dominant hydrophobic surface layer.

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GLOSSARY

AFM	atomic force microscope
BA-L	DuPont's Zonyl intermediate (fluorohydrocarbon)
c, c_A	mass concentration of faster permeant (A) in the feed, ppm
c', c_A'	mass concentration of faster permeant (A) in the permeate, ppm
c_B	mass concentration of slower permeant (B) in the feed, ppm
c_B'	mass concentration of slower permeant (B) in the permeate, ppm
cc	cubic centimeter
DMAc	dimethylacetamide
DSC	differential scanning calorimetry
EPDM	ethene-propene terpolymer
EPR	ethylene/propylene rubber
FTIR	fourier transform infrared
g	gram
GC	gas chromatography
GC(P&T)	gas chromatography (purge & trap)
GFT	Gesellschaft Für Trenntechnik
GPC	gel permeation chromatography
gpm	gallon per minute
h	hour
IC	inorganic carbon
J'	permeate flux or permeation rate, g/(h. m^2 of membrane area)
kg	kilogram
L	liter
m	meter
mL	milli liter
MDI	methylene bis-phenyl diisocyanate
MRT	Membrane Technology and Research Inc.
M.S	mass spectrometry
MTBE	methyl-tert-butylether
NBR	nitrile-butadiene ruber
PA	polyamide
PBTESP	poly(1,3-bistriethyl silyl-1-propyne)
PDMS	polydimethylsiloxane
PEBA	polyether-block-amid
PEI	polyetherimide
PES	polyethersulfone
POC	purgeable organic carbon
ppb	parts per billion
PPO	polypropylene diol
ppm	parts per million
PS	polysulfone
PSI	pervaporation index
psi	pressure per square inch

PTESP	poly(1-triethyl silyl-1-propyne)
PTFE	poly tetrafluoroethylene
PTMSP	poly(1-[trimethylsilyl]-1-propyne)
PVA	poly(vinylalcohol)
PVP	polyvinylpyrrolidone
rpm	rotation per minute
SBR	styrene-butadiene rubber
SMM(s)	surface modifying macromolecule(s)
t_g	glass transition temperature, °C
TC	total carbon
TCE	trichloroethane
THF	tetrahydrofuran
TOC	total organic carbon
VOC(s)	volatile organic chemical(s)
XPS	X-ray photoelectron spectroscopy
wt.	weight
6-PP	6-pentyl-alpha-pyrone
α	separation factor
β	enrichment factor
μ	micro

CHAPTER 1

INTRODUCTION

An estimated 1.6 to 5.0 million tons of volatile organic chemicals (VOCs) enter and pollute the environment each year (Shen and Sewell, 1988). The main types of water contaminations with VOCs are industrial wastewater and contaminated groundwaters. The latter arises from improper disposal of these common industrial solvents or from leaking tanks. Although contaminated groundwaters only contain ppb level of VOCs, it renders them unfit for human consumption. Cleanup of these contaminated groundwaters is difficult, expensive and takes many years. Because of their widespread use in industry, VOCs are the most common contaminants found at U.S. superfund sites. Conventional treatment methods for removal and recovery of VOCs include air stripping, adsorption, advanced oxidation and distillation are effective only at specific VOC concentration levels. Some of these techniques also result in release of gaseous VOC emissions (Brewer, 1991).

Separation of VOCs from liquid streams via membrane pervaporation followed by concentration of VOCs in the permeate by compression-induced condensation is an alternative that could help overcome the shortfalls of existing technologies. Pervaporation can be used for a wide range of VOC concentration levels ranging from dehydration membranes for higher

VOC concentrations to organophilic membranes for lower VOC concentrations. It can be used for water pollution reduction, and for VOC recovery and reuse. Although pervaporation is the least developed process, it was ranked as the best technology for organic/organic separations in a report commissioned by the U.S. Department of Energy (Baker, 1991). This ranking clearly demonstrates the potential future impact of this technology on the chemical process and environmental fields. Pervaporation could be used for both groundwater cleanup as well as for VOC recovery and reuse from industrial waste streams.

In general, membranes made from hydrophobic elastomeric polymers have been known to be highly organophilic and effective in VOC removal from water by pervaporation (Koops and Smolders, 1991). To date, most practical membrane applications have been reported with polydimethylsiloxane (PDMS), ethylene/propylene rubber (EPR) or polyether-block-amid (PEBA) materials (Fleming and Slater, 1992; Néel, 1995). PDMS composite membranes for the removal and recovery of trace organics from water are commercially available (Bengston and Böddeker, 1988; Kaschemekat et al., 1988). PDMS membranes however, require chemical treatment to control swelling which results in the reduction of both permeation rate and selectivity due to the absorption of feed components (Blume and Baker, 1987; Eustache and Histi, 1981).

Membrane efficacy requires large contact surface areas (Kesting, 1971; Matsuura, 1993). PDMS composite membranes however, due to their weak mechanical properties require specially designed modules. Since these modules usually do not allow for a high surface to volume ratio, a large number of modules are required for most applications (Blume and Baker, 1987).

There is hence an urgent requirement for the development of an organophilic membrane having sufficient mechanical strength to enable its use in high surface area to volume ratio configurations. Given the limitations of the mechanical strength of PDMS and the practical limitations of time and economics for the development of entirely new membrane materials, incorporating organophilic selectivity in existing membrane materials of proven mechanical stability may be the best approach.

Polyethersulfone (PES), polyetherimide (PEI) or polysulfone (PS) are some such membrane materials whose selectivity may be tailored through the incorporation of surface modifying additives, referred to in this study as surface modifying macromolecules (SMMs). These SMMs increase the hydrophobicity of the membrane surface and hence enhance their organophilic properties. This is a reasonable approach since both surface chemistry and morphology play an important role in permeate transport (Kesting, 1971: Matsuura, 1993) and that hydrophobicity of the surface favors organic selectivity (Koops and Smolders, 1991; Fleming and Slater, 1992).

This work has therefore concentrated on modifying PES membrane by incorporating SMMs to develop surface hydrophobic pervaporation membrane and on evaluating the performance of such membranes for removal and recovery of chloroform from aqueous streams. The primary objective of this thesis is to evaluate the impact of the various membrane preparation steps on membrane performance for such applications.

CHAPTER 2

LITERATURE REVIEW

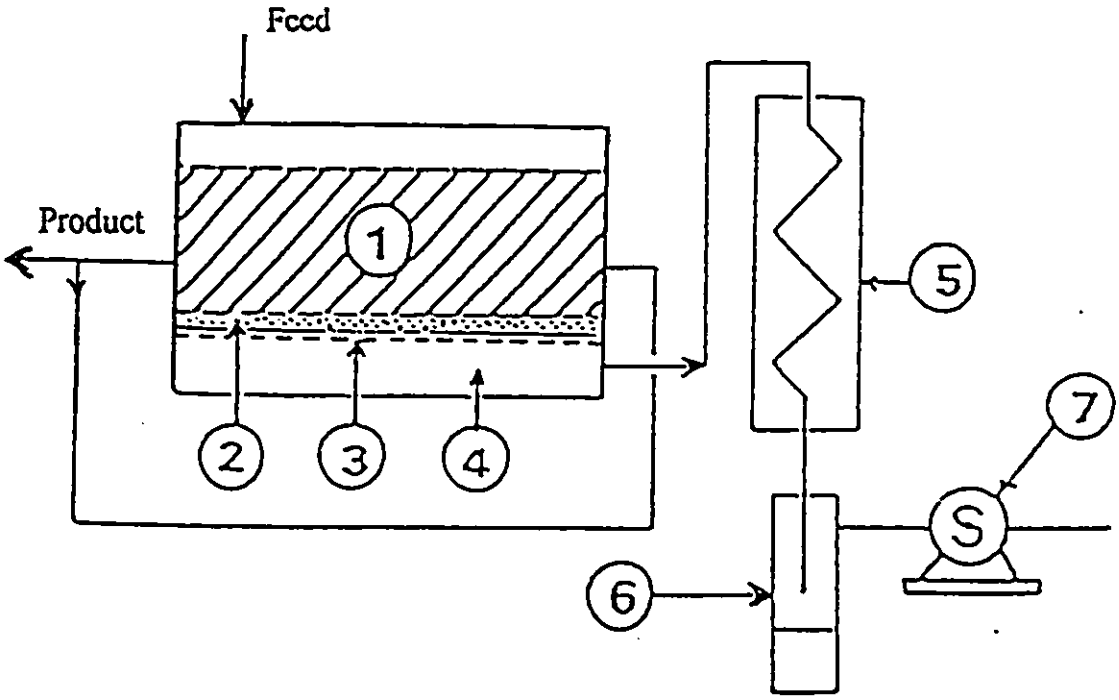
Interest and research in the field of pervaporation was greatly increased in the past ten years. There have been nearly 200 patents awarded and 300 papers presented on pervaporation from 1984 to 1989 (Slater and Hickey, 1989). This chapter, briefly reviews past and on going research on pervaporation.

2.1 Introduction to Pervaporation Process

The characteristics of pervaporation membrane separation, including some general assessments of the effects of process conditions have been reviewed by Noble and Stern (1995), Ho and Sirkar (1992) and Huang and Rhim (1991).

Pervaporation is a process, based on a permselective membrane, used to separate mixtures of dissolved solvents. In this process, a liquid feed-mixture contacts one side of the membrane and the permeate (or pervaporate) evolves in the vapor state from the opposite side of the membrane, which is kept under vacuum. Pervaporation is characterized by the imposition of a barrier (membrane) layer, generally made of polymeric materials, between a liquid and a gaseous/vapor phase, with mass transfer occurring selectively across the

barrier from the liquid to the gas/vapor side. Because of the unique phenomenon of phase change, this technique, which was originally called 'liquid permeation', has subsequently been termed 'pervaporation'. The permeate obtained can be finally collected in a liquid state after condensation (Figure 2.1).



1. Liquid feed-mixture
2. Membrane
3. Sintered support
4. Permeate
5. Condenser
6. Permeate receiver
7. Vacuum pump

Figure 2.1 Pervaporation Process (Néel et al., 1985)

The transport of the permeate through the pore-free permselective membrane involves three successive steps (Huang, 1991): a) upstream partitioning of the feed-components

between the flowing liquid mixture and the swollen upstream layer of the membrane, i.e. selective sorption into the membrane on the feed side; b) diffusion of the penetrants through the unevenly-swollen permselective barrier; and c) permeate desorption at the downstream (vapor or gas) side of the film.

Hence, the selectivity and permeation rate are governed by the solubility/sorption and diffusivity of each component of the feed mixture to be separated. Mulder et al. (1985) suggested that for liquid mixtures, separation is possible because the membrane can preferentially transport one component over the other, even if the driving forces for the components are equal. Nevertheless, the prediction of selectivity is often difficult, since the transport of one component through the membrane is affected by the presence of the other component(s) as in the case of binary permeation.

Solubility or sorption are thermodynamic properties, while diffusivity is a kinetic property. The coupling of transport of permeants can be divided into two parts, a thermodynamic part and a kinetic part (Brun et al., 1985a). Thermodynamically, the change in concentration of one component in the membrane is caused by mutual interactions between the permeants in the membrane, as well as by interactions between the individual components and the membrane material. The kinetics of diffusion of the individual permeants is controlled by their diffusion coefficients, which are in turn a function of their own concentration as well as that of the other permeants.

There are several relationships, which are usually derived from the Flory-Huggins thermodynamic theory, to describe the equilibrium sorption of low molecular weight components in polymers (Flory, 1953). These include: (i) the sorption of pure liquid in an amorphous polymer; (ii) the sorption of binary liquid mixtures in an amorphous polymer; (iii) the sorption of pure liquid in a crosslinked polymer; and (iv) the sorption of pure liquid in a semi-crystalline polymer (Huang and Rhim, 1991). The expression for the sorption of pure liquid in an amorphous polymer is generally described as being largely dependent on the interaction parameter between the penetrant and the polymer (Mulder, 1991). This parameter generally increases as the affinity between the penetrant and the polymer decreases. For binary sorption, the interaction parameters are generally concentration dependent. The expression for pure liquid sorption in crosslinked polymer reflects the restriction on swelling, which results in a decrease of the concentration of liquid in the polymer. For the sorption of pure liquid in a semi-crystalline polymer, the expression accounts for the decrease in component concentration by assuming that the crystallites can be considered as physical crosslinks, having the same effects as chemical crosslinks. In addition, the model assumes that crystallites are impermeable to penetrants.

Diffusion mechanisms can be considered as either 'molecular' or 'free volume' mechanisms. The former theory considers the diffusion process to comprise of specific postulated motions of penetrant molecules and polymer chains (Dibenedetto, 1963; Dibenedetto and Paul, 1964; Paul and Dibenedetto, 1965). The latter is based on an oversimplified view of molecular processes, but relates the diffusion coefficients to the free volume ('hole or void space') of the system on the basis of a fluctuation analysis

(Vrentas and Duda, 1976, 1977). The diffusion coefficient, in most cases, is a function of the concentration of the components in the membrane. Several commonly used expressions were summarized by Huang and Rhim (1991).

Néel (1991) suggested that the transition from the liquid to vapor is a multistage process that is much more complex than a single vaporization step, and that the composition of the pervaporate differs widely from that of the mixed vapor obtained after equilibrium conditions.

Vaporization on the permeate side of the membrane (desorption step) is generally considered to be a fast, non-selective step if the partial pressure is kept low (Aptel et al., 1976; Huang and Rhim, 1991). It has been shown that the permeate flux at low pressures remains fairly constant, but drops off sharply and becomes dependent on the rate of vaporization when the pressure on the down stream side approaches the partial vapor pressure of the liquid component (Aptel et al., 1976; Huang and Rhim, 1991).

2.2 Pervaporation Flux and Selectivity

A satisfactory quantitative explanation of binary permeation through polymeric membranes has not yet been achieved. However, some qualitative assessments are available. In general, the effect of a mixture's composition on the permeation rate and selectivity is very noticeable (Huang and Rhim, 1991), but precise quantification is complicated because of the complex nature of the mutual interactions involved. The permeation rate of one component could be influenced negatively or positively by the

presence of the other component (Huang and Lin, 1968; Brun et al., 1985a). The order of magnitude of the selectivity was found to be lower than the ratio of the permeation rates of pure components (Huang and Rhim, 1991). This behavior is usually attributed to the plasticizing effect of the permeants on the membrane. Hence, a linear dependence of the permeant diffusivity is not suitable to account for large plasticizing effects. Many investigators (Huang and Lin, 1968; Brun et al., 1985a; Mulder and Smolders, 1985; Rautenbach and Albrecht, 1980) suggested that the diffusivity of each component is a function of permeant concentration which is related to the free volume of the polymer. This free volume, in turn, depends on the local composition of the ternary system permeant A / permeant B / membrane.

The behavior of a pervaporation membrane used to separate a binary liquid mixture (component A and B) of given composition is characterized by two experimental parameters, namely the permeate flux or permeation rate, J' [expressed in g/(h.m^2 of membrane area)] and selectivity of the barrier, which may be quantified by the following two alternative dimensionless ratios separation factor, α and enrichment factor, β. They are defined as

$$\alpha = \frac{c'_A / c'_B}{c_A / c_B} = \frac{c'(1-c)}{c(1-c')} \qquad (2.1)$$

$$\beta = \frac{c'}{c} \qquad (2.2)$$

where $c_A = c$ = mass concentration of the faster permeant (A) in the feed
$c'_A = c'$ = mass concentrations of the faster permeant (A) in the permeate
c_B and c'_B = mass concentration of the slower permeant (B) in the feed and in the permeate, respectively.

The numerical values of these two parameters can be readily related to one another by means of the following relationships:

$$\alpha = \frac{1-c}{1-\beta c}\beta \tag{2.3}$$

$$\beta = \frac{\alpha}{1+(\alpha-1)c} \tag{2.4}$$

The physical meaning of α is not very clear because the two penetrants are not transported independently through the membrane due to strong coupling effects (Hwang and Kammermeyer, 1975). Even then, α is undoubtedly more significant than ß from the physico-chemical point of view since it increases to infinity as the membrane approaches perfect semipermeability (c' then being very close to 1). On the other hand, the use of the parameter ß makes it easier to formulate the mathematical equations governing membrane performance (production capacity, operation yield and energy cost) (Néel et al., 1983).

A comparison between the ratios α and ß clearly shows that the former is larger than the latter. ß systematically assumes a rather low value if the feed mixture is rich in the faster-permeating component. Also from the above equations, it can be seen that α and ß values can only be determined if the feed composition is known.

The selectivity and permeation rate of a membrane usually exhibit an inverse dependence, that is, when one factor increases the other decreases (Huang and Rhim, 1991). Hence it is useful to define a composite performance index that accounts for both. Huang and Rhim

(1991) defined a pervaporation separation index (PSI) to be the product of the separation factor and the permeation rate.

$$PSI = J_t.\alpha_{A/B} \qquad (2.5)$$

where, J_t is the total permeation rate, g/(h.m^2) and PSI has the unit of g/(h.m^2).

This index is useful as a comparative value to evaluate membranes. A complete evaluation of the membrane performance, therefore, requires kn[illegible] variation of the flux (J') and the separation factor (α) associated with char[illegible]ition.

To collect these data, experimental investigations are usually carried out with laboratory pervaporation cells, as described in the section 3.4. It is also worth stressing that selectivity and flux measurements are not equally reliable (Néel, 1995). In fact, the experimental errors of the selectivity values are rather small provided that measurements are carried out under a low downstream pressure, i.e., if there is no significant pressure drop across the sintered metal support. On the other hand, flux values are more questionable because the transfer area is not exactly known, due to contact between the membrane and its support i.e. the sintered support may be blocking permeants from desorbing from the membrane. Comparative measurements made by Blackadder and Keniry (1972), while investigating the pervaporation transport of pure *p*-xylene at 30°C through a 75 μm thick homogeneous sheet of polyethylene mounted over five different supports yielded experimental flux values ranging from 26 to 61 g/ (h.m^2). It is hence clear that the geometry of the support may significantly affect the observed transport rate and

that experimental flux values measured with a given laboratory pervaporation cell support configuration must only be compared with those obtained from cells with an identical support configuration. Reliable flux and selectivity data should be collected only when the steady-state transport regime has been attained. Establishment of a steady-state regime in a laboratory test is generally preceded by a transient period of 30 minutes to several hours, depending on the composition of the feed and the nature of the membrane (Néel, 1995). During this period flux and selectivity apparently change with time. These variations are governed by the sorption kinetics of the feed mixture and by the polymeric barrier material. They often involve complex migration phenomena, which may significantly deviate from Fickian diffusion (Windle, 1985). These transient behaviors are generally considered a temporary phenomena which do not interfere significantly once the steady-state transport regime is established.

Membrane aging has also been known to significantly affect performance of the membrane (Nemeh and Peterghem, 1994; Huang and Wei, 1994) and is also a practical consideration for evaluation studies.

2.3 Background of Pervaporation

As early as 1906, Kahlenberg reported some qualitative observations concerning the selective transport of hydrocarbon/alcohol mixtures through a thin rubber sheet (Kahlenberg, 1906). The term pervaporation was first introduced by Kober (1917) who observed that "a liquid in a collodion bag, which was suspended in the air, evaporated, although the bag was tightly closed". Farber(1935) at the University of Toronto presented

the results of work using pervaporation for concentrating protein solutions. Schwob (1952, 1963) dehydrated water/alcohol mixtures by means of a thin (20 μm) regenerated cellulose film (Cellophane). Heisler et al.(1956) reported their findings on dewatering of ethanol solutions through regeneration of cellulose in 1956.

Initially, homogeneous membranes were used for pervaporation. The low magnitude of permeation flow- rates through these homogenous dense films seemed to prevent its further development for industrial applications. The development of the " phase-inversion" membrane making method by Loeb and Sourirajan in the 1960s to manufacture high-flux asymmetric membranes provided a possible solution to overcome the earlier problem of low flux (Néel, 1991).

The first major research effort in pervaporation was undertaken in the late 1950s by Binning and associates at the American Oil Company (Amoco) in Texas (Ho and Sirkar, 1992). They conducted a series of investigations on the separation of hydrocarbon mixtures using cellulosic and polyethylene membranes. Binning et al., (1958) reported the use of membrane pervaporation for dehydration of a ternary azeotrope of isopropanol-ethanol-water from the overhead of a distillation column. The group also separated an equi-volume mixture of *n*-heptane and iso-octane through unnamed "thin polymer films" (Binning et al., 1961b). Several papers discussed azeotropic benzene/methanol separation and reversal of selectivity with different membranes. The experiments showed that aromatics and olefins permeate faster than paraffins, and linear hydrocarbons permeate faster than branched isomers(Binning et al., 1961b, Lee, 1961). This process was used to

improve the octane number of gasoline. More than 10 patents were issued to Amoco in those years citing members of the research group as inventors(Binning and Kelley, 1959; Binning and Lee, 1960a, 1960b, 1960c; Binning, 1960; Stuckey, 1960; Binning and Stuckey, 1960; Binning and Johnson, 1961; Binning, 1961; Binning et al., 1961a, 1962).

Meanwhile, systematic studies on pervaporation and vapor permeation were started in France by Néel and others(Fries and Néel, 1965; Aptel et al., 1969, 1972, 1973, 1974a, 1974b). Their experiments clearly demonstrated that pervaporation and distillation could be associated to fractionate mixtures of close boiling-temperature liquids, or mixtures leading to azeotropes. Thus, this new membrane technique became a competitor to sophisticated and energy-consuming processes, such as extractive and low-pressure distillation.

In addition to the development of better membrane materials, the energy crisis in the 1970s refocused interest in separation technologies that possessed a high potential for energy savings. This greatly enhanced the commercialization of pervaporation.

In the mid 1970s, Gesellschaft Für Trenntechnik (GFT), a German company, commercialized an economical pervaporation process for dehydrating ethanol that produces high purities rivaling those achieved by azeotropic distillation (Fleming and Slater, 1992). Following pilot trails in Europe, the first industrial applications were in Brazil and the Philippines for the production of ethanol via continuous fermentation of sugar cane, bagasse, and sweet sorghum. The fermented material contained 5 to 7%

ethanol and it was concentrated by primary distillation to a mash containing 80 to 85% ethanol, followed with vacuum pervaporation to 96 wt. % (Ballweg et al., 1982). The primary advantages for the GFT process were as follows. First, no additives were necessary for the final separation. Second, energy demand was reduced, because only the fraction of the liquid, which permeate across the membrane, has to be vaporized. Third, only a small vacuum pump was required, because the condensing permeate continuously created a driving vacuum force. Fourth, closed-loop operation, with only a small volume of recycled permeate. Fifth, much lower capital cost. Sixth, recovery of the initial thermal energy supplied as low-pressure steam(<90 psi).

In the late 1970s and continuing into early 1980s, other integrated distillation/pervaporation plants were built in Europe and Asia. Most of these were of moderate capacity, typically with ethanol recovery of 1,000 to 50,000 L/day (Fleming and Slater, 1992). As the cost of the permselective membrane modules decreased, and the selectivity increased (99.85% ethanol purity became easily attainable), the integrated process gained industrial acceptance. Today, a number of commercial pervaporation plants exist for ethanol dehydration. In 1980, a 150,000 L/day ethanol dehydration plant in Betheniville, France, became the largest pervaporation facility in the world (Rapin, 1988).

2.4 Polymers & Membranes for Pervaporation

Most polymers used in the preparation of pervaporation membranes can be divided into two classes: glassy polymers and rubbery polymers or elastomers (Koops and Smolders, 1991). This distinction is made on the basis of the state of the polymer at room

temperature. Polymers with a glass transition temperature (t_g) below room temperature are in the rubbery state and are, therefore, classified as rubbery polymers or elastomers. Polymers having a glass transition temperature above room temperature are classified as glassy polymers. Glassy polymers can be further classified as crystalline, semi-crystalline and amorphous polymers.

Three types of polymers have been identified as suitable for making membranes for the pervaporation of aqueous-organic or organic-organic mixtures (Tyagi, 1993). These are: 1) glassy (amorphous) polymers which interact preferentially with water (Böddeker and Bengtson, 1991); 2) Elastomeric polymers (elastomers) which interact preferentially with the organic component of the aqueous-organic mixture water (Böddeker and Bengtson, 1991; Nijhuis et al., 1988); and 3) ion exchange polymers which may be viewed as crosslinked electrolytes and usually interact preferentially with water (Tyagi, 1993).

Glassy polymers are generally used for the dehydration of aqueous-organic mixtures. A modified polyvinylalcohol (PVA) membrane is commercially produced by the GFT company for the dehydration of aqueous streams. Glassy polymeric membranes can also be used for the separation of an organic component from an aqueous-organic or organic-organic mixture. For example, polyethylene membranes were used for separating organic mixtures (Michaels et al., 1962; Siegel and Coughlin, 1970; Fels and Huang, 1970; and Huang and Lin, 1968). A novel glassy polymer namely, Poly(1-[trimethylsilyl]-1-propyne) (PTMSP) was investigated for the separation of alcohol-water mixtures (Hickey et al., 1992). The polymer PTMSP was reported to be more alcohol selective than a rubbery

polymer of polydimethylsiloxane (PDMS). Membranes made from several copolymers [poly(1-triethylsilyl-1-propyne)(PTESP), Poly(1,3-bistrimethylsilyl-1-propyne)(PBTMSP) and Poly(1,3-bistriethylsilyl-1-propyne) (PBTESP)] resulted in membranes with a higher ethanol selectivity than PTMSP (Inaba et al., 1989). However, the co-polymer membranes were unstable and a decrease in both permeation rate and selectivity was observed with time. This phenomenon could be avoided by adding 1 to 4 wt. % PDMS.

Organic components permeate preferentially with respect to water through hydrophobic elastomeric polymers due to the absence of polar groups in the flexible chains and thus are effective in VOC removal from water by pervaporation (Koops and Smolders, 1991). Polymers with these properties are excellent candidates as membrane materials for the removal of organics from aqueous-organic mixtures. Polyesters, polyvinylchlorides, ethylene/propylene rubber (EPR), PDMS and co-polymers such as polyether block amides (PEBA) are some of the polymers presently used for the removal of organics from aqueous-organic mixtures by pervaporation (Fleming and Slater, 1992; Néel, 1995; Néel, 1991; Böddeker and Bengtson, 1991). The pervaporation behavior of elastomeric membranes for removal of trichloroethylene and toluene from aqueous solutions were investigated in detail by Nijhuis et al., (1988).

Gesellschaft Für Trenntechnik (GFT), has successfully developed a pervaporation process for the dealcoholization of beers, wines and liquors using PDMS composite membrane (Escudier et al., 1988). Processes for the removal and recovery of trace organics from groundwater and waste water using PDMS composite membranes are commercially

available (Bengston and Böddeker, 1988; Kaschemekat et al., 1988). However, PDMS membranes require chemical treatment to control swelling due to the absorption of feed components. This swelling is responsible for loss of productivity (Blume and Baker, 1987; Eustache and Histi, 1981). In addition, concentration polarization, the term used to describe the fact that the retained species accumulate in higher concentration near the membrane surface than that of the bulk, is also a major impediment in the use of pervaporation through membrane made of PDMS, EPR or PEBA to remove trace organics from contaminated waters (Néel, 1995; Psaume et al., 1988; Côté and Lipski, 1988; Nijhuis, 1990; Raghunath and Hwang, 1992).

The efficient use of membranes requires large surface areas (Kesting, 1971; Matsuura, 1993). However, PDMS composite membranes, due to their poor mechanical properties, need modules with special physical configurations. Since these modules usually do not allow for a high surface to volume ratio, a number of modules are required for higher efficiency (Blume and Baker, 1987). The resulting additional capital cost contributes to the limited use of these membranes. The use of PDMS based membranes will diminish further because of their low solvent resistance, which contributes to swelling and loss of selectivity (Eustache and Histi, 1981). Therefore, there is a need to develop a membrane which has good selectivity for organics while overcoming the disadvantages of PDMS based membranes.

2.5 Pervaporation Applications

As pervaporation membranes preferentially transport one component over others, they can efficiently separate azeotropic mixtures as well as, concentrate substances present at low concentrations in the feed. The mixtures to be separated can be of water/organic or organic /organic in nature. Pervaporation applications can be divided into three major sections. These are: a) dehydration of organic/water mixtures such as alcohols, esters, ethers, ketones, hydrocarbons, acids, amines, etc.; b) removal/concentration of organics from diluted organic/water mixtures like esters, ethers, chlorinated hydrocarbons, aromatic compounds, etc.; and c) separation/removal/concentration of organics from organic/ organic mixtures.

Among these applications, the removal/concentration of organics from aqueous solutions is of particular interest.

As it is clear from the discussion under Section 2.3, the pervaporation process for dehydration of ethanol or other organics mixtures is a well established commercial process, only the other two applications are reviewed here.

2.5.1 Removal/Concentration of Organics from Organic/Water Mixtures

Separation/concentration of organics from dilute aqueous solutions is a very important research topic for pervaporation (Fleming and Slater, 1992). As mentioned earlier, pervaporation preferentially transfers the minority components of choice through polymeric membranes from feed to permeate. This application is very appropriate for

environmental and biotechnology industries, as both need removal or recovery of organics from dilute solutions (Böddeker and Bengtson, 1991). Specially, removal/ separation/ concentration of volatile organic compounds (VOCs) is attracting more and more interest and is being widely investigated (Brüschke, 1988). The removal of VOCs by pervaporation and vapor permeation is well summarized in a recent book edited by Huang (1991).

As stated in the previous section, separation of organics from aqueous solutions requires membranes made of elastomeric polymers. These include PDMS and copolymers (namely copolymers of styrene and styrene derivatives), polyurethane and polyether block amide (PEBA). A detailed survey of the various membranes and test feed mixtures has been conducted by Böddeker and Bengtson (1991). These include mixtures of alcohol, aromatic hydrocarbon, chlorinated hydrocarbon, acids, ethers, ketones etc. Only a part of it covering aromatic and chlorinated hydrocarbons together with some new data are presented in Table 2.1 and Table 2.2.

Volatile hydrophobic solvents, such as chloroform, 1,1,2-trichloroethane, benzene, toluene and naphtha, were effectively separated with an enrichment factor exceeding 200 from industrial waste streams, using Membrane Technology and Research Inc. (MTR) membranes (Kaschemekat et al., 1989). Moderately hydrophobic solvents, such as methyl ethyl ketone and ethyl acetate, were separated with typical enrichment factors of 50 - 100. Hydrophobic solvents such as acetone, isopropanol and ethanol were separated with enrichment factors of 5-20. For thin-film PDMS composite membrane, the order of

enrichment for organics was chloroform > ethyl acetate>1,1,2 -trichloroethane ≈ acetone » isopropanol ≈ ethanol ≈ methanol ≈ n-propanol (Blume and Baker, 1987). It was reported that enrichment changed from 200 fold for chloroform to 2 -10 fold for alcohols.

Table 2.1 Separation/ Concentration of Dilute Aromatics from Water

Membrane material	Organic compound	Feed conc.	Permeate /retentate[3] conc.	Separation factor, α	Flux,	References
		ppm	ppm		g/(m^{2}h)	
PEBA[1]	Phenol	50000	300[3]			Kondo & Sato, 1994
PEBA	Phenol	100	7500	76	1.3	Böddeker et al., 1990
PEBA	2-Methyl phenol	100	15000	152	2.8	Böddeker et al., 1990
PEBA	2,5-Dimethyl phenol	100	21000	215	3.5	Böddeker et al., 1990
EPDM[2]	Toluene	250	850000	60000	≈7.5	Nijhuis et al., 1988

[1] PEBA = Polyether block amides
[2] EPDM = Ethene-propene terpolymer
[3] retentate concentration

The separation of tetrahydrofuran (THF)-water solutions by pervaporation has been examined by Mencarini et al.(1994) using a silicone composite membrane. It was reported that a selectivity of 205 and a THF flux of 1.1 kg/(h·m^2) were achieved at benchmark conditions of 50°C feed temperature, 2 torr downstream pressure and feed concentration of 4.4 wt % THF.

Cultivation of trichoderma viride yields the volatile lactose 6-pentyl-alpha-pyrone(6-PP) as the principal metabolite in concentrations of up to 1 g/L. It was separated from the culture

medium and enriched by pervaporation using hydrophobic membranes (Bengtson and Böddeker, 1992). Virtually complete removal of 6-PP from an inactive cultural medium was achieved by batch pervaporation.

Table 2.2 Separation / Concentration of Chlorinated Hydrocarbons from Water

Membrane material	Chlorinated Hydrocarbon	Feed conc.	Permeate conc.	S.factor α/ Enrinch. factor ß*	Total Flux,	References
		ppm	ppm		g/(m²h)	
Thin-layer PDMS[1]	Chloroform	1000 2000	200000 400000	200*	≈500	Blume & Baker, 1987
PDMS	Chloroform	220	90000	500		Schönberger, 1984
PDMS	Chloroform	1000	590000	1400		Schönberger, 1984
PDMS	Chloroform	5000	910000	2100		Schönberger, 1984
Thin-layer PDMS	1,1,2-tri chloroethane	1000 - 3,000	100000 300000	100*	0.5 L/ (m² h)	Blume & Baker, 1987
PDMS tubing	Chloroform	100 200 400	490000 670000 860000	9700 10100 15300		Nguyen & Nobe, 1987
SBR[2]	Chloroform	80 800 1700	580000 940000 970000	17000 19000 21000		Brun et al., 1985b
NBR[3]	Chloroform	80 800 1700	580000 950000 980000	18000 24500 31000		Brun et al., 1985b
EPDM	Trichloro-ethylene	500	900000	40000	≈17.0	Nijhuis et al., 1988

[1] PDMS = Polydimethylsiloxane
[2] SBR = Styrene-butadiene rubber
[3] NBR = Nitrile-butadiene rubber
* The values indicate enrichment factor,

Methylene chloride can be successfully concentrated from methylene chloride/water mixtures by pervaporation (Peterson et al., 1993). Experiments were performed using a

feed solution consisting of a 1% methylene chloride/99% water, using a poly [bis (phenoxy) phosphozene] based membrane. In these experiments a separation factor of approximately 10,000 was obtained by concentrating the methylene chloride to 99 % in the permeate. The flux was 0.003 - 0.05 L/(h·m^2) at 24 °C and 200 torr permeate pressure.

In treating groundwater, it is reported that although high levels of VOC removal are possible by pervaporation, it is more economic to combine pervaporation with a second technology in a hybrid process (Athayde et al., 1995). A cost comparison of carbon adsorption and a pervaporation/carbon adsorption hybrid system for reducing the trichloroethylene (TCE) content of a 10-gpm groundwater stream from 100 ppm to less than 1 ppb is shown in Table 2.3

Table 2.3 Comparison of System Economics for TCE Removal from Groundwater Carbon Adsorption vs Pervaporation/Carbon Adsorption Hybrid (Athayde et al, 1995)

System	Relative Capital Cost	Relative Annual Operating Cost	3-Yearly Relative Project Cost	5-Yearly Relative Project Cost
Carbon Adsorption	1.00	1.00	1.00	1.00
Pervaporation /Carbon Hybrid	7.10	0.39	1.04	0.80

Lipski and Côté (1990) reported that the treatment cost for trichloroethylene (TCE) by a pervaporation unit was \$0.56/m^3 for a transverse flow model, \$ 1.10/m^3 for a spiral wound model, \$ 1.41/m^3 for an inside flow hollow fibre model (wide bore fibers) and

$3.80/m^3 for another inside flow hollow fibre model (narrow bore fibers). For comparison, the cost of conventional technologies ranges from $0.10/m^3, for air stripping alone (an environmentally undesirable solution), to $0.80/m^3, for treatment trains including stripping with activated carbon off-gas treatment or activated carbon aqueous phase treatment.

2.5.2 Organic-Organic Separation

Separation of organic/organic mixtures represent the least developed and the largest potential commercial application for pervaporation. The earliest interest in pervaporation was focused in this type of application (Binning and James, 1958a, 1958b) for benzene/cyclohexane separation. Since then, various organic mixtures have been tested with membranes made of various materials. A representative list is given in Table 2.4.

There is however no literature except those presented as a part of this on going large research project, using membranes like those developed for this project, i.e. membranes prepared with newly synthesized surface modifying macromolecules.

2.6 Concept of Surface Modification

The success of pervaporation depends on the performance of the membrane. New membranes can be developed by a) the optimization of existing membrane manufacturing methods, b) the development of new materials and c) the modification of the surface of existing membranes. There is a limit as to what process optimization can do; for example, it can not change the mechanical properties of the PDMS membrane. The development of

new materials is often economically unfeasible due to small size of the current pervaporation membrane market. So, modification of the surface of existing membranes seems to offer greater possibilities of improvement in terms of both engineering and economic feasibility. This is supported by the fact that significant changes to the pervaporation membrane selectivity towards organic compounds and permeation rate can be achieved by modification of surface hydrophobicity. Particularly since surface chemistry and morphology play an important role in permeate transport (Kesting, 1971; Matsuura, 1993), and surface hydrophobicity favors organic selectivity (Koops and Smolders, 1991; Fleming and Slater, 1992). Furthermore, using the converse hypothesis that hydrophilicity favors dehydration (Yoshikawa et al. 1984a, 1984b), Huang and Xu (1988), Huang et al. (1988) and Xu and Huang (1988) modified the surface chemistry of membranes to increase hydrophilicity and successfully improved the water selectivity of their membranes.

Surface modified membranes should hypothetically have enhanced organic or water selectivity relative to membranes made without surface modifying additives. For instance, in the case of the polyvinyl alcohol (PVA) membranes modified by cyclodextrin, the selectivity changed from ethanol selective to water selective when crosslinking time was changed from 1 to 8 hours (Yamasaki and Mizoguchi, 1994). In addition, PVA membranes containing cyclodextrin were found capable of concentrating *n* - propanol from *n* - propanol and iso-propanol mixture (Miyata et al., 1994).

Table 2.4 Separation of Organic from Organic/Organic Mixtures

Membrane material	Organic mixture	Feed conc. mol%	Separat. factor, α	Flux, kg /(m² h)	Reference
Polypropylene	Acetone Butanol	50 50		0-0.025	Ohya et al., 1988
PTFE/PVP[1]	Butanol Cyclohexane	10 90	23.5	0.3	Aptel et al., 1976
PTFE/PVP	Chloroform *n* - Hexane	65 35	3.9	2.65	Aptel et al., 1976
Modified poly (Phenylene oxide)	Methanol MTBE[2]				Doghieri et al., 1994
Polyvinylalcohol composite	IPA *n* - Hexane	10 90	>900	<0.01	Schneider, 1987
Polyvinylalcohol composite	IPA Toluene	10 90	>900	<0.02	Schneider, 1987
Polyethylene	IPA Benzene	25-70 30-75		0.1-2	Carter & Jagannadhaswamy, 1964
Cellulose	Ethanol Heptane				Okada and Matsuura, 1991
Grafted Membrane	*n* - Hexane Benzene	20 w% 80 w%	6-50	12-0.8	Schneider, 1987
Modified Celluloseester	Iso-octane *n* - Hexane	50 50	2.33	7.2	Schneider, 1987

[1] PTFE/PVP = Membrane obtained by grafting polyvinylpyrrolidone onto a thin polytetrafluoroethylene film

[2] MTBE = Methyl-tert-butylether

Surface modification techniques have been used to improve the transport properties of membranes in a variety of processes. In pervaporation, so far emphasis has been on controlling the swelling and/or the hydrophobicity of membranes used in dehydration. Some of the methods applied include grafting (Huang and Xu, 1988), cross-linking (Huang at el., 1988; Xu and Huang, 1988; Kang et al., 1990) and plasma polymerization (Inagaki et al., 1988; Masuoka et al., 1988, 1992). All of these methods are potentially useful for modifying polymer surface energetics, but there are some deficiencies associated with each of them (Pham, 1995). An ideal technique would provide flexibility in application and ample controllability to prevent over-modification to the point of damaging the polymer surface. It also has to limit its modification to the surface, so that

the bulk properties of the polymer are kept relatively intact. Plasma techniques and surface fluorination can not be easily controlled, and the mechanism of these processes are not yet fully understood; hence, surfaces produced by these methods usually encounter problems such as irreproducibility and irreversible surface damage (Néel, 1991). Cross-linking is only useful for producing solvent resistant surfaces; its use in modifying the surface energetics is rare. Chemical coating and grafting require specific conditions which somewhat limit their uses. An attractive alternative is the use of surface active additives as a component of the membrane making solution. This method offers advantages such as simplicity of application, and better control with regard to reproducibility.

The development of surface modifying macromolecules (SMMs) do not follow a rigid theoretical approach (Pham, 1995). However, there are four theoretical aspects which would serve as the basis for qualitative assessment of what an SMM should be. These aspects include (i) the thermodynamics of interfacial phenomena; (ii) the thermodynamics of polymer blends or mixtures; (iii) the polyurethane chemistry which governs the synthesis of SMMs; and (iv) the theory of pervaporation. The theory of pervaporation has been reviewed above while the other three aspects have been thoroughly covered by V. A. Pham in his M.A.Sc thesis (Pham, 1995).

Surface modifying macromolecules are active at the interface between two phases (Fang et al., 1995). SMM has the ability to migrate preferentially toward a polymer - air interface during membrane making.

The effect of SMMs and solvent evaporation time on the surface hydrophobicity and performance of PES membranes for separation/extraction of organics from aqueous-organic mixtures by pervaporation was investigated (Fang et al., 1994, 1995). For this study, novel fluorohydrocarbons introduced by DuPont, named Zonyl intermediates and surfactants, were targeted as the starting materials for synthesis of poly-fluoro-etherurethanes. This selection was based on the following information. The Zonyl intermediates can induce critical surface tensions of 3-5 dynes/cm in comparison to 18.5 for PTFE and 21-24 for PDMS (DuPont, 1988). Study results showed that fluorinated polyurethanes could be readily synthesized to have mechanical properties ranging from that of tough plastics to those of elastomers, while having a low surface energy, and fluorine-enriched surfaces in both air and water environments (Yu et al., 1990). The successful incorporation of fluorine based moieties at the polymer membrane surface would also enhance thermal and oxidative stability (Munekata, 1988) and yield surface with high chemical resistivity (Hunston et al., 1978). From the above statements, it was concluded that synthesized poly-fluoro-etherurethanes would have the physical properties of a polyurethane elastomer and hydrophobic properties that not only surpass those of PDMS but also those of PTFE.

As a part of the study conducted by Pham (1995) and Fang et al. (1994, 1995), eight different SMMs were synthesized in triplicate. Each had different proportions of the components and they were prepared by the following method. Methylene bis-phenyl diisocyanate (MDI) was reacted with polypropylene diol (PPO) of average molecular weight 425 to form a prepolymer. The prepolymer was then reacted with the

fluorotelomer, Zonyl BA-L ™ supplied by DuPont (BA-L). The fluorotelomers were received as a mixture of fluorotelomers, whose structure is CF_3-$(CF_2)_m$-$(CH_2)_2$-OH, with a variable number (m) of CF_2 repeat units ranging from 4 to 12. It was distilled at 0.025 mm Hg to yield three major fractions. Descriptions of each fraction are presented in Table 2.5. The fractions used in these synthesizes were with boiling temperature in the range of 50-55°C and 70-90°C. A 2^3 factorial design was used to study the effects of reactant stoichiometry, prepolymer reactant concentration and chain length of polyfluoroalcohol on SMM properties and reproducibility of the SMM synthesis (Pham, 1995). The bulk SMM polymers were characterized with differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and elemental analysis. The compatibility between PES (the base polymer of membranes) and SMM polymers was studied by DSC. SMMs were found to have migrated to the PES surface, rendering it more hydrophobic. This migration effect was confirmed by water droplet contact angle measurements and X-ray photoelectron spectroscopy (XPS). Both the advancing and the receding contact angle increase significantly with an increase in the SMM concentration in the casting solutions up to 0.5 wt. % and level off at higher SMM concentrations (Fang et al., 1995). The significant increase in contact angle suggests that the PES/SMM membrane has a more hydrophobic surface than the PES membrane. The general structure of surface modifying macromolecule is shown in Figure 2.2.

It was reported that chloroform separation from chloroform/water mixture increased with an increase of fluorinated SMM in the casting solution, and exhibited the highest

separation at 1.0 to 1.5 wt. percentage of SMM and then decreased, but the flux kept increasing (Fang et al., 1994, 1995). At the highest point, the chloroform concentration was reported to be 15,000 ppm in the permeate using a 1000 • 10 ppm chloroform/water mixture as feed. Composition of chloroform was analyzed by a Waters differential refractometer R401. Another finding was that the selectivity of PES membranes in the separation of chloroform/water mixture is reversible by changing the evaporation period during membrane making.

Table 2.5 Physicochemical Properties Pertinent to Fluorotelomers (DuPont's Zonyl BA-L™)(Pham, 1995)

BA-L fraction	m[1]	Vapor temperature range[2], °C	Average Molecular wt.	Physical state
Low	4-8	50-55	443	colorless liquid
Medium	8-10	60-65	490	soft, white solid
High	≥10	70-90	589	white solid

[1] approximate number of (CF_2) unit based on DuPont's literature.
[2] at 0.025 mm Hg

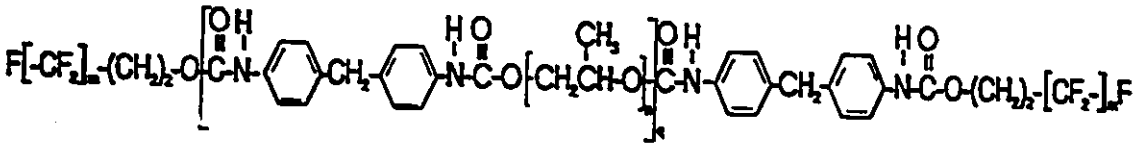


Figure 2.2. The Chemical Structure of Surface Modifying Macromolecule (SMM).

1,1,2- trichloroethane (TCEA) was successfully concentrated by pervaporation using a surface modified butylacrylate grafted membrane (Yamaguchi et al., 1994). A permeation rate of 0.232 kg/m^2 h and a separation factor of 1096 were achieved for a feed stream consisting of 0.135 wt.% TCEA.

Deng et al. (1994) has studied the effect of lamination on the performance of PDMS/ aromatic polyamide (PA) membranes. As two membranes were laminated, both component membranes contributed to the overall selectivity of the bilayer membrane.

It was found that when the surface of a ultrathin silicone - polycarbonate membrane is coated with a thin silicone material, the membrane becomes isopropanol selective (Feng and Huang, 1992). Single pass concentration enrichments of 4.1 to 11.8 fold were obtained for aqueous solutions isopropanol with <6 wt.% isopropanol using the poly(dimethyl siloxane) and the silicone-coated ultrathin silicone-polycarbonate copolymer membranes.

2.7 Summary

Elastomeric membranes having organophilic characteristics and good mechanical properties are required for the removal, recovery, separation or concentration of organics from aqueous-organic or organic-organic mixtures. Normally, a hydrophobic membrane surfaces favor organophilicity, but, most of the presently available hydrophobic elastomers have some shortfalls. The research presented in this thesis is a part of on going project at the University of Ottawa on pervaporation membranes incorporating SMMs to over come

these short falls. It has been found that fluorinated SMMs can be successfully synthesized and blended with PES to cast membranes of higher surface hydrophobicity. These membranes also have better mechanical strength than PDMS membranes. But these membranes still need optimization, characterization, and performance evaluation in respect to environmental contaminants removal as well as its reproducibility.

The specific objectives of this thesis were as follows. First, to investigate the impact of PVP, which is an additive in the membrane casting solution, on the membranes performance. Second, to investigate the impact of several membrane preparation variables, which were previously not controlled, to ascertain if they were responsible for the variations in repeat experiments. These include studies on the impact of a) casting solution mixing period; b) solution age (period between solution filtration and the membrane casting); c) membrane age (period from the end of solvent exchange method to the membrane pervaporation testing). Third, to reevaluate impact of SMM on membrane performance. Fourth, to study the morphology of the membrane surface. And finally to evaluate membranes prepared using a different SMM named SMM58.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Overview

As mentioned, this research was part of a larger on going project for development of a novel type of pervaporation membrane suitable for environmental applications. Within the project and this thesis membrane performance was evaluated in terms of the pervaporation of dilute chloroform aqueous solutions. This work focused on a) optimization of the casting solution composition by varying PVP percentage in it, followed by an evaluation of several membrane preparation variables; and b) reevaluation of the impact of SMM addition on membrane performance. Figure 3.1 presents the key steps involved in membrane preparation. These include: i) casting solution mixing period; ii) solution age (period between solution filtration and the membrane casting); and iii) membrane age (period from the end of solvent exchange method to the membrane pervaporation testing).

The experimental methods used in this study will be described under the following subheadings: a) materials; b) membrane making; c) pervaporation experiments; d) membrane morphology study; and e) analytical methods.

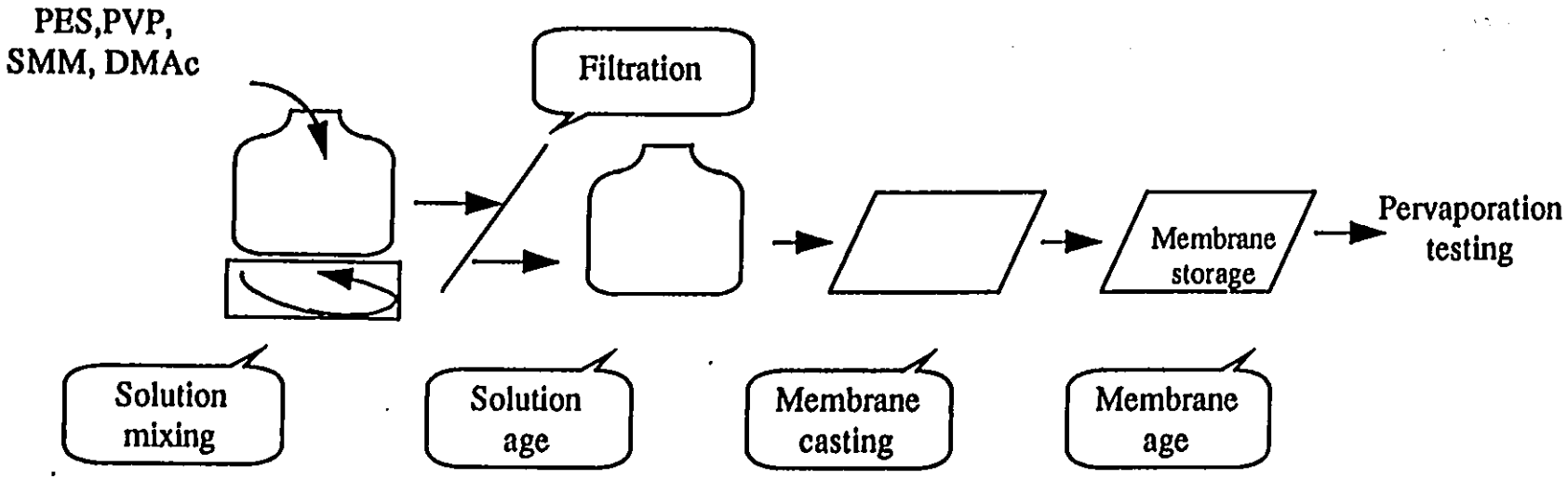


Figure 3.1 Membrane Preparation Steps

3.2 Materials

Materials used for this study were of analytical grade and were used without further modification, unless otherwise stated.

The conventional polymeric membrane material used was polyethersulfone (PES) of Victrex 4800P [ICI Advanced Materials, Billingham, Cleveland, England], the chemical structure of which is shown in Figure 3.2. The properties for which PES is qualified as an outstanding membrane material are t_g of 230 °C, thermal and oxidative stability, excellent strength and flexibility, and resistance to extremes of pH (Kesting, 1985). The pore former used was polyvinylpyrrolidone (PVP) powder of molecular weight 10,000 [Aldrich Chemical Company, Inc., Milwaukee, WI], and the solvent used was dimethylacetamide (DMAc) [BDH Inc., Toronto, ON]. Two of the eight surface modifying macromolecules (SMMs) synthesized by Pham (1995) as a part of this project, were used in this study. One was surface modifying macromolecule named MPB322LR, prepared from MDI : PPO: BA-L (low fraction) in the proportion 3 : 2 : 2, respectively, hereafter referred as SMM. The other was surface modifying macromolecule named MPB212HN, prepared from MDI : PPO: BA-L (high fraction) in the proportion of 2 : 1: 2, respectively, hereafter referred as SMM58. SMM was used in all membrane casting solutions with the exception of those associated with the evaluation of the impact of SMM58 on membrane performance.

Potassium hydrogen phthalate, A.C. S. of 99.98 % purity, [Fisher Chemicals, Fair Lawn, NJ] was used for total organic carbon (TOC) standard preparation. Deionized water [Milli-Q water plant at Pollution Control Laboratory, D108, CBY, University of Ottawa] was used where

needed. The bottles were wrapped with parafilm "M" laboratory film [American National Can $_{Co}$, Neenah, WI] to avoid leaks. Ethyl alcohol of 99 % [BDH Inc, Toronto, ON] was used for the solvent exchange method. Chloroform with purity of 99.9% [BDH Inc., Toronto, ON] was used for gas chromatoghaph (purge and trap) {GC (P & T)} standard preparation and were needed. Ortho phosphoric acid [BDH Inc., Toronto, ON] was used for TC analysis.

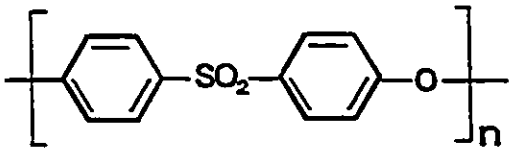


Figure 3.2 The Chemical Structure of Polyethersulfone (PES).

3.3 Membrane Making

The membrane making involves: a) solution preparation; b) membrane preparation and c) drying by the solvent exchange method

3.3.1 Solution Preparation.

SMM, polyethersulfone (PES), polyvinylpyrrolidone (PVP) and dimethylacetamide (DMAc) were used for preparation of the membrane casting solutions. PVP was used as a non-solvent additive. PVP, which is water soluble, acted as a pore former. It also increases the viscosity of the casting solution as well as acted as compatibilizer to improve miscibility between PES and

SMM to reduce the phase separation in the solution, which was a problem when using SMM concentrations beyond 2.0 wt.%. DMAc was used as the solvent.

Preparation of casting solutions involves several general steps. For some of the experiments however certain steps were modified, these modifications are described after the general procedure. The steps of the general procedure are:

a) Drying of PES and PVP in a convective oven for at least four hours before use, the oven temperatures were at 150°C and 60°C respectively.

b) Weighing predetermined quantities (based on the desired composition of the casting solution) of the chemicals and transferring them to a 250 mL glass bottle (colorless or amber). The bottles were previously cleaned with soap and hot water, rinsed with deionized water and DMAc solvent and dried in a convective oven for at least 48 hours. Since PES is highly hygroscopic, Teflon tape was used to provide an effective leak proof seal in between the cap and the bottle mouth. In addition to that, the capped bottles were then wrapped in parafilm to avoid moisture entering into the bottle.

c) Mixing of the solution, prepared with DMAc, PES, PVP and SMM, until it becomes homogeneous. In this study, solutions were mixed at 160 rotation per minute (rpm) in a G24 Environmental Incubator Shaker [New Brunswick Scientific Co. Inc., Edison, NJ] operating at 55°C. The mixing time varied with the specific experiment.

d) Filtration of the solutions in a pressure filter driven by nitrogen gas at a pressure of 35 to 40 psi. Filter cloth was used as a filter media. The filtered solution was then stored in another sealed bottle of the same type.

e) Degassing of the filtered solutions by putting the sealed solution bottles in a convective oven at 55°C for a predetermined period of time, normally 24 hours.

f) Cooling of the degassed solutions in a freezer at 0°C for at least 48 hours to increase the solution's density which aids the casting process.

Each batch of casting solution was large enough to cast several sets of membranes. Steps e) and f) were repeated each time the solution was used for membrane casting.

The compositions and specific preparation conditions for the different casting solutions used were as follows:

A) Optimization of PVP Concentration:

For PVP optimization, the PVP concentration of the casting solution was varied from 0 to 8.0 wt % while PES and SMM concentrations were maintained at 25.0 wt % and 1.0 wt %, respectively, the balance was dimethylacetamide (DMAc) solvent. Three series of solutions namely 'B', 'D' and 'BB' were prepared. The solutions under 'B' series covered PVP percentage of 0.5 and 1.0 to 8.0 wt. % (at increments of 1.0 wt. %). 'D' series solutions contained PVP additions of 0 to 3.5 wt. % at increments of 0.5 wt. % and 'BB' series covered 1.25 to 2.25 wt. % of PVP at increments of 0.25 wt. %. The solutions were mixed for 3 to 6 days, degassed for 24 to 48 hours and then cooled for 48 to 144 hours. The solutions were removed from the freezer just before membrane casting.

B) Determination of the impact of solution mixing period, solution age and membrane age.

Solution mixing period is the homogenization period between adding the compounds together and the filtration of the solution. Solution age is the period for which filtered solution is stored before casting, and membrane age defined as the period between the end of drying by the

solvent exchange method and its use for pervaporation testing. Three solutions named H(M73), F(M140) & G(M306) were prepared with mixing times of 73, 140 and 306 hours, respectively. The PVP, PES, SMM and DMAc concentrations in these solutions were 1.5 wt. %, 25.0 wt. %, 1.0 wt. % and 72.5 wt. %, respectively. These solutions were degassed for 96 hours, and then cooled for 48 hours at 0°C prior to their first use for membrane casting. For subsequent castings, the solutions were degassed for 24 hours and then cooled for 48 hours at 0°C. The solutions were removed from the freezer immediately before casting.

C) Reevaluation of the impact of SMM.

Two casting solutions, called "Q" and "R", were prepared. The main difference between them was that, "Q" contained SMM while "R" did not. In solution "Q", PVP, PES, SMM and DMAc concentrations were maintained at 1.5 wt. %, 25.0 wt %, 1.0 wt % and 72.5 wt. % respectively, while in solution "R", the concentrations of PVP, PES and DMAc were 1.5 wt. %, 25.0 wt % and 73.5 wt %, respectively. These solutions were mixed for 13 days, then they were degassed for 48 hours and cooled for 268 hours before the first membranes were prepared. Before preparation of the second batch of membranes from solution Q, the solution was degassed for 48 hours and then cooled for 48 hours. The solutions were removed from the freezer just prior to casting.

D) Evaluation of the impact of SMM58 on the membrane performance

A solution called "M" was prepared with PVP, PES, SMM58 and DMAc concentrations of 1.5 wt. %, 25.0 wt. %, 1.0 wt. % and 72.5 wt. %, respectively. The solution was mixed for 6 days, degassed for 48 hours and then cooled for 96 hours. The solution was removed from the freezer just prior to casting.

3.3.2 Membrane Preparation

Membranes were cast on a glass plate to a nominal thickness of 0.025 cm. Immediately after casting, the films were transferred to a convection oven preheated to 95°C where they were kept for seven minutes; this was referred to as the evaporation period. This evaporation period of seven minutes was chosen based on earlier work with PES membranes (Fang et al., 1994). The films were then gelled by immersing the membrane and glass plate into ice-cold water. The membranes were kept in the gelation medium overnight, they were then dried by the solvent exchange method described below.

3.3.3 Solvent-Exchange Method

Membranes used in this thesis were dried by a solvent exchange technique. In this technique, the water in the membranes after the gelation process was replaced by ethyl alcohol through successive immersions in ethyl alcohol /water solutions. Each immersion lasted 24 hours. The ethyl alcohol content in the solution was progressively increased viz. 25, 50, 75, 100 vol. %. Then, the membranes were removed from ethyl alcohol and were subsequently air dried at room temperature for 24 hours in a fume hood to yield the final dry membranes. Each dried membrane was kept in a separate polyethylene zip loc bag.

3.4 Pervaporation Experiments

The pervaporation experimental setup used initially for the PVP optimization tests was not equipped with a by-pass trap. All other experiments were carried out with the newly installed pervaporation setup described below, which includes a by-pass trap (Figure 3.3).

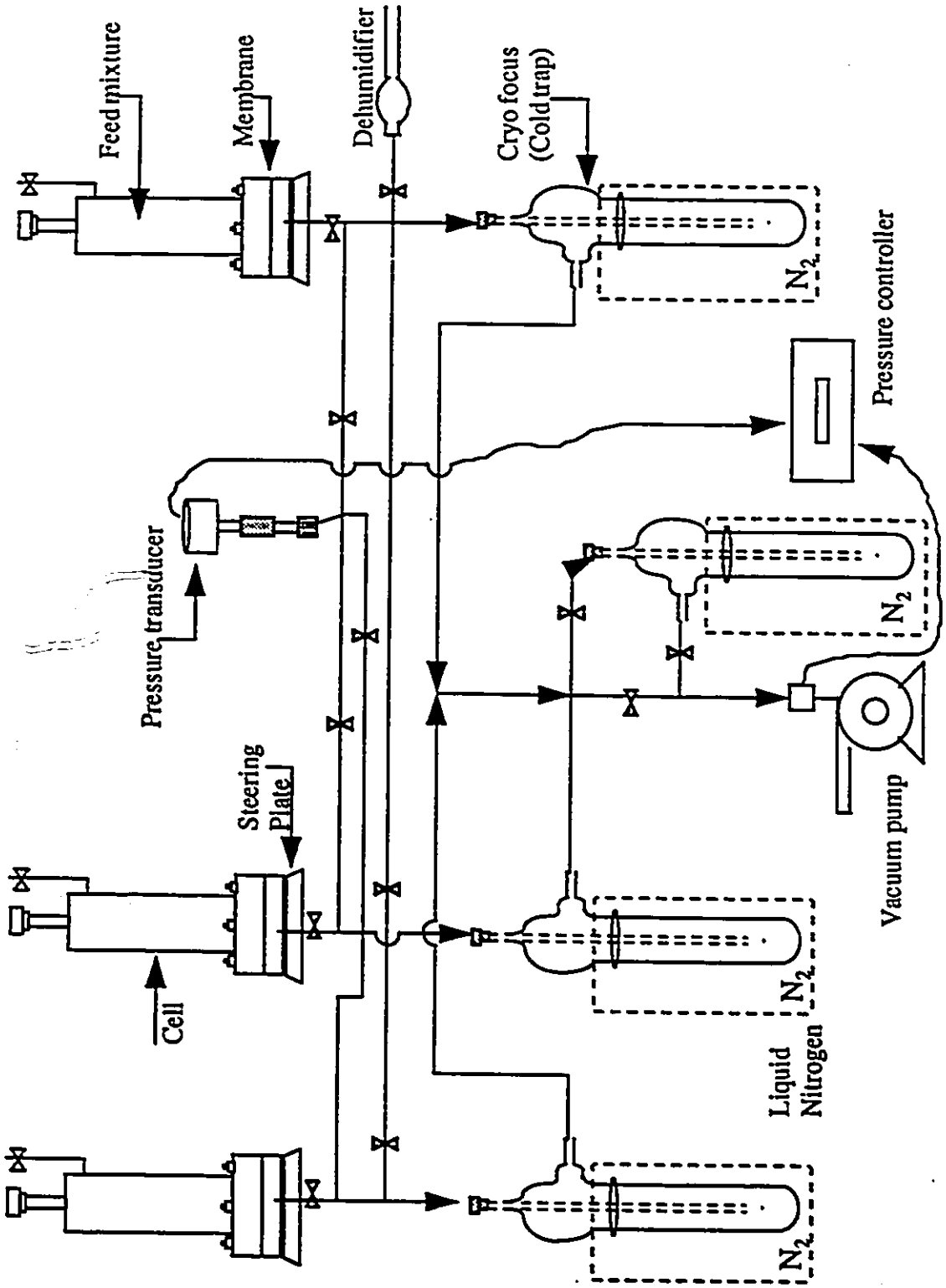


Figure 3.3 Pervaporation Experimental Setup

A new pervaporation experimental setup was designed, installed and commissioned. The system includes three feed reservoirs/cells (Figure 3.4) connected to their individual cold traps for collection of the permeate and to a vacuum pump [Welch Vacuum Technology, Inc., Skokie, IL] on the down-stream side, which drives the process. The traps are connected to the vacuum pump via a by-pass trap. The pressure is controlled by a pressure controller [MKS Type 651, MKS Instrument, Inc., Andover, MA]. Prior to the commissioning, the new setup was tested for moisture content, leak rate and system losses.

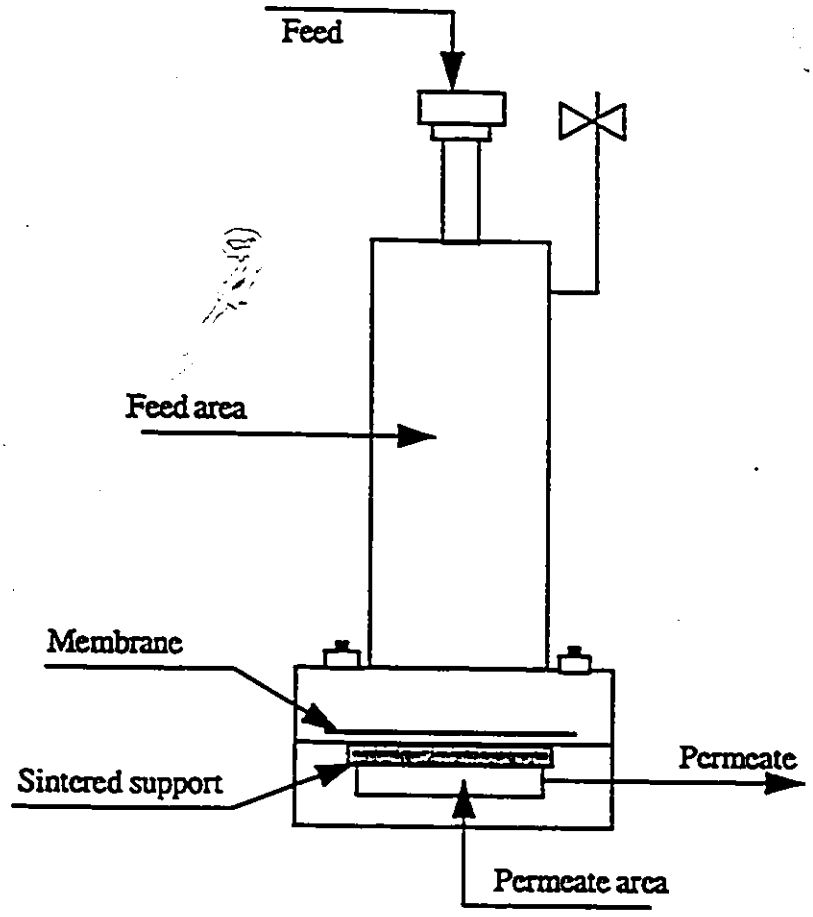


Figure 3.4 Static Cell Used In Pervaporation Experiment.

The cells used for the pervaporation experiments were of 300 ± 10 mL capacity static cells. The cells are stainless steel chambers consisting of two detachable parts. The two parts of the cell are clamped and sealed tight using rubber O-rings. The membrane is placed in between these two detachable parts on a stainless steel sintered support embedded in the lower part of the cell through which the membrane permeated vapor/gas is withdrawn under a vacuum. The upper part of the cell contains the feed solution at atmospheric pressure. The feed solution was kept homogenous and concentration polarization was avoided by continuous stirring during the experiment. Mixing was accomplished by a magnetic stirrer fitted in the cell about 0.6 cm above the membrane surface. The effective area of the membrane in the cell was 9.6 cm^2. The system including the membranes was tested for leaks by applying a vacuum prior to each run. Feed liquid was charged into the cell and the vacuum was applied on the downstream side of the membrane. The permeate, which was in vapor form, was then condensed and collected in a cold trap cooled by liquid nitrogen. The permeate collected during the first 90 minutes was discarded using the by-pass trap. Each test run lasted for 10 to 13 hours. At the end of each test run, the cold traps along with the permeate were removed from liquid nitrogen. Both ends of the traps were sealed with parafilm and immediately immersed into ice cold water, where it was kept for 8-10 minutes to defrost the permeate. The permeate, which was still primarily (frozen) solid, was then pushed with a clean metal wire into a pre-weighed sample collecting vial. The permeation rate was determined by measuring the mass of sample collected during the testing period. Immediately after weighing, the vial was again immersed into ice cold water to completely melt the permeate. The liquid permeate was then analyzed. Precautions were taken during permeate handling to minimize air contact. The composition of the sample was determined by gas chromatography (G.C), mass spectrometry (M.S) and total organic carbon

analysis (TOC). Earlier reported works (Fang, 1995) showed that the chloroform concentration in the permeate could be accurately measured by either total carbon (TC) or GC analysis and both could be accurately correlated. Accordingly, most of the analysis in this thesis is based on this approach. All pervaporation experiments were carried out at room temperature (23-25°C). The pressure downstream of the membrane was less than 1 mmHg, unless otherwise stated.

Pervaporation experiments were carried out for: a) Optimization of the PVP percentage in the casting solution; b) Determination of the impact of solution mixing period, solution age and membrane age on pervaporation performance; c) Reevaluation of the impact of SMM on the membranes for removal of environmental contaminants; and d) Evaluation of membrane prepared using SMM58. Chloroform was used as a representative environmental contaminant in this study.

3.4.1 Optimization of PVP Percentage in the Casting Solution

Pervaporation experiments were carried out with membranes prepared from the solutions (B, D & BB Series) having PVP concentrations varying from 0 to 8 wt %. The performance of these membranes were evaluated using aqueous feed solutions with concentration of 10 ppm and 100 ppm $CHCl_3$. The permeation rate was determined by weighing the permeate and dividing it by the time period of it's collection. The composition of the permeate was analyzed in terms of total carbon using a total carbon analyzer.

3.4.2 Effect of Solution Mixing Period, Solution Age and Membrane Age on Pervaporation Performance

From the solution H(M73) with a 73 hour mixing time, membranes H1(M73), H2(M73) and H3(M73) were prepared with solution ages (the period for which filtered solution is stored before casting) of 144, 216 and 312 hours, respectively. From the solution F(M140) with a mixing time of 140 hours, membranes F1(M140), F2(M140) and F3(M140) were prepared with solution ages of 144, 216 and 312 hours, respectively. And membranes G1(M306), G2(M306) and G3(M306) were prepared using a casting solution with a mixing time of 306 hours and solution ages of 144, 216 and 312 hours, respectively. Pervaporation experiments were carried out at different membrane ages.

Three other membranes namely HH(M73), FF(M140) and GG(M306) were prepared from the above H(M73), F(M140) and G(M306) solutions, respectively. They were cast at the same time but were tested immediately after drying by the solvent exchange method. These membranes were different from the earlier nine membranes as they were prepared at the same time from solutions having different length of mixing time (i.e 73, 140 and 306 hours, respectively) and different solution ages (i.e 1008, 1344 and 1008 hours, respectively).

Feeds used in these experiments were 10 ± 1 ppm, 11 ± 1 & 100 ± 1 ppm $CHCl_3$/water mixtures. The permeation rates were measured by weighing and permeates were analyzed for total carbon.

3.4.3 Reevaluation of the Impact of SMM on Membrane for Removal of Chloroform.

Q1, Q1x and Q2 membranes were prepared with solutions "Q", which contains SMM while membrane R1 was prepared with solution "R", which does not contain SMM. Pervaporation experiments were carried out with these membranes with a 10 ppm $CHCl_3$ feed solution. Clean water tests were also done with a coupon of Q2 membrane using deionized water as feed. This clean water test was done as a control to determine the cleanliness of the membrane. Q2x membrane was prepared from solution "Q" and was dried in air for 8 days and then vacuum dried for 4 days, in addition to the normal 24 hours air drying included in solvent exchange method. Membrane Q2x was also tested with 10 ppm $CHCl_3$ feed solution. In contrast to other sets of experiments, the fresh feeds and used feeds were analyzed by TOC and gas chromatoghaph (Purge & Trap) to determine concentration of purgeble organic carbon (POC) and chloroform, respectively. The permeation rates were determined by weighing. The permeates were analyzed by TOC analyzer for TC, G.C. (Purge & Trap) and G.C.- M.S. to determine their composition.

3.4.4 Evaluation of Membrane Prepared Using SMM58.

Pervaporation experiments were carried out with membranes prepared from solution "M" having the PVP, PES, SMM58 and DMAc concentrations of 1.5 wt. %, 25.0 wt. %, 1.0 wt. % and 72.5 wt. %, respectively. The performance of the membrane was evaluated using aqueous feed solutions with 10 ppm and 100 ppm $CHCl_3$ concentration. The permeation rate was determined by weighing the permeate and dividing it by the time period of it's collection. The composition of the permeate was analyzed in terms of total carbon using a total carbon analyzer.

3.5 Study of Membrane for Residual Solvent and Morphology

Two membranes were tested to detect any residual solvent. For this purpose, Fourier Transform Infrared spectra were recorded on a piece of Q2x after the normal 24 hours of air drying included in solvent exchange method and on a piece of F1(M140) which was additionally vacuum dried for 48 hours.

The change in surface morphology of the membrane with aging was studied using an Atomic Force Microscope (AFM). Photographs were taken to record the change in surface morphology of membrane Q1 with aging.

3.6 Analytical Methods

The following analytical methods were used during this work:

3.6.1 Total Carbon Analyzer

The purgeable organic carbon (POC) of the feed & the used feed and the total carbon (TC) of the permeate were determined by a total carbon analyzer [DC-190, Dohrmann Division, Rosemount Analytical, Santa Clara, CA,]. The oven temperature of the total carbon analyzer was 680°C. The carrier gas was ultrapure grade compressed oxygen (> 99.99 %) [Air Products, Ottawa, ON] at a flow rate of 200 ± 10 cc/min. Twenty percent ortho phosphoric acid was used in the inorganic carbon (IC) chamber of the TOC. The sample size was 20 µL for TC and 10 mL for POC analysis. Gastight syringes [Hamilton Co., Reno, NV] were used for sample injection. For TC analysis, manual injection mode was used due to the small quantity of sample generated by the experiments. Total organic carbon could not be analyzed

due to the requirement of simultaneous injections into TC and IC ports for which the amount of the sample was insufficient. The principle of operation and standard preparation is as per the manufacturer's manual and the standard methods (APHA, 1992).

The system also provides manual capability to measure POC by purging the sample with 200 ± 10 cc/minute of oxygen or air at room temperature. For this study, the samples were purged for 6 minutes. The gas containing the POC is passed through a lithium hydroxide scrubber to remove CO_2, and then passed directly to the combustion tube for oxidation.

Special care was taken to clean the glass ware used in handling and analysis of the samples. Standard solution was prepared in a volumetric flask and kept in amber boro silicate bottles with Teflon-lined closures. These bottles were cleaned via the following steps: a) cleaned with soap and hot water; b) rinsed five times with distilled water; c) kept over night with chromic/ sulfuric acid cleaning solution; d) rinsed five time with deionized water; e) kept over night with deionized water to leach any cleaning agent and f) dried over night at 80 °C in a convection oven.

POC standard was prepared from chloroform as 9.72 ppm POC. Standard preparation involved the following steps: a) A 1000 mL volumetric flask (cleaned by the above procedure) was filled up to the graduation mark with deionized water; b) a cleaned stirring bar was added; c) the water was degassed for 5 minutes; d) 67 µL of chloroform was injected deep into the water by immersing the syringe needle; e) flask was capped and f) gently agitated for about 5 to 10 minutes until chloroform was dissolved. The standard was used immediately after preparation.

3.6.2 Gas Cromatograph (Purge & Trap)

The composition of the permeate was also analyzed with a gas chromatograph (purge and trap). This equipment includes a Tekmar Liquid Sample Concentrator LSC -2 [Tekmar Company, Cincinnati, OH], which is a purge and trap (P&T) unit for the concentration of compounds, and a Varian - Vista Series 6000 Gas Chromatograph [Varian Instrument Group, Walnut Creek Division, Walnut Creek, CA]. The GC system had a Flame Ionization Detector (FID), operated with a packed column (Carbopack B 60/80 Mesh, 1% SP-1000, 8 feet by 1/8 inch SS) [Supelco Canada Ltd., Oakville, ON], and a Waters 820 Chromatography Data Station as an integrator [Waters, Water Chromatography Division, Millipore Corporation, Milford, MA]. Purge and trap unit is used as the aqueous samples could not be injected directly into the gas chromatograph, since water could affect the chromatographic column.

The samples were diluted with 5 mL deionized water to inject into the purger. The dilution factor was 100. A detailed description of this setup and its operation were presented by Lamarche (1986).

3.6.3 Gas Chromatograph And Mass Spectrometry

The compositions of the permeates were analyzed at the Ottawa-Carleton Universities Mass Spectrometry Center, University of Ottawa, by a Gas Chromatograph [Model HP 5890, Series II, Hewlett Packard, Palo Alto, CA] and a Kratos Mass Spectrometer, Model Concept, Series II H. The gas chromatograph was fitted with 30 m long capillary column [DBS, J & W Scientific, Folsom, CA]. The GC thermal program consists of 2 minutes holding time at 40°C followed by heating 10°C/min. The mass spectrometer's accelerating voltage was 8 Kv and the

ionization was at 70 ev. The volume of the sample injected was 1 μL, and the GC's split/splitless system reduced the amount going to the detector by 20 fold.

3.6.4 Infrared Spectrometer

The Fourier Transform Infrared (FTIR) spectra were recorded during this study to detect presence of any residual solvent in the membrane after the normal 24 hours of air drying included in the solvent exchange method. A membrane dried for a further 48 hours in a vacuum was also examined. The spectra were obtained using a Bomem MB100 spectrometer [Bomem, Vanier, PQ] at the Chemistry Department, University of Ottawa. The instrument was equipped with a KBr beam-splitter, limiting its useful range to the mid infrared region, about 5000 to 450 cm^{-1}. The MB100 was equipped with a deuterium triglycine sulfate (DTGS) detector. Obtaining a routine spectrum involved signal averaging 25 scans at 4 cm^{-1} resolution, leading to an acquisition time of about 70 seconds. The spectra was processed using Spectra Calc software [Galactic Industries Corp., Salem, NH] on an IBM compatible personal computer. The infrared spectra are presented as absorbance against wave length number [$\log_{10} (I_0 / I)$ vs cm^{-1}].

3.6.5 Atomic Force Microscope

The effect of membrane aging on the surface morphology of the membrane was studied with a Nanoscope III tapping mode atomic force microscope (TM AFM), equipped with 1553D scanner [Digital Instruments, Santa Barbara, CA] and located at the Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa.

CHAPTER 4

RESULTS AND DISCUSSION

The results have been presented in the sequence in which the experiments were carried out and are discussed in the light of the objectives and the findings of that experimental run. Each subsequent experiment was based on the questions raised by the results of the preceding experimental run. The results obtained from each subsequent experiment were superimposed on the findings from previous experiments to develop a composite understanding of the phenomena observed. At the end of this chapter, all the findings are re-discussed in the light of those results which have the highest overall impact.

4.1 PVP Optimization Experiments

Pervaporation experiments carried out as per Section 3.4.1 with the membranes from 'B', 'D' and 'BB' series for PVP optimization using 10 ppm $CHCl_3$/water mixture feed, The results obtained are given in Table 4.1. The effect of PVP percentage in the casting solution on the TC concentration in the permeate is shown in Figure 4.1.

Initial runs were conducted on membranes designated as series 'B'. They covered PVP additions of 0.5 and 1.0 to 8.0 wt.% (at increments of 1.0 wt.%). These results showed a peak TC concentration in the permeate at 2.0 wt.% PVP. To further confirm and investigate this peak, 'D' series membranes were tested. These had been cast from solutions containing 0 to 3.5 wt.% of PVP at increments of 0.5 wt.%. Very high levels of TC concentration in the permeate were recorded for membranes of this series with 1.5 and 2.5 wt.% of PVP. But the membrane with 2.0 wt.% PVP showed a completely divergent trend with a low TC concentration in the permeate. To further investigate this anomaly, membranes of the 'BB' series were prepared and tested, these had been cast from solutions with 1.25 to 2.25 wt.% PVP at increments of 0.25 wt.%. A continuously decreasing trend of TC concentration in the permeate was observed for this series.

Table 4.1 Results from PVP Optimization Test Using 10 ppm $CHCl_3$/water Mixture Feed

PVP %	TC Conc. in permeate, ppm TC			Flux, g/(h. m^2)		
	B Series	D Series	BB Series	B Series	D Series	BB Series
0.00		348			18.52	
0.50	149	575		18.97	19.67	
1.00	88	818		13.03	13.15	
1.25			1581			17.46
1.50		3407	1405		18.26	30.76
1.75			678			10.17
2.00	1056	516		23.11	9.21	
2.25			646			15.32
2.50		2829			35.78	
3.00	684	942		23.23	28.24	
3.50		347			24.22	
4.00	490			39.09		
5.00	547			41.44		
6.00	282			55.58		
8.00	115			73.44		

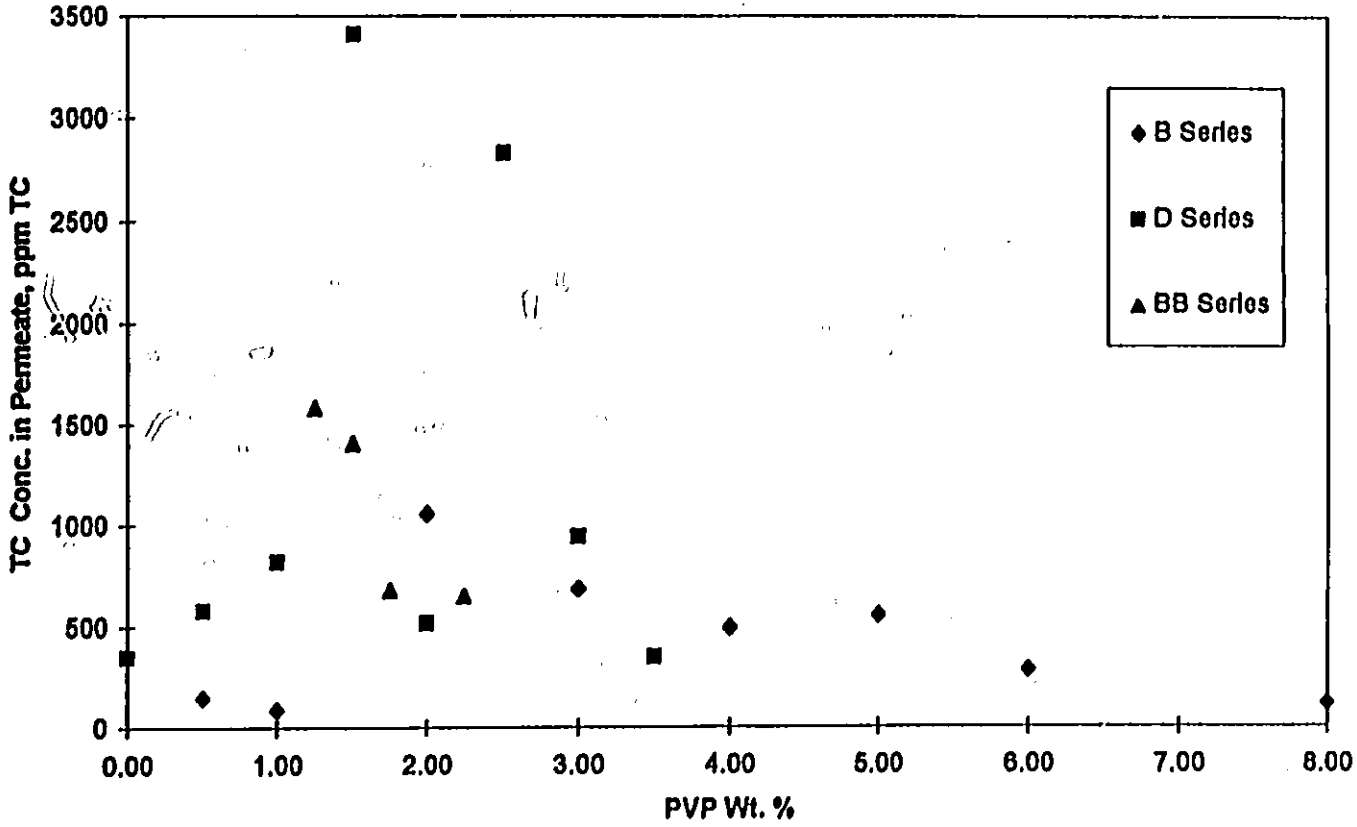


Figure 4.1 TC Conc. in Permeate from PVP Optimization Test Using 10 ppm CHCl3/ Water Mixture Feed

From these results it was evident that the PVP percentage alone was not responsible for the levels of TC concentration recorded in the permeate. It therefore became necessary to conduct further investigations to find out what other factor(s) were responsible for these discrepancies.

On the other hand, from Figure 4.2, it is seen that membrane permeation rate (flux) increases continuously with an increase in PVP concentration in the membrane casting solution for 'B' series. This may have been due to the fact that, PVP is readily water soluble and acts as a pore former in the membrane matrix. The increase of PVP concentration thus increases the number/size of pores in the membrane which ultimately increases the flux. There is however considerable scatter in the data for flux and while a general trend can be discerned for 'B' series, there is not any well defined correlation with PVP percentage and the flux for membranes of the other series ('D' and 'BB').

The results obtained from the experiments with the above membranes from 'B', 'D' and 'BB' series for PVP optimization using 100 ppm $CHCl_3$/water mixture feed, are given in Table 4.2. The effect of PVP percentage in the casting solution on the TC concentration in the permeate and on the flux are plotted in Appendix A-1 and Appendix A-2, respectively. It was observed from these plots that, the membranes of 'B' series also showed a peak TC concentration at 2.0 wt.% of PVP, while membranes of 'D' and 'BB' series showed the same pattern of TC concentration in the permeate as with 10 ppm $CHCl_3$/water mixture feed. The flux patterns were also similar to those observed with 10 ppm $CHCl_3$/water mixture feed. It was hence not possible to reach any definite conclusions regarding correlation of selectivity or flux with PVP percentage in the casting solution and further investigations were planned.

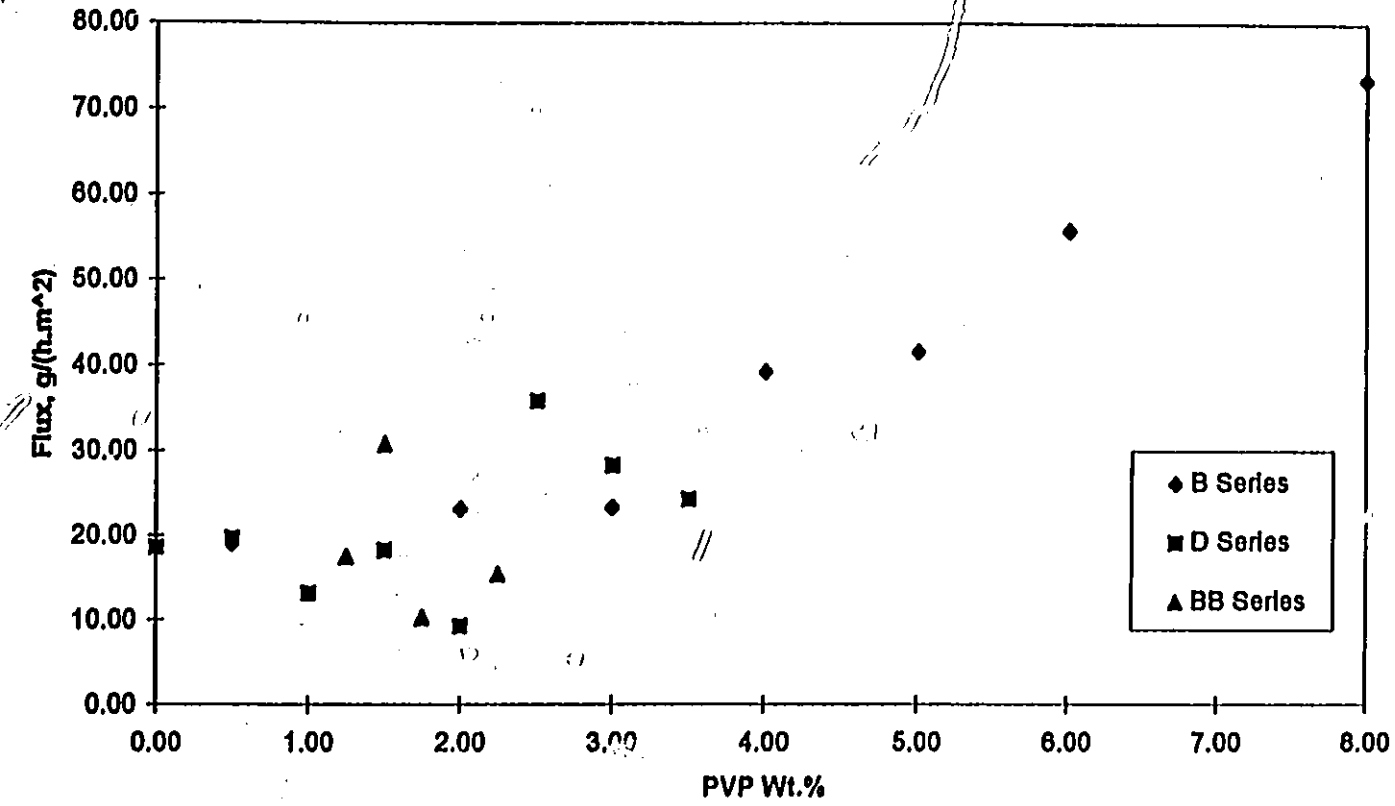


Figure 4.2 Effect of PVP on Flux Using 10 ppm CHCl3/Water Feed

Table 4.2 PVP Optimization Test Results Using 100 ppm $CHCl_3$/water Mixture Feed

PVP %	TC Conc. in permeate, ppm TC			Flux, g/(h.m^2)		
	B Series	D Series	BB Series	B Series	D Series	BB Series
0.00		325			14.29	
0.50	153	1414		18.61	14.21	
1.00	118	1321		13.67	14.99	
1.25			1016			13.00
1.50		2485	849		26.11	18.45
1.75			1272			13.60
2.00	989	315		24.30	9.27	
2.25			1086			18.97
2.50		1413			35.89	
3.00	673	514		26.18	26.61	
3.50		249			23.43	
4.00	465			34.59		
5.00	520			46.59		
6.00	166			59.82		
8.00	47			84.93		

4.2 Effect of the Solution Mixing Period, Solution Age and Membrane Age on Pervaporation Performance

To investigate the data scatter and the extreme high values observed in some of the previous experiments a number of tests were conducted varying several parameters which could have potentially caused the scatter. These parameters were solution mixing period, solution age (period lapse between solution filtration and membrane casting) and subsequently also membrane age (period lapsed between the completion of drying by the solvent exchange method and the initiation of pervaporation testing). The H, F and G Series membranes were prepared with casting solutions H(M73), F(M140) and G(M306) that were mixed for 73, 140 and 306 hours respectively. The numbers 1, 2 and 3 indicate that the solution ages were 144, 216 and 312 hours, respectively and thus these membranes are identified as H1(M73),

H2(M73), H3(M73), F1(M140), F2(M140), F3(M140), G1(M306), G2(M306) and G3(M306), respectively. The results from the 10 ppm $CHCl_3$/water feed experiments are presented in Table 4.3. The data in this table are the results obtained from the first day use of these membranes after dry storage in polyethylene zip bags.

Table 4.3 Results from Effect of Solution Mixing Period & Solution Age Tests with 10 ppm $CHCl_3$/water Mixture Feed [First Day Data Only]

Solution	TC conc. in permeate, ppm TC			
age, hrs	Mixing, hr	73	140	306
	Membrane series	H(M73)	F(M140)	G(M306)
144		416	500	652
216		677	356	693
312		452	509	1197
	Flux, g/(h.m^2)			
	Membrane series	H(M73)	F(M140)	G(M306)
144		6.38	9.31	8.84
216		7.66	11.16	8.16
312		10.14	4.90	6.51

H(M73) : Membrane series prepared from the solution mixed for 73 hours.
F(M140) : Membrane series prepared from the solution mixed for 140 hours.
G(M306): Membrane series prepared from the solution mixed for 306 hours.

The membrane age was not envisaged as a factor influencing either the selectivity or permeability at this stage and hence there was no control over this factor in these experiments.

The effects of solution mixing period on TC concentration in the permeate are shown in Figure 4.3 and on the flux in Figure 4.4. From these figures, it was found that there was no clear correlation of the solution mixing period with the TC concentration in the permeate and the flux.

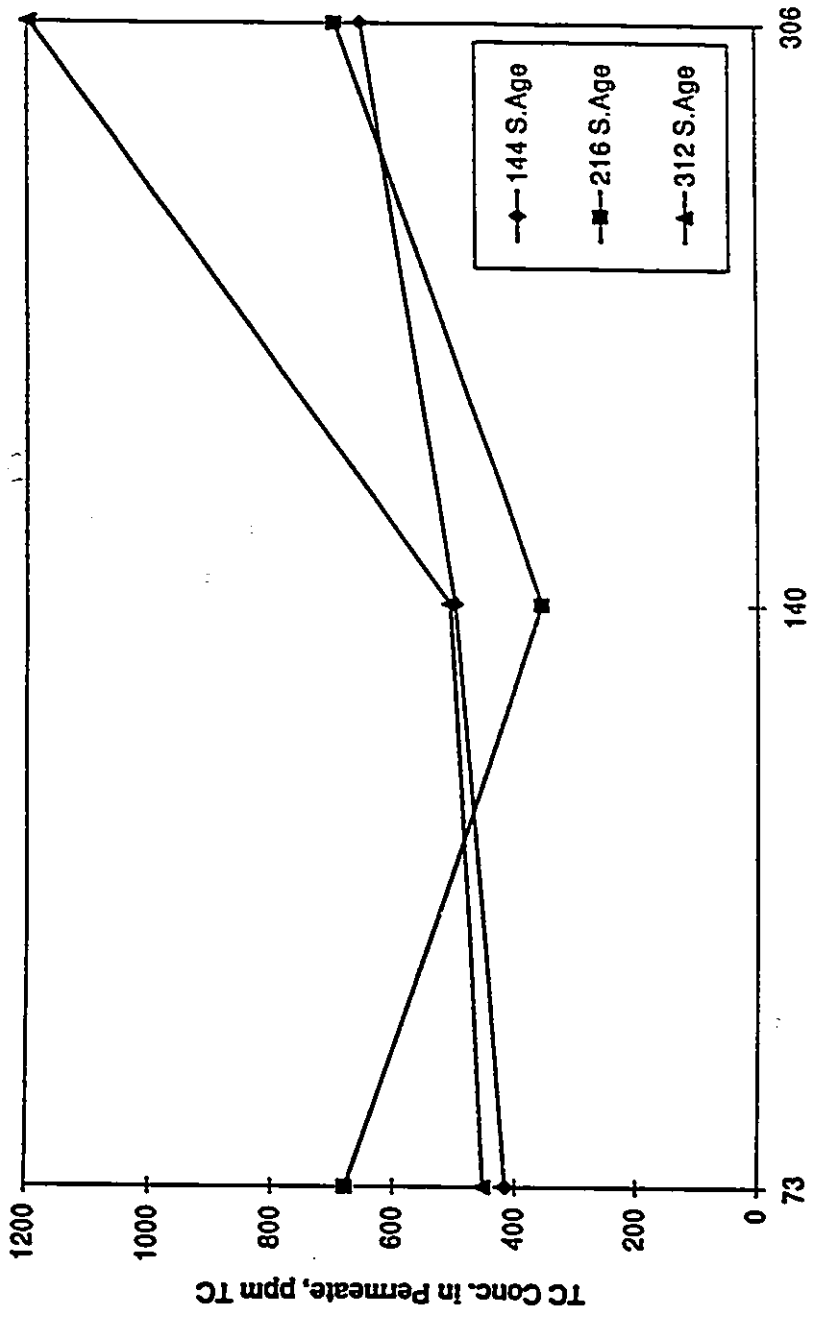


Figure 4.3 Effect of Solution Mixing Period on TC Conc. in Permeate Using 10 ppm CHCl3/Water Mixture Feed

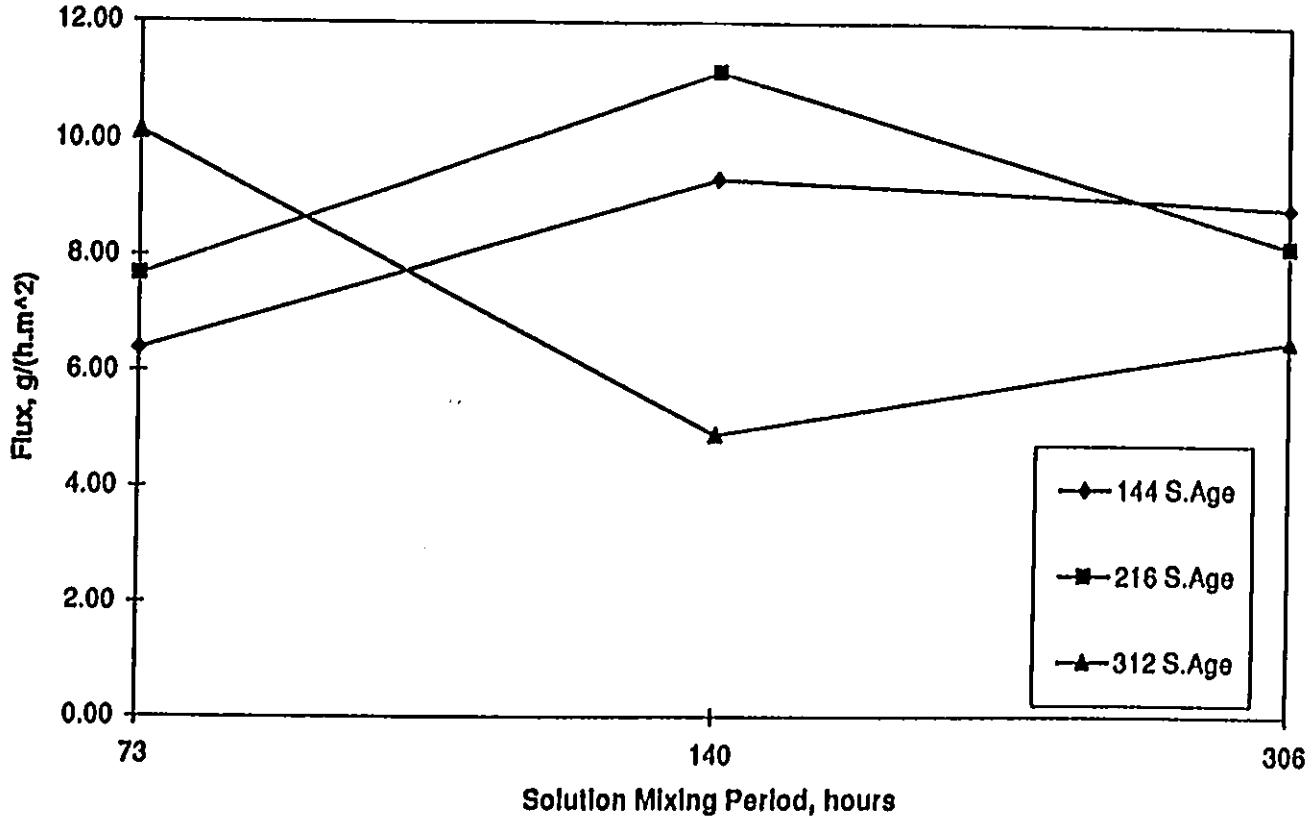


Figure 4.4 Effect of Solution Mixing Period on Flux Using 10 ppm CHCl3/Water Mixture Feed.

The effects of solution storage age on TC concentration in the permeate are shown in Figure 4.5 and on the flux in Figure 4.6. These figures show no discernable correlation of the solution age on the performance of these membranes.

The tests were repeated with 10 ppm $CHCl_3$ /water mixture feed for two or three days. After completion of these tests, experiments were carried out with 100 ppm $CHCl_3$ /water mixture feed, without removing the membranes from the cells. The results are given in Table 4.4.

Table 4.4 Results from Effect of Solution Mixing Period & Solution Age Tests with 100 ppm $CHCl_3$/water Mixture Feed

Solution age, hours	TC conc. in permeate, ppm TC		
	H(M73)	F(M140)	G(M306)
144	194	261	180
216	303	198	273
312	201	299	585
	Flux, g/(h.m^2)		
	H(M73)	F(M140)	G(M306)
144	7.95	11.25	13.09
216	7.28	13.49	10.39
312	10.30	5.91	8.93

H(M73) : Membrane series prepared from the solution mixed for 73 hours.
F(M140) : Membrane series prepared from the solution mixed for 140 hours.
G(M306): Membrane series prepared from the solution mixed for 306 hours.

The effects of solution mixing period on TC concentration in the permeate from these tests with 100 ppm $CHCl_3$ /water mixture feed are shown in Appendix A-3 and on the flux in Appendix A-4. The effects of solution storage age on TC concentration in the permeate are shown in Appendix A-5 and on the flux in Appendix A-6. It was observed from the figures in Appendix A-3 to A-6 that there were no obvious influence of the solution mixing period or the

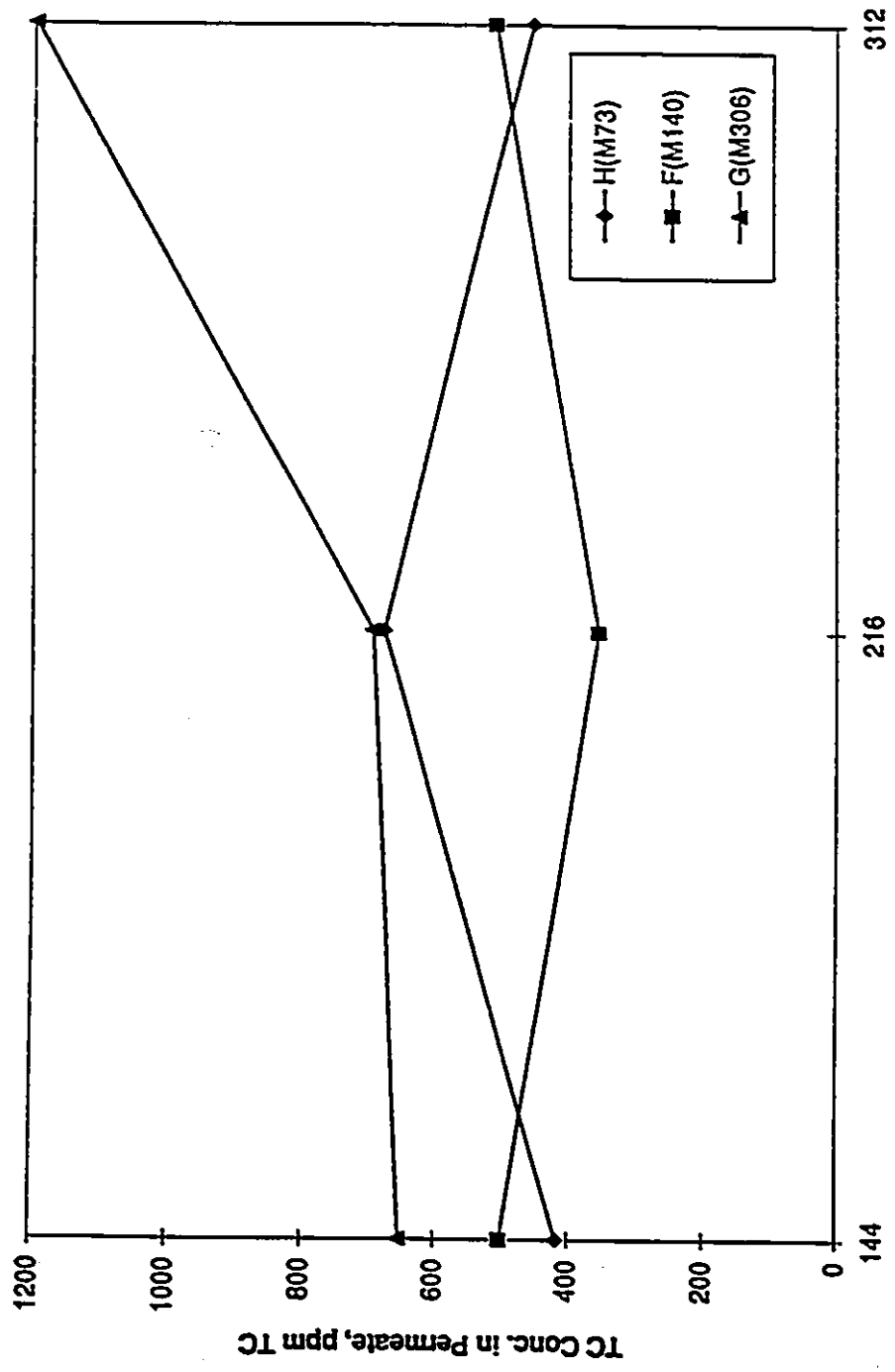


Figure 4.5 Effect of Solution Age on TC Concentration in Permeate using 10 ppm Chloroform/Water Mixture Feed

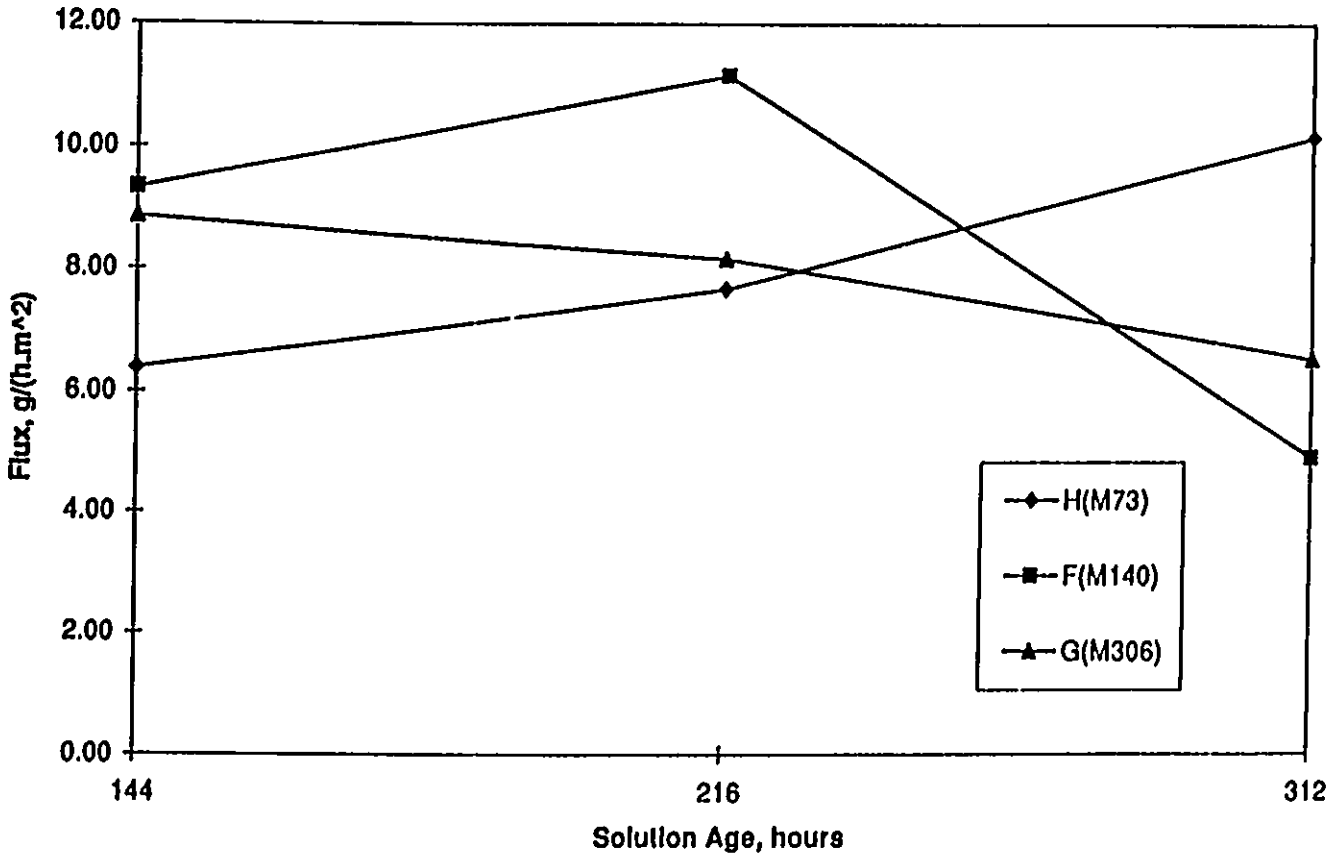


Figure 4.6 Effect of Solution Age on Flux Using 10 ppm CHCl3/Water Mixture Feed.

solution age on the performance of the membranes. As a conclusion it could be stated from Figures 4.3 through 4.6 and Appendixes A-3 through A-6, that there was no substantial effect of the solution mixing period or solution age on the performance of these membranes.

To verify this conclusion, three other membranes, namely HH(M73), FF(M140) and GG(M306) were prepared from solutions H(M73), F(M140) and G(M306) simultaneously from solutions having different mixing periods (73, 140 and 306 hours, respectively) as well as different solution ages (1008, 1344 and 1008 hours, respectively). These membranes were tested immediately after completion of drying by the solvent exchange method with 10 ppm $CHCl_3$/water mixture feed. As shown in Table 4.5, the TC concentration in the permeate was found to be very high in the first day test results. To investigate the likely cause for this high value, these first day results were combined with the first day results from earlier experiments and the TC concentration in the permeate versus membrane storage age was plotted as shown in Figure 4.7. It was found that the TC concentration in the permeate continuously decreases with an increase in period for which the membranes have been stored between drying and testing (membrane age).

These results indicated that there was a profound negative effect of membrane storage age on the TC concentration in the permeate and this was found to be having significantly more influence than any of the other factors investigated in the earlier experiments, i.e. PVP concentration in the casting solution, the solution mixing period or the solution age.

Table 4.5 Effect of Membrane Age on Membrane Performance [Data from First Day of Operation with 10 ppm $CHCl_3$/Water Mixture Feed]

Membrane	TC Conc. in Permeate, ppm TC			Flux, g/(h.m^2)		
Age, days	H(M73)	F(M140)	G(M306)	H(M73)	F(M140)	G(M306)
0						
1	4426	3699	2948	16.43	17.48	13.33
2						
3						
4						
5						
6						
7						
8			1197			6.51
9						
10						
11						
12			693			8.16
13						
14		509			4.90	
15			652			8.84
16						
17						
18	452	356		10.14	11.16	
19						
20						
21		500			9.31	
22	677			7.66		
23						
24						
25	416			6.38		

H(M73) : Membrane series prepared from the solution mixed for 73 hours.
F(M140) : Membrane series prepared from the solution mixed for 140 hours.
G(M306): Membrane series prepared from the solution mixed for 306 hours.

Flux from the first day test results versus membrane age are plotted in Figure 4.8. It was noted that the flux did not follow any general pattern with membrane aging. Membranes of some series showed a decrease in the permeation rate with aging while others did not.

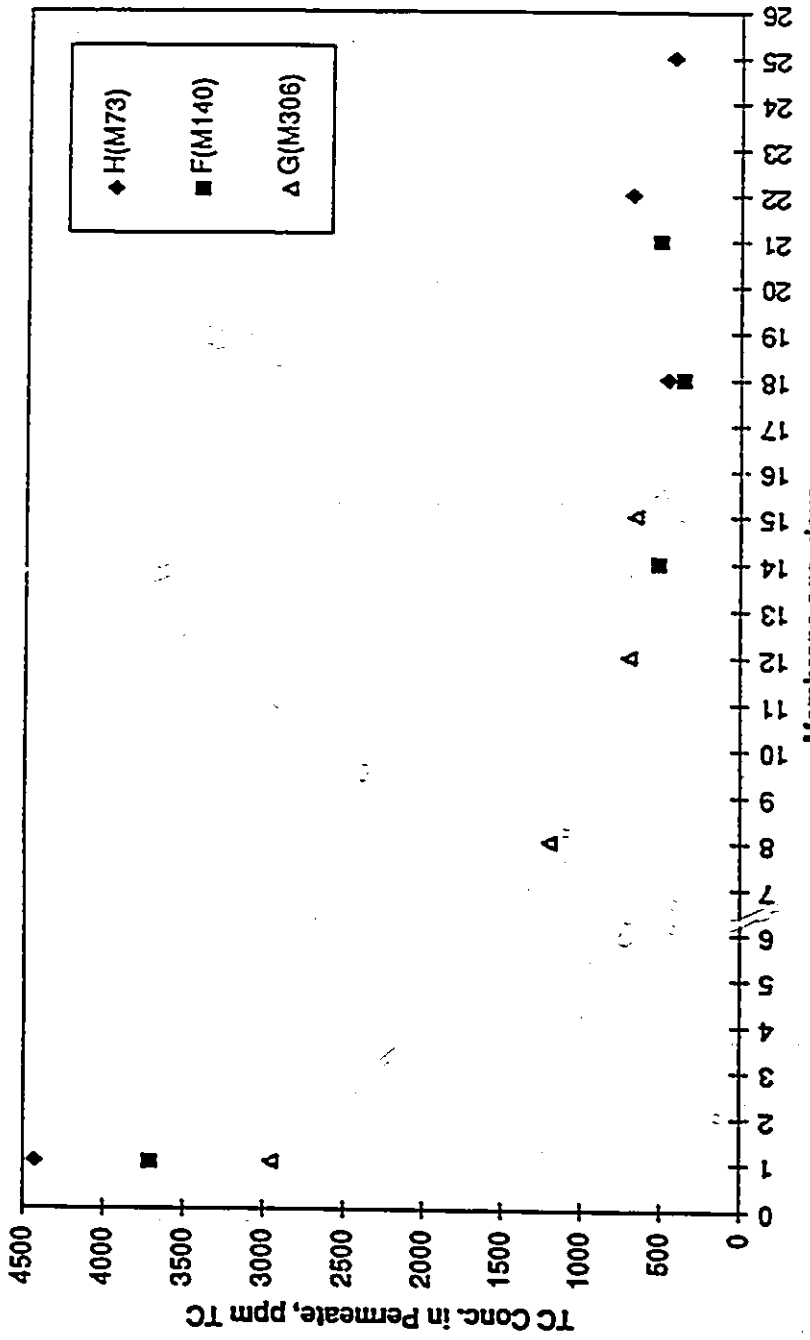


Figure 4.7 Effect of Membrane Storage Age on TC Conc. in Permeate Using 10 ppm CHCl3/Water Feed [Results from 1st. Day Operation Only]

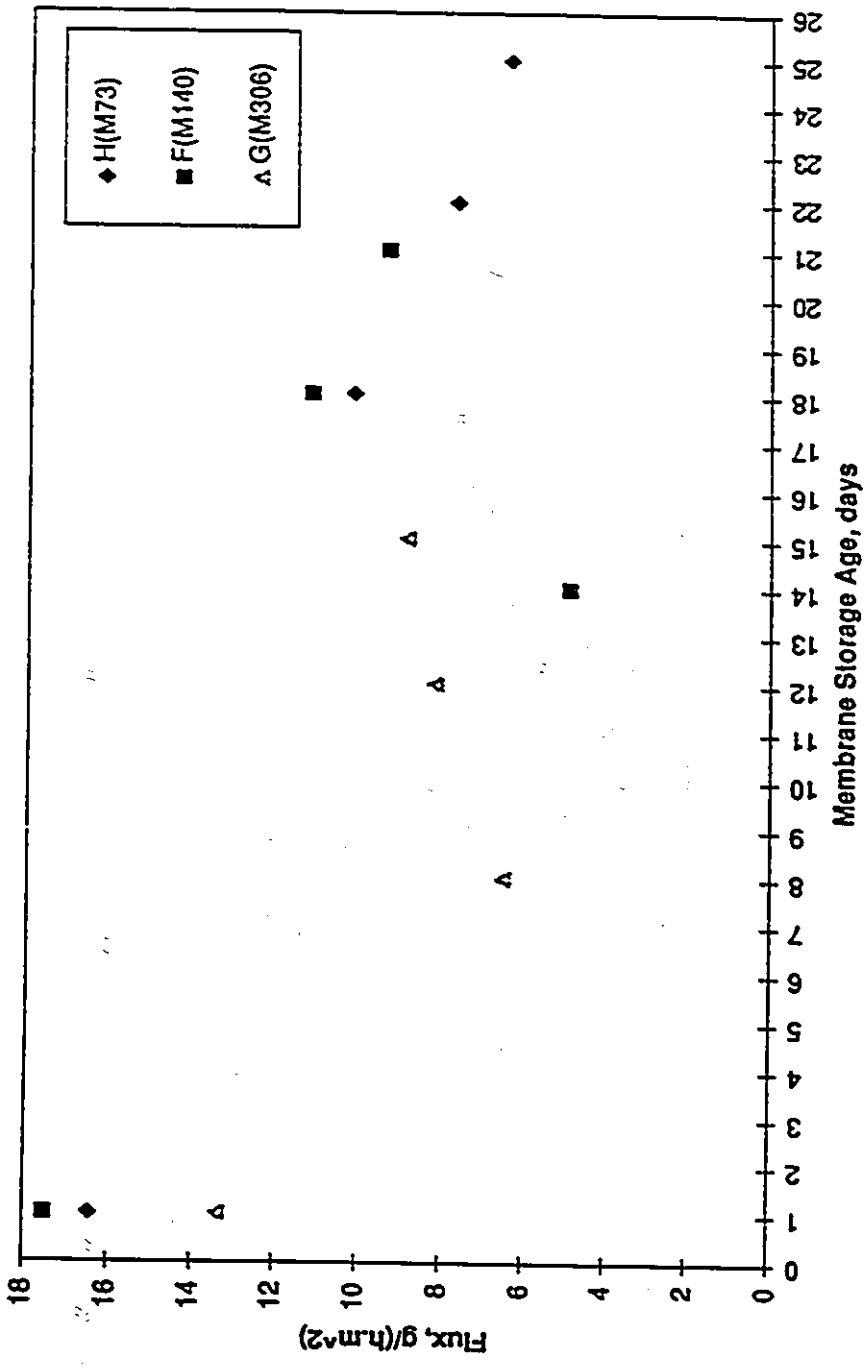


Figure 4.8 Effect of Membrane Storage Age on Flux from 10 ppm CHCl3/Water Feed [Results from 1st. Day Operation]

To determine the effect of period of use on membrane performance, tests with 10 ppm $CHCl_3$/water mixture feed were repeated for two or three days with the same coupons of H1(M73), H2(M73), H3(M73), F1(M140), F2(M140), F3(M140), G1(M306), G2(M306) & G3(M306) membranes and 5 days with HH(M73), FF(M140) & GG(M306) membranes without removing them from the cells, i.e. cells were not opened and only the feed was changed.

The results from the tests conducted with HH(M73), FF(M140) and GG(M306) membranes are presented in Table 4.6. TC concentration in the permeate versus operation period (period of use) are plotted in Figure 4.9 and flux versus operation period in Figure 4.10. It was found that the TC concentration in the permeate decreased very sharply but that the flux did not change substantially.

Table 4.6 Effect of Operation Period on Performance of Membrane at Its Early Storage Age Using 10 ppm $CHCl_3$/water Mixture Feed

Operating days	TC Conc. in Permeate, ppm TC			Flux, g/(h.m^2)		
	Membranes			Membranes		
	HH(M73)	FF(M140)	GG(M306)	HH(M73)	FF(M140)	GG(M306)
0						
1	4426	3699	2948	16.43	17.48	13.33
2	1018	1222	1177	16.98	15.80	12.32
3	833	712	614	16.98	17.10	12.56
4	404	454	371	17.29	17.96	12.17
5	292	321	301	17.51	17.06	10.85

HH(M73) : Membrane prepared from solution mixed for 73 hours and stored (solution age) for 1008 hrs.
FF(M140) : Membrane prepared from solution mixed for 140 hours and stored (solution age) for 1344 hrs.
GG(M306) : Membrane prepared from solution mixed for 306 hours and stored (solution age) for 1008 hrs.

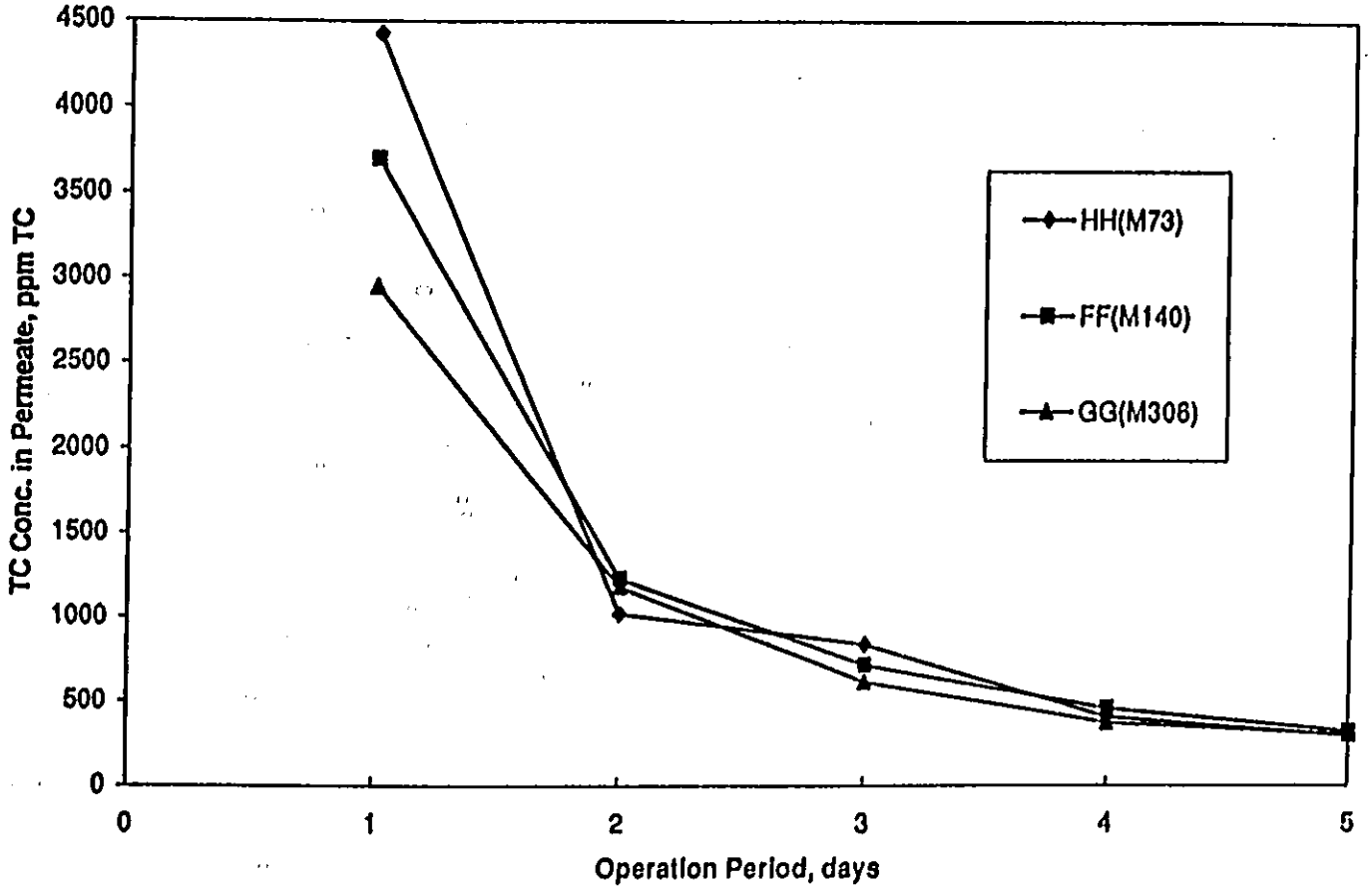


Figure 4.9 Effect of Operation Period on TC Conc. In Permeate Using 10 ppm CHCl3 /Water Feed [Membranes at Early Age]

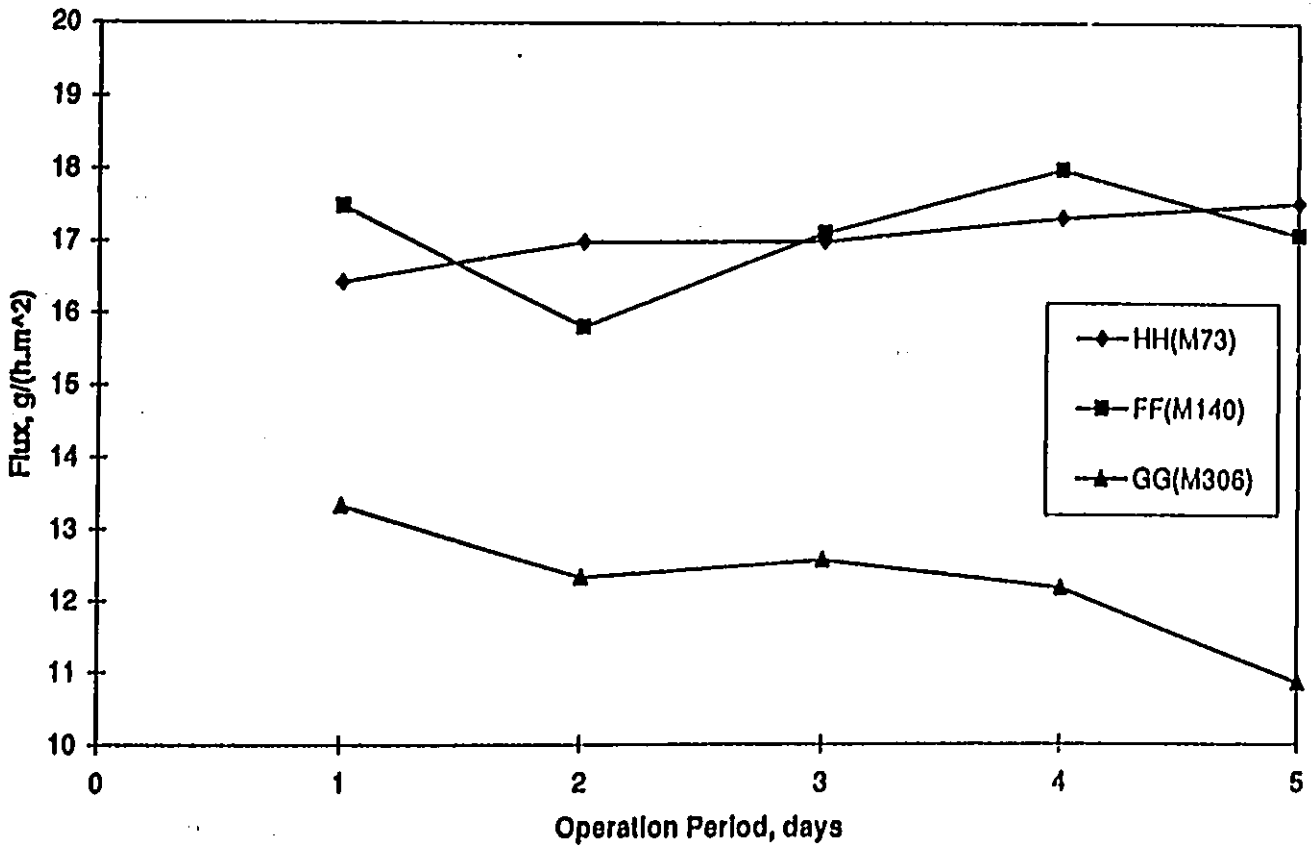


Figure 4.10 Effect of Operating Period on Flux Using 10 ppm CHCl3/Water Feed [Membranes at Early Storage Age]

The TC concentration in the permeate obtained from repeat tests with the other membranes, which had longer storage ages, are given in Table 4.7 and the effect of operation period is shown in Figure 4.11. It was found that the TC concentration in the permeate had decreased but not as sharply as for the membranes with low storage ages.

Table 4.7 Effect of Operation Period on TC Concentration in Permeate at Membrane Storage Age more than Two Weeks Using 10 ppm $CHCl_3$/water Mixture Feed

Operation	TC Concentration in the permeate, ppm TC						
period,day	H1(M73)	H2(M73)	H3(M73)	F1(M140)	F2(M140)	F3(M140)	G1(M306)
0							
1	416	677	452	500	356	509	652
2	383	499	349	497	435	518	596
3	400	558	336				537

H1(M73), H2(M73) & H3(M73) membranes were prepared from solution mixed for 73 hours and stored (solution age) for 144, 216 & 312 hours, respectively.

F1(M140), F2(M140) & F3(M140) membranes were prepared from solution mixed for 140 hours and stored (solution age) for 144, 216 & 312 hours, respectively.

G1(M306) membrane was prepared from solution mixed for 306 hours and stored (solution age) for 144 hours.

Flux results from these tests are given in Table 4.8. From Figure 4.12, where flux values from the repeat tests are plotted, it could be stated that the flux had very slightly increased with the use of the membranes. This may be due to the fact that the permeation rate partially depends on the solute diameter and the free volume available for the transport of permeant molecules. When the membrane is in contact with the feed solution for a substantial period of time, the solution may be partially dissolved in the polymer matrix and may cause it to swell slightly (Néel, 1995). The swelling may increase the free volume which may in return increase the flux.

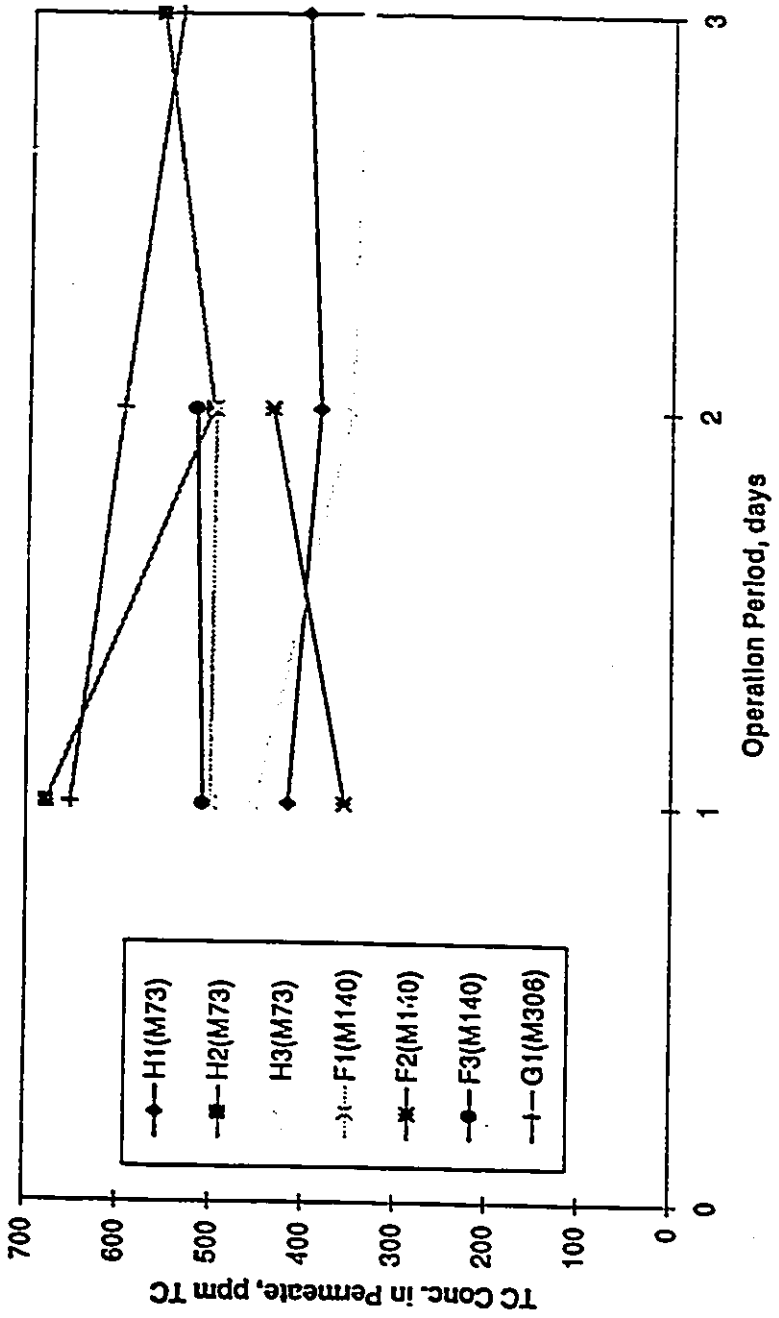


Figure 4.11 Effect of Operation Period on TC Concentration in Permeate Using 10 ppm CHCl3/Water Feed [Membranes with Longer Storage Age]

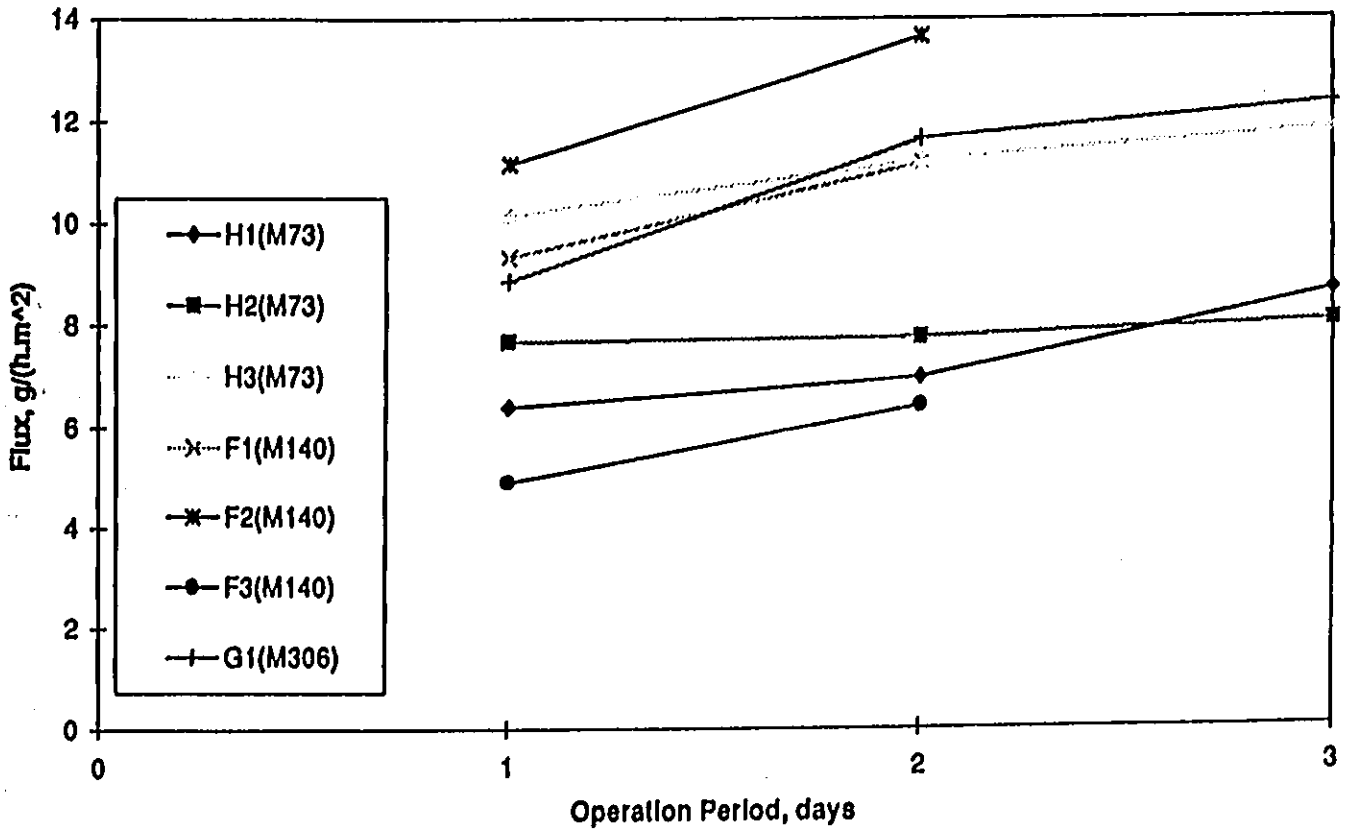


Figure 4.12 Effect of Operation Period on Flux Using 10 ppm CHCl3/Water Feed [Membranes with Longer Storage Age]

Table 4.8 Effect of Operation Period on Flux at Membrane Storage Age more than Two Weeks Using 10 ppm $CHCl_3$/water Mixture Feed

Operation period,day	Flux, g/(h.m^2)						
	H1(M73)	H2(M73)	H3(M73)	F1(M140)	F2(M140)	F3(M140)	G1(M306)
1	6.38	7.66	10.14	9.31	11.16	4.90	8.84
2	6.95	7.73	11.21	11.15	13.65	6.39	11.64
3	8.64	8.03	11.82				12.36

H1(M73), H2(M73) & H3(M73) membranes were prepared from solution mixed for 73 hours and stored (solution age) for 144, 216 & 312 hours, respectively.

F1(M140), F2(M140) & F3(M140) membranes were prepared from solution mixed for 140 hours and stored (solution age) for 144, 216 & 312 hours, respectively.

G1(M306) membrane was prepared from solution mixed for 306 hours and stored (solution age) for 144 hours.

4.3 Reevaluation of the Impact of SMM

Pervaporation experiments were carried out according to the method stated in section 3.4.3. with membranes of "Q" and "R" series. The main difference between them was that, "Q" series contained SMM while "R" series did not. During these tests, a detailed material balance of chloroform and the composition of the permeate was planned. For this purpose, the feed & retentates were analyzed by TOC Analyser and GC (Purge & Trap) and the permeates were analysed by TOC Analyser, GC (P & T) and GC-MS. The ethanol which was detected by GC (P&T) could not be quantified, as ethanol is not easily purgeable from water. The area shown in the tables below is used only for a qualitative assessment. The results obtained from the GC-MS analysis are purely qualitative. The findings of these tests are summarized below:

First, the TC concentration in the permeate given in Table 4.9, decreases with the use of the membrane except membrane Q2x which was well dried [8 days in air and 4 days in vacuum]. This phenomena was observed independent of feed composition as membrane Q2-2 was tested

with deionized water as feed and other membranes were tested with 11 ± 1 ppm chloroform solutions as feeds.

Table 4.9 Permeate Analyzed by TOC Analyzer Obtained from Reevaluation of the Impact of SMM Tests

Operating period, days	Q1x	Q1	Q2-1	Q2-2	Q2x	R1
	ppm TC	ppm TC	ppm TC	ppm TC	ppm TC	ppm TC
1	1754	1303	584	995	52	1554
2	760	522	701	579	90	1282
3	380	376	275	364		
4			179	126		
5			122	51		
6			120	60		

Q1x, Q1 & Q2-1 membranes were prepared from solution containing 1 wt.% of SMM and tested with 11 ± 1 ppm $CHCl_3$/water feed.

Q2-2 1 membrane was prepared from solution containing 1 wt.% of SMM and tested with deionized water as feed.

Q2x membrane was prepared from solution containing 1 wt.% of SMM, dried additionally for 8 days in air and 4 days in vacuum and was tested with 11 ±1 ppm $CHCl_3$/water feed.

R1 membrane was prepared from solution containing no SMM and tested with 11 ± 1 ppm $CHCl_3$/water feed.

The TC concentration in the permeate versus operation period of the membranes is shown in Figure 4.13. The pattern of this decrease in TC concentration in the permeate matches that observed during earlier experiments conducted to determine the effect of operation period on membrane performance (Figure 4.9).

Second, the results of the permeate analysis by GC (P&T) and GC-MS are given in Table 4.10. The results indicated that there was trace or no chloroform in the permeate but ethanol was detected and its concentration continuously decreased with operation period and membrane aging. These results indicate that the ethanol, which was used for drying by solvent exchange was possibly retained in the membrane and leached out from the membrane during use. The

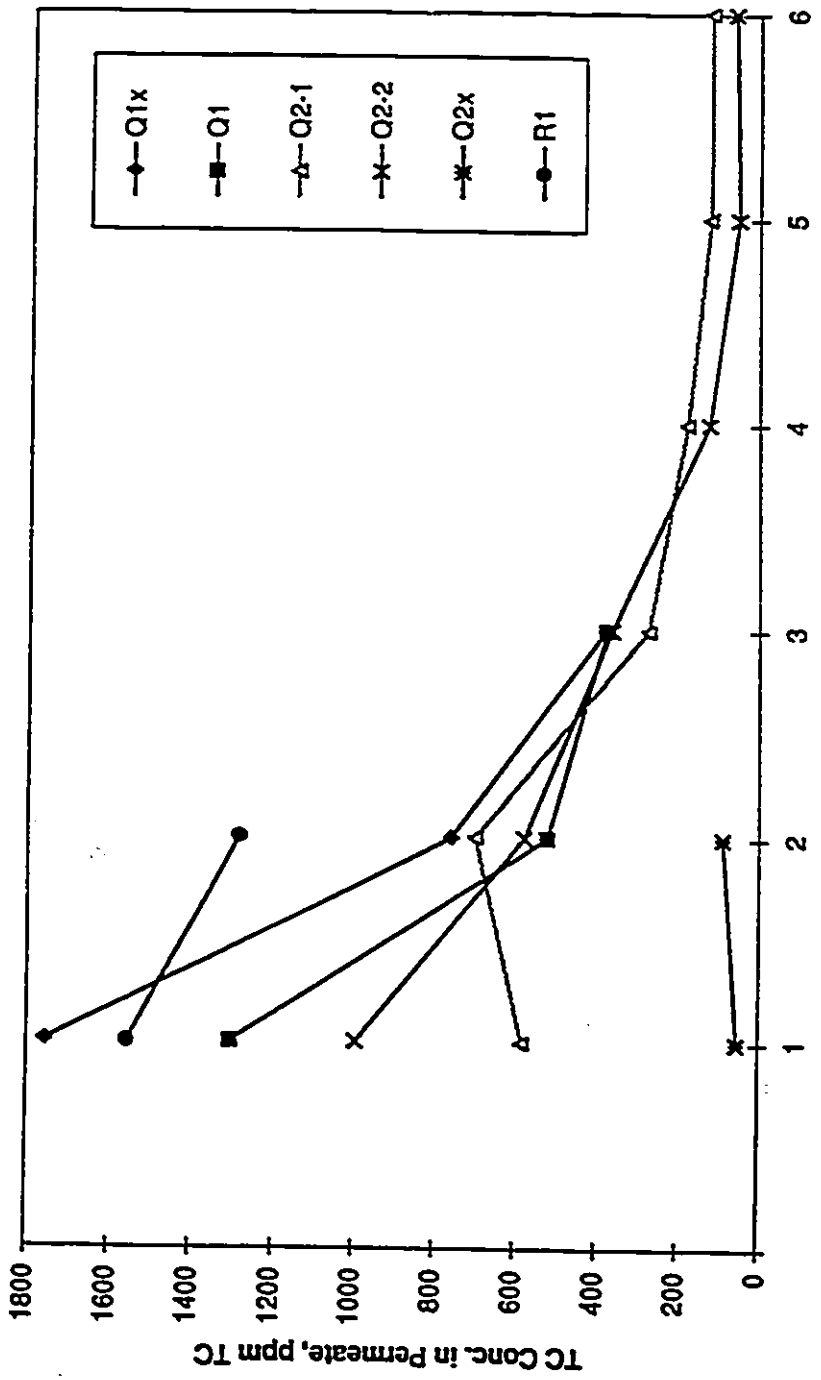


Figure 4.13 Effect of Operation Period on TC Conc. in Permeate Obtained from Reevaluation of the Impact of SMM Tests

Table 4. 10 Permeate Analysis Results from G.C. (P&T) and G.C.-M.S. Obtained from Reevaluation of the Impact of SMM Tests

Membranes	Operation Period, days	G.C. (Purge & Trap)		G. C. - M. S.	
		CHCl3, ppm	Ethanol*	CHCl3**	Ethanol**
Q1x	1	*****	*****	ND***	DD****
	2	1.5	4.00x10^8	ND	DD
	3	0.5	1.27x10^8	ND	DD
Q1	1	3	4.45x10^8	ND	DD
	2	1.5	4.32x10^8	ND	DD
	3	0.7	1.72x10^8	ND	DD
R1	1	30	4.06x10^8	ND	DD
	2	0.5	7.26x10^8	ND	DD
Q2x	1	ND	ND	ND	DD
	2	ND	0.29x10^8	ND	DD
Q2-1	1	File lost	File lost	ND	DD
	2	1.5	2.89x10^8	ND	DD
	3	0.8	1.93x10^8	ND	DD
	4	0.6	0.48x10^8	ND	DD
	5	ND	0.16x10^8	ND	DD
	6	ND	0.27x10^8	ND	DD
Q2-2	1		4.17x10^8	ND	DD
	2	0.7	1.05x10^8	ND	DD
	3	0.8	0.93x10^8	ND	DD
	4	0.4	0.14x10^8	ND	DD
	5	ND	ND	ND	DD
	6	ND	0.11x10^8	ND	DD

* The quantity of ethanol is expressed in area of the GC peak. But as ethanol is not good purgeable compound, this area is given only in qualitative term.

** GC-MS identified chloroform and ethanol in qualitative terms only.

*** ND = not detected

**** DD = detected

***** The concentration was low then expected, so dilution factor was high for the range used.

TC detected using TOC analyzer could be attributed to the carbon in ethanol. The leaching was obviously higher at an early membrane age (i.e. shortly after preparation) and decreased with membrane aging as some of the ethanol partially evaporated from the membrane during storage. The presence of ethanol was further confirmed from the Fourier Transform Infrared (FTIR) spectra which were recorded during this study. The spectra presented in Appendix A - 7 show the presence of residual ethanol after 24 hours of normal drying. Even after 48 hours of vacuum drying, a trace of ethanol was detected. This indicates that the 24 hours of normal drying was not adequate for total removal of residual ethanol. This observation is supported by Huang and Wei (1994), who had dried the membranes in air for a period of 7 days and then by vacuum for 12 hours to eliminate residual solvent. To verify that the TC concentration observed in the permeate was the result of ethanol leaching from the membrane into the permeate and not due to enrichment of chloroform, repeat experiments were conducted by Yi Fang (1995) and John Minnery (1995). The permeates were analyzed by a GC (Varian Aerograph Series 1400) with a newly installed column [12' x 0.25" O.D. S.S. 15%, Carbowax, 20M CHROM.W.H.M.D.S 60/80]. The results reported by them confirmed that there was no chloroform enrichment in the permeate.

Third, the analytical results of the feeds and the retentates presented in Table 4.11 show that the POC values analyzed by TOC analyzer of the retentates, ranged from 8.9 % lower to 2.40 % higher than the feed, except that in the cases where deionized water was used as feed. In the latter case, the difference is higher as it was approching the detection limits of the TOC analyzer. The chloroform concentrations of the feeds and retentates analyzed by GC (P&T) showed that the retentates concentrations ranged from 2.46 % higher to 13.06 % lower than

Table 4.11 TOC and G.C. (Purge & Trap) Analysis Results of Feed & Retentates Obtained from Reevalution of the Impact of SMM Tests.

Membrane/ Operation period, days	TOC Analyser			G.C. (Purge & Trap)			
	Feed	Retentate	Difference	Feed	Retentate	Difference	Retentate
	ppm POC	ppm POC	%	ppm CHCl3	ppm CHCl3	%	Ethanol*
Q1x							
1	1.17	1.11	5.13	10.72	9.18	14.38	ND**
2	1.14	1.12	1.75	10.01	9.76	2.46	Trace
3	1.11	1.02	8.11	10.43	9.27	11.13	Trace
Q1							
1	1.17	1.09	6.84	10.72	9.61	10.42	ND
2	1.14	1.07	6.14	10.01	10.14	-1.34	Trace
3	1.11	1.06	4.50	10.43	9.07	13.06	Trace
R1							
1	1.17	1.13	3.42	10.72	9.70	9.58	ND
2	1.14	1.12	1.75	10.01	10.25	-2.46	0.14x10^8
Q2x							
1	1.25	1.28	-2.40	11.57	10.46	9.65	ND
2	1.28	1.20	6.25	11.48	10.68	7.00	ND
Q2-1							
1	1.40	1.31	6.43	11.28	10.77	4.55	Trace
2	1.29	1.19	7.75	12.29	11.17	9.09	ND
3	1.37	1.33	2.92	11.17	10.21	8.60	ND
4	1.35	1.23	8.89	11.68	10.66	8.80	ND
5	1.25	1.22	2.40	11.57	10.28	11.20	ND
6	1.28	1.21	5.47	11.48	10.57	7.98	ND
Q2-2							
1	0.25	0.26	-4.00	ND	NA***		NA
2	0.26	0.24	7.69	ND	NA		NA
3	0.32	0.30	6.25	ND	NA		NA
4	0.34	0.31	8.82	ND	NA		NA
5	0.22	0.22	0.00	ND	NA		NA
6	0.20	0.16	20.00	ND	NA		NA

* The quantity of ethanol is expressed in area of the GC peak. But as ethanol is not good purgeable compound, this area is given only in qualitative term.

** ND = not detected

*** NA = not analysed

the feed. But chloroform was either not detected or observed only in trace amounts in the permeate by GC (P&T) and GC-MS (Table 4.10). Therefore, these differences observed between the feeds and the retentates could be due to losses during the transfer of the feed and the retentates from the volumetric flask into the cell and from the cell into the sample vial and/or due to errors in analysis but was definitely not due to any enrichment of chloroform in the permeate. In addition to this, as chloroform is a solvent for PES, the possibility of chloroform reacting with the PES membrane could not be ignored completely. It was also noticed from the GC (P&T) analysis that in some cases, traces of ethanol were found in the retentates which further confirmed that ethanol was coming from the membrane as it was not completely removed by the normal drying cycle.

Fourth, flux data presented in Table 4.12 and the effect of operation period on flux displayed in Figure 4.14 show that the permeation rates did not change significantly with use. It was noted for membrane Q2x, which was *extra* dried that the permeation rate was lower. This phenomena of decreasing permeation rate with storage period (membrane age) was also reported by Huang and Wei (1994) for a latex membrane.

Table 4.12 Flux Data Obtained from Reevaluation of the Impact of SMM Tests.

Operation Period, days	Q1x $g/(h.m^2)$	Q1 $g/(h.m^2)$	Q2-1 $g/(h.m^2)$	Q2-2 $g/(h.m^2)$	Q2x $g/(h.m^2)$	R1 $g/(h.m^2)$
1	17.88	15.11	17.94	22.16	6.43	18.51
2	17.40	15.42	12.99	19.55	11.67	17.38
3	16.45	12.69	15.85	16.85		
4			23.45	19.23		
5			17.63	16.03		
6			15.26	19.20		

Legends are same as that of Table 4.9.

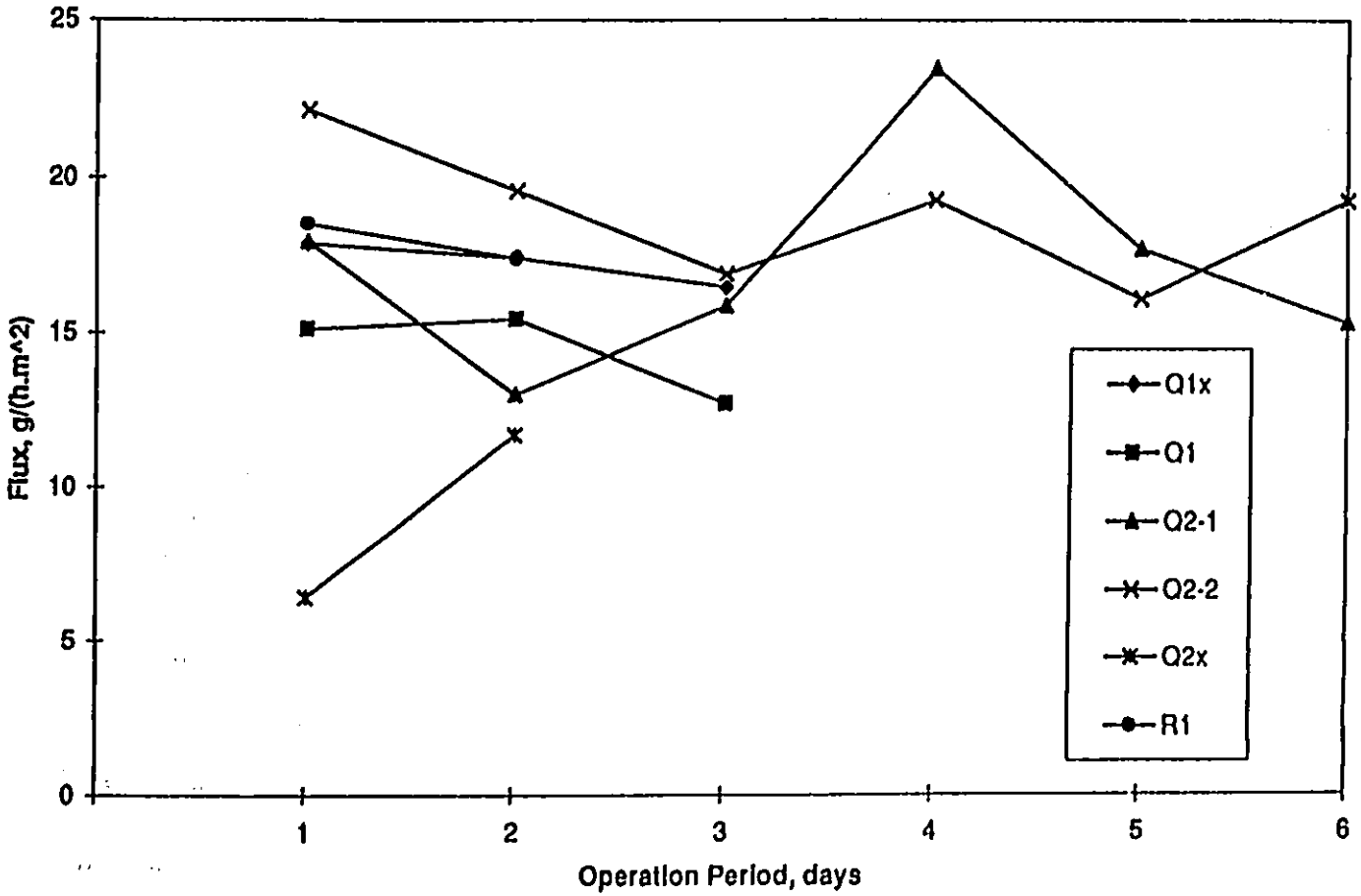


Figure 4.14 Effect of Operating Period on Flux Obtained from Reevaluation of the Impact of SMM Tests

The question remains as to why the various batches of membranes yield similar pattern of results during the PVP optimization tests conducted in this study and during the SMM optimization experiments conducted by Fang et al. (1994). That is, why did the TC concentrations (chloroform concentration ?) in the permeate increased, reached a maximum and then decreased. The reason for this might be that batches of membranes of different compositions were prepared at the same time and they were tested at different membrane ages. Initially, the membrane which was tested first, might have shown a higher value of TC in the permeate as compared to that of the other membranes which were tested later. When the second batch of membranes was prepared, the membranes prepared with a composition similar to that yielding the highest earlier separation in the first batch, were given priority and tested first. Hence repeat testing tended to show the same pattern of results. Even then, the final question remains, as to why it was concluded that there was chloroform enrichment in the permeate in earlier studies (Fang et al. 1994, 1995). It had not been envisaged in these studies that ethanol may be leaching out of the membrane. Hence during GC calibration, peak positions were determined only for pure chloroform, water and a chloroform/water mixture. One peak was identified as the chloroform peak and the other as water peak. During the analysis of the permeate, again only two peaks were observed and unfortunately, since the ethanol peak lies closer to the original chloroform peak, this peak was erroneously treated as being due to chloroform. This has since been confirmed by repeat experiments conducted and analyzed by Yi Fang (1995) and John Minnery (1995) which were conducted as a result of the findings presented here.

In summary, it can be concluded that chloroform was not being concentrated in the permeate. The chloroform concentration in the permeate reported earlier by Fang et al., (1994, 1995) was primarily due to the carbon from ethanol which was leaching from the membrane. Thus, PES membranes prepared incorporating the newly synthesized SMM, do not appear to be very good for chloroform enrichment from dilute aqueous solutions as the paper by Fang et al. (1995) stated. The initial perception was that incorporating hydrophobic SMM to PES (which is a water selective glassy amorphous polymer with several other very favorable properties) would change the surface to an extent that would overcome its bulk intrinsic hydrophilic properties. This was based on the possible creation of a substantial surface layer by suitable adjustment of the SMM percentage in the casting solution and evaporation period during membrane casting, i.e. allowing enough SMM migration to the surface to significantly alter selectivity. It was also felt that the pore size of the PES membrane could also be enlarged by optimizing the level of PVP additions. It was thus expected that this approach would favour the formation of a hydrophobic surface layer, while utilizing the superior mechanical attributes of PES substrate. It however appears that the membrane produced by a 7 minute evaporation period and 1 wt. percent of SMM did not build up a sufficiently enriched or thick hydrophobic surface and as a result the bulk intrinsic hydrophilic properties of the PES continued to dominate.

As it was concluded that the TC concentration measured in the permeate was not due to chloroform enrichment but due to ethanol leaching out from the membrane, conducting statistical analysis of the results obtained from the earlier experiments i.e., i) effect of solution

mixing period; ii) effect of solution age; and iii) effect of membrane age is meaningless. Actual chloroform measurements would be required for such an exercise to be worth while.

4.4 Membrane Morphology Study

The aging effect on the membrane morphology was studied using an atomic force microscope. The images are presented in Appendix A-8 through A-10. The images were taken at 0 hour, 24 hours and 240 hours of the membrane age, respectively. It was found that the membrane surface was becoming smoother and smoother with the aging of the membrane.

4.5 Performance Evaluation of the Membrane Prepared Using SMM58

Membranes were prepared from solution "M", which incorporated 1 wt.% SMM58. The surface of these membranes was found to be non-uniform. Pervaporation tests with these membranes were carried out at a membrane age of 48 days and the results are given in Table 4.13. As this experiment was carried out before discovering that chloroform was not concentrating in the permeate, the permeates were analyzed for TC using the TOC analyzer only. The TC concentrations in the permeate were found less than those of the membranes tested at membrane age of 25 days (Table 4.5), but were more than that of a well dried membrane (Q2x, Table 4.9). As no detailed analysis of the permeate was done, the actual composition is not known.

Table 4.13 Performance of Membranes Prepared Using SMM58.

	10 ppm CHCl3/Water feed			100 ppm CHCl3/Water feed		
	Membrane M1	Membrane M2	Membrane M3	Membrane M1	Membrane M2	Membrane M3
TC Conc. in Permeate, ppm	222	173	174	144	198	147
Flux, g/(h.m^2)	12	15	16	12	12	17

M1, M2 & M3 were prepared from solution containing 1 wt % of SMM58.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. The addition of 1 weight percent SMM into a PES/PVP/DMAc membrane casting solution increases hydrophobicity of the membrane surface, however, there was no evidence that chloroform is enriched in the permeate.

2. The enrichment in total carbon content in the permeate, mistaken as chloroform enrichment, was due to leaching out of residual ethanol from the membrane.

3. It appears that the surface hydrophobicity introduced by adding SMM into the casting solution is insufficient to completely overcome the intrinsic hydrophilic properties of the basic PES membrane.

4. It was observed that solution mixing time and solution age had no significant effect on either selectivity or flux.

5. The residual ethanol leaching out from membranes decreases with membrane age and period of use. It can almost be eliminated by an additional 4 days of vacuum drying.

5.2 Recommendations

1. The experiments on pervaporation of water/chloroform mixtures by membranes containing SMM should be repeated using gas chromatography as an analytical tool.

2. The effect of membrane preparation variables on pervaporation performance should be re-studied.

3. Future evaluations should include blank experiments using deionized water as feed to identify leaching from membranes.

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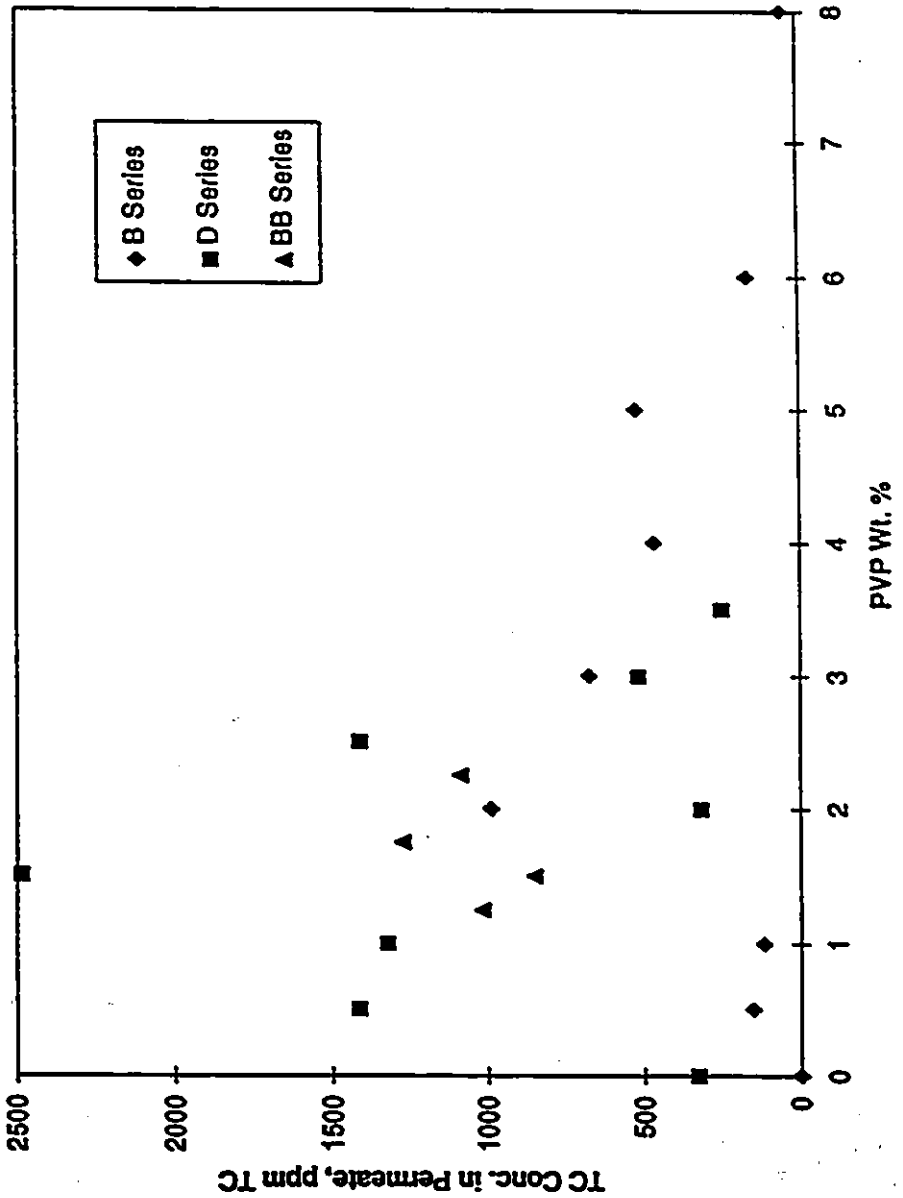
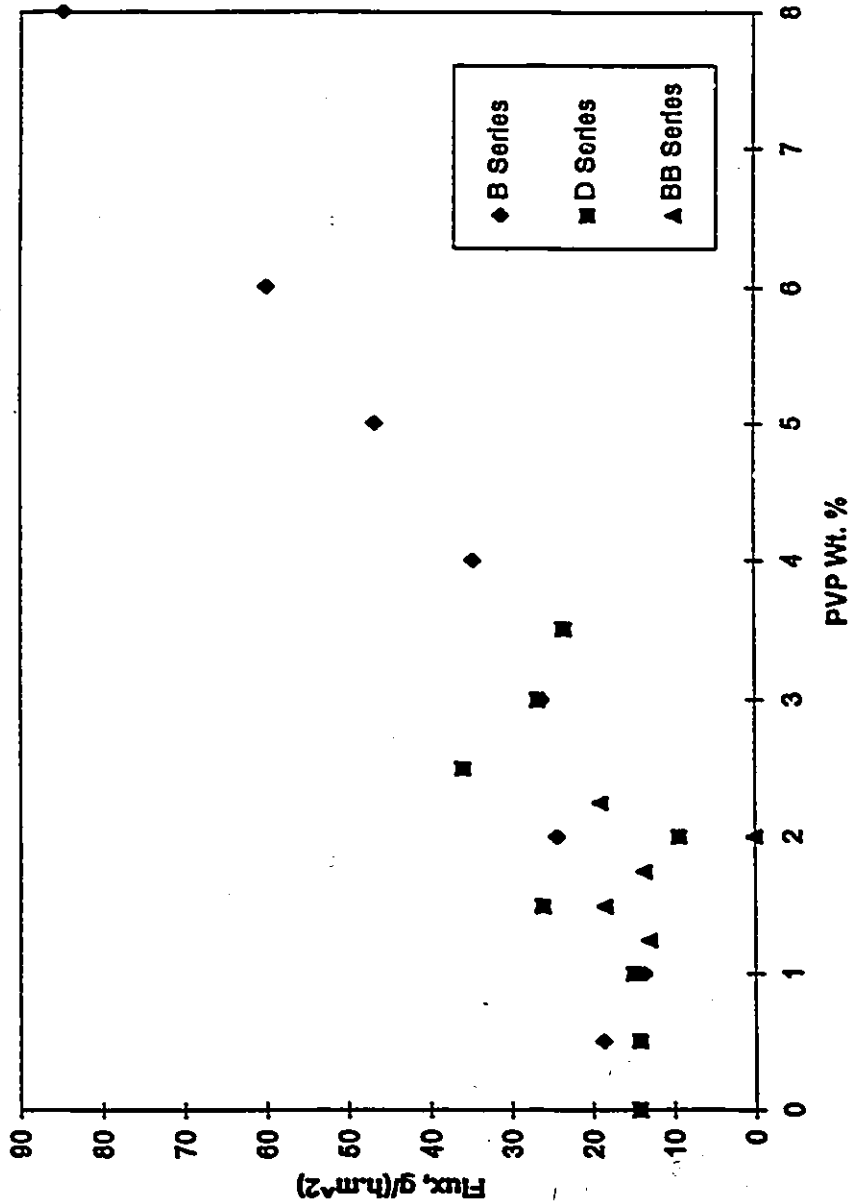
APPENDIX A-1

TC CONCENTRATION IN THE PERMEATE FROM PVP OPTIMIZATION TESTS USING 100 PPM $CHCL_3$/WATER MIXTURE FEED



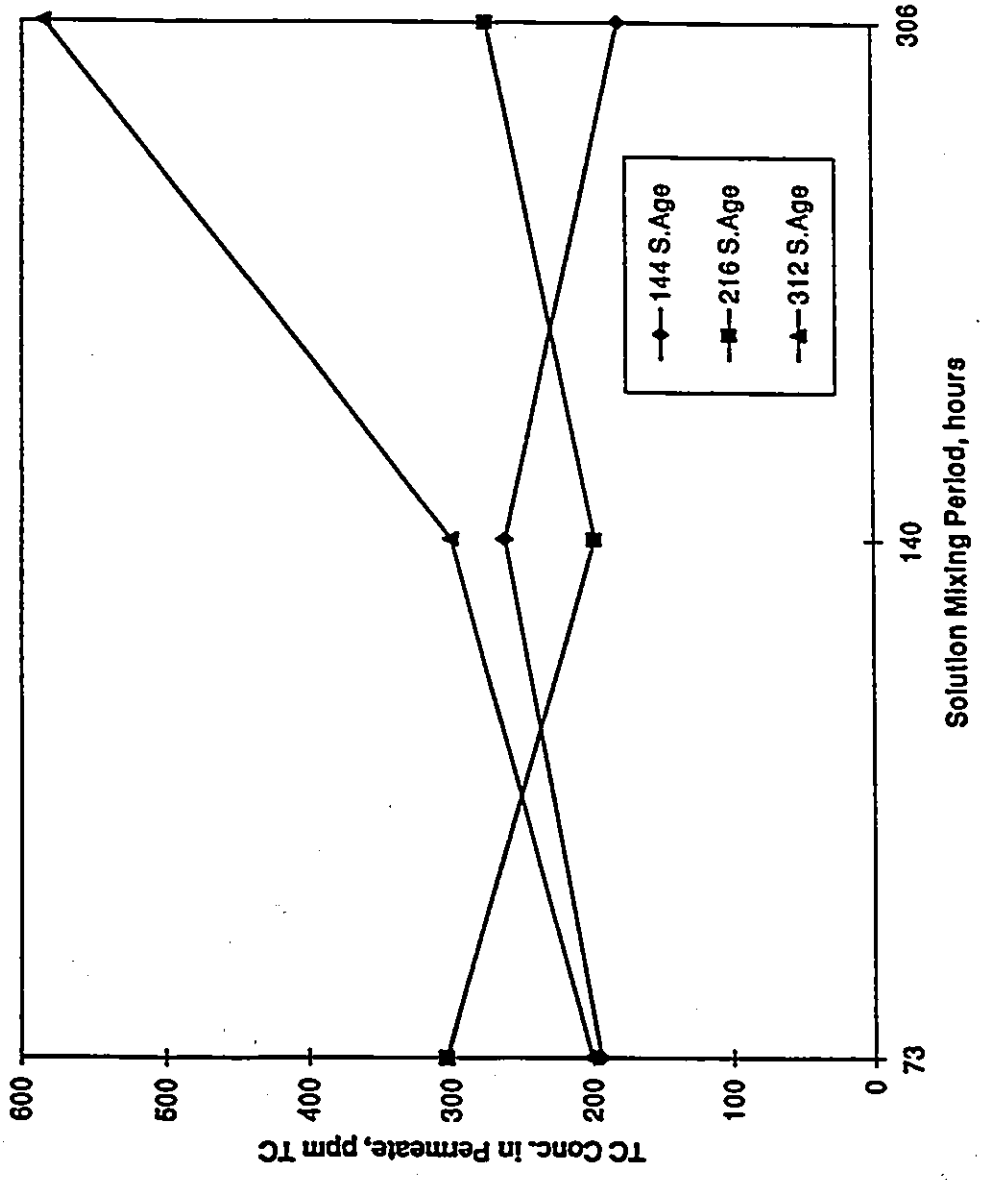
APPENDIX A-2

EFFECT OF PVP ON FLUX WITH 100 PPM $CHCL_3$/WATER MIXTURE FEED



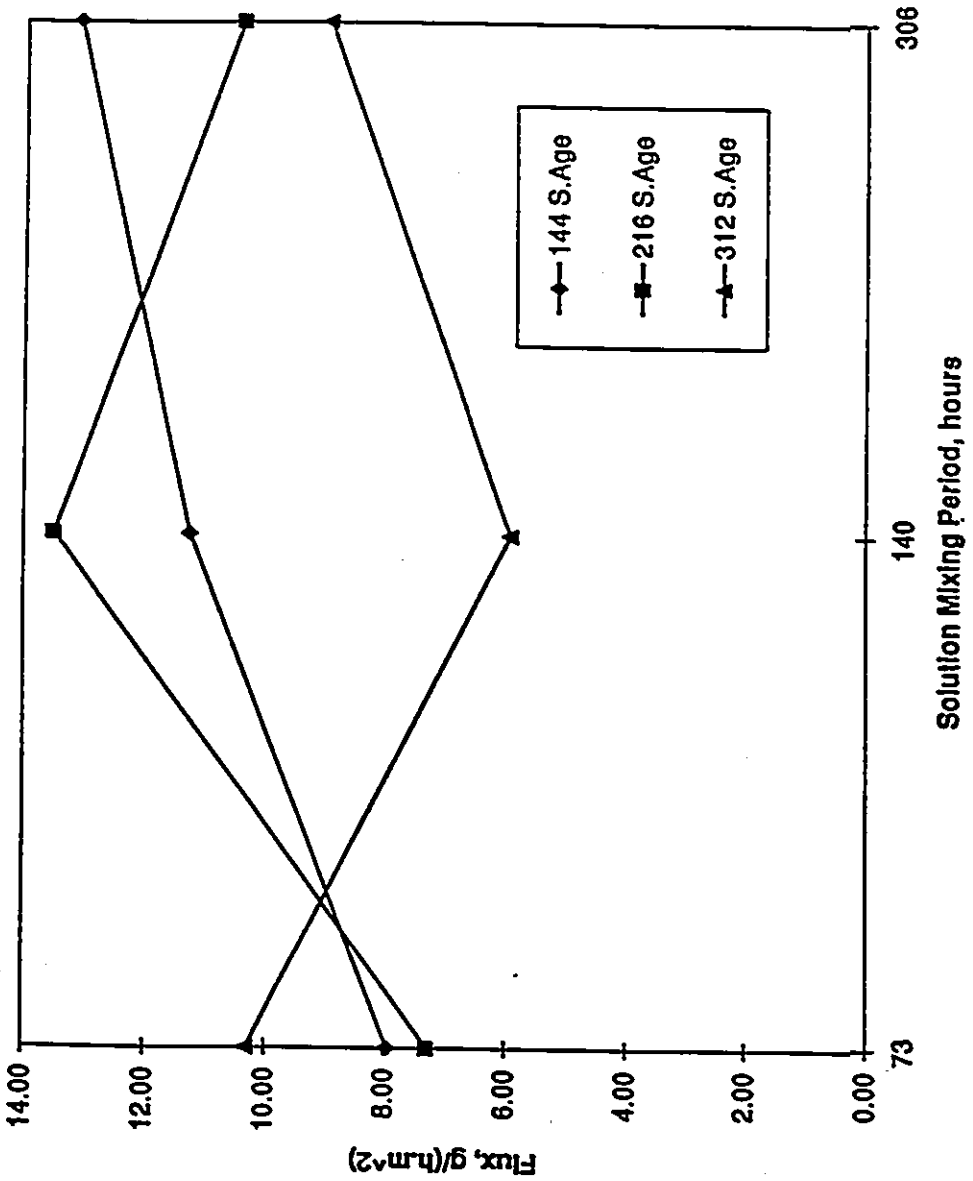
APPENDIX A-3

EFFECT OF SOLUTION MIXING PERIOD ON TC CONC. IN PERMEATE USING 100 PPM $CHCL_3$/WATER MIXTURE FEED



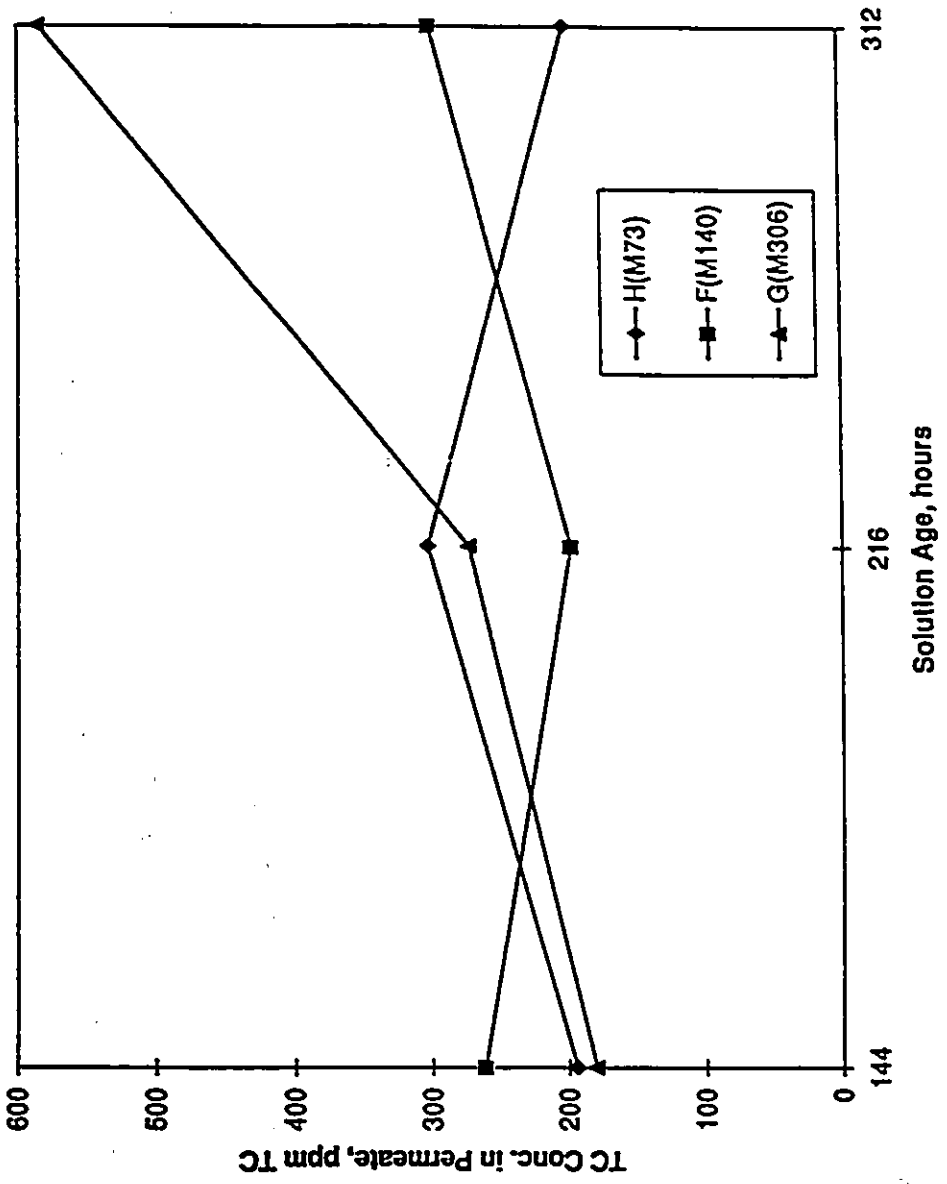
APPENDIX A-4

EFFECT OF SOLUTION MIXING PERIOD ON FLUX USING 100 PPM $CHCL_3$/WATER MIXTURE FEED



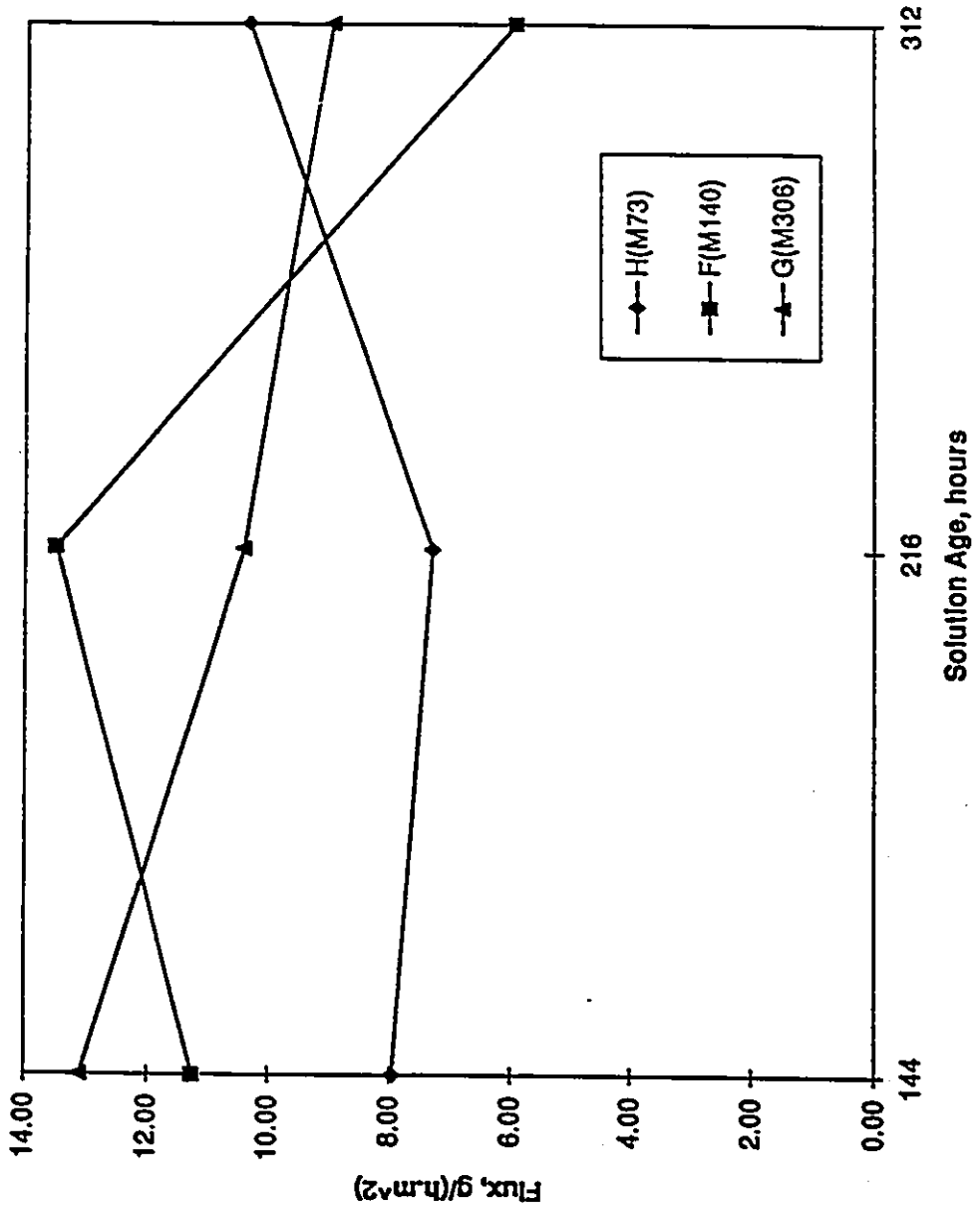
APPENDIX A-5

EFFECT OF SOLUTION AGE ON TC CONC. IN PERMEATE USING 100 PPM $CHCL_3$/WATER MIXTURE FEED



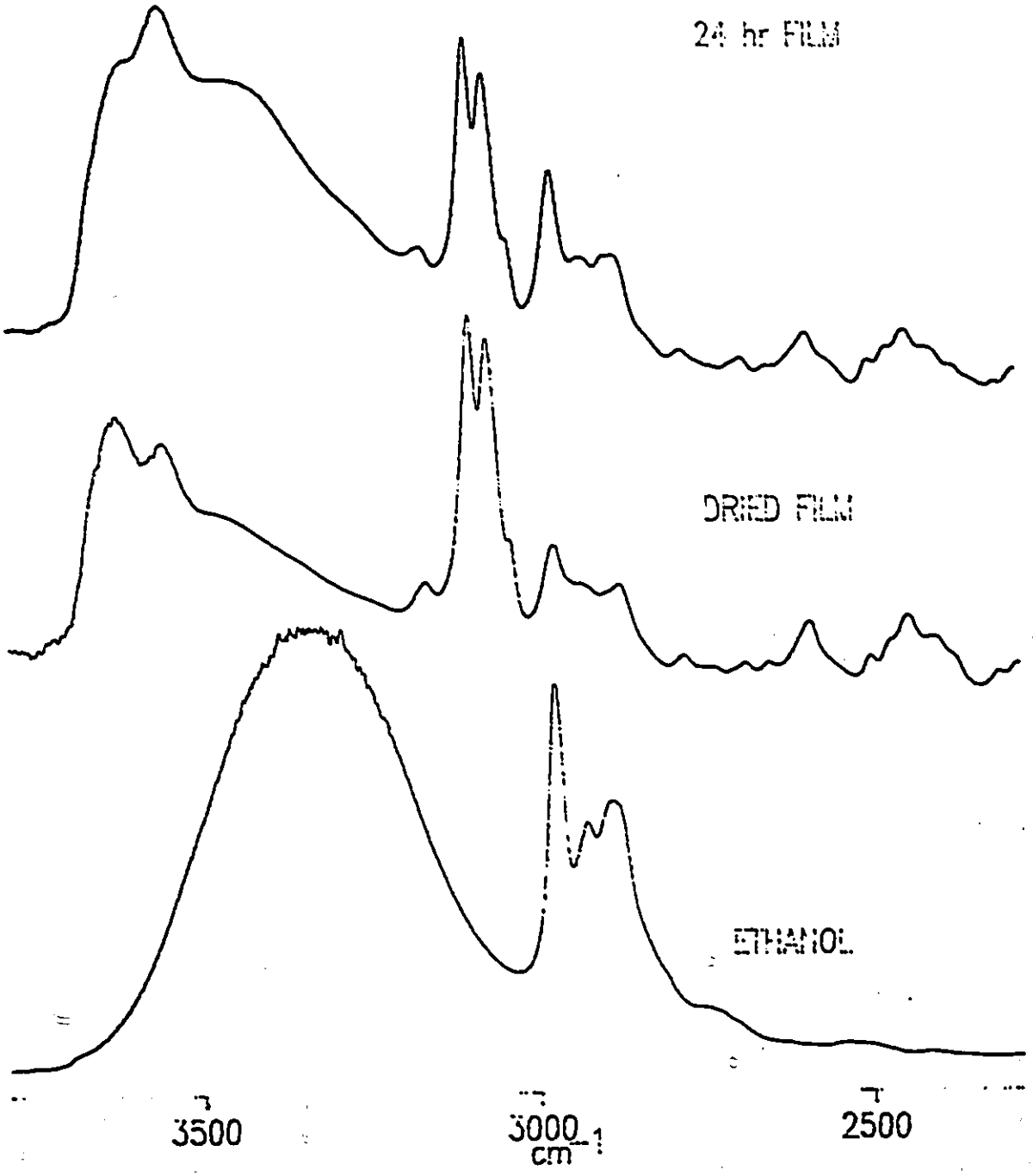
APPENDIX A-6

EFFECT OF SOLUTION AGE ON FLUX USING 100 PPM $CHCL_3$/WATER MIXTURE FEED



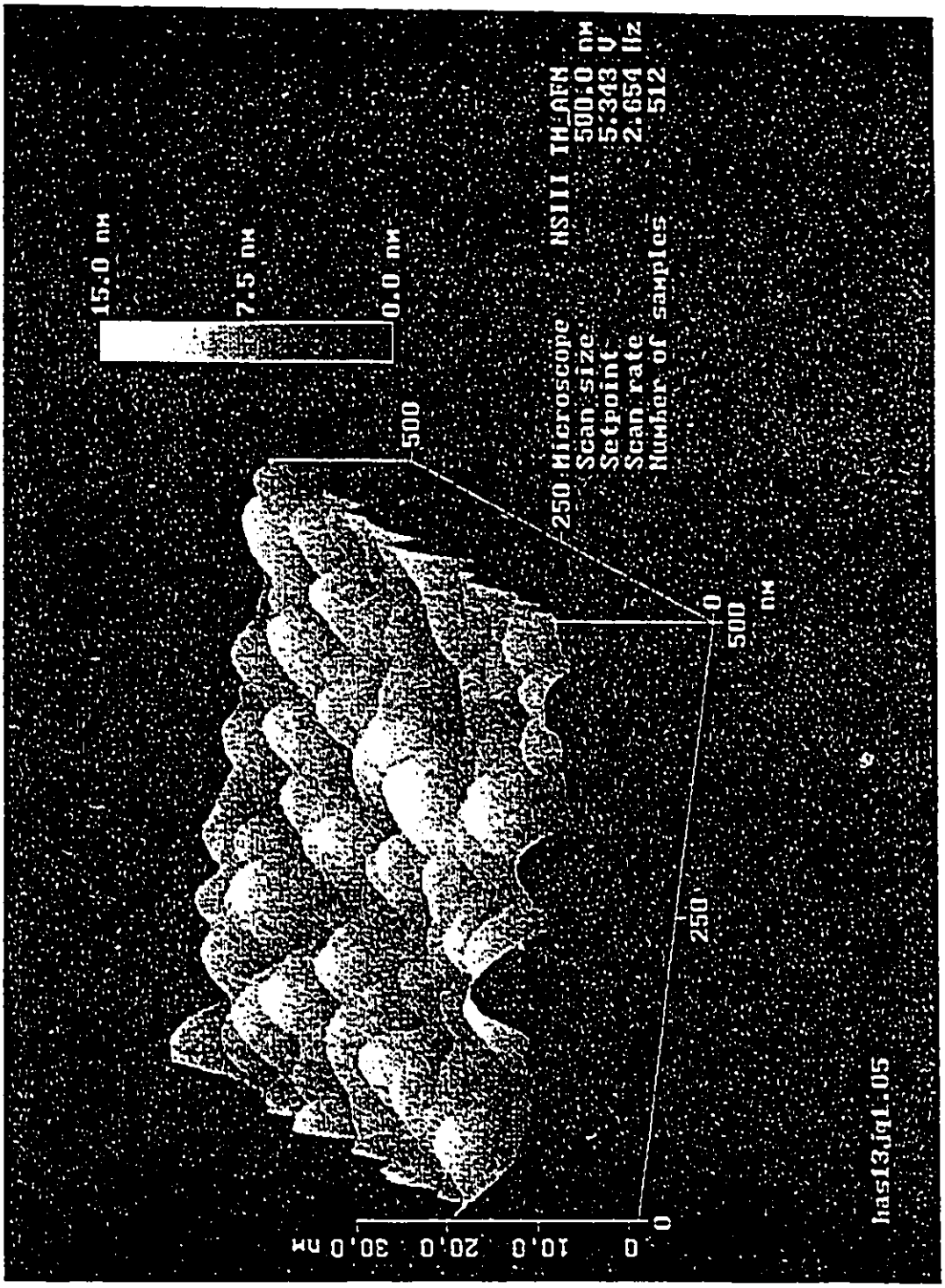
APPENDIX A-7

FOURIER TRANSFORM INFRARED SPECTRA OF THE MEMBRANE



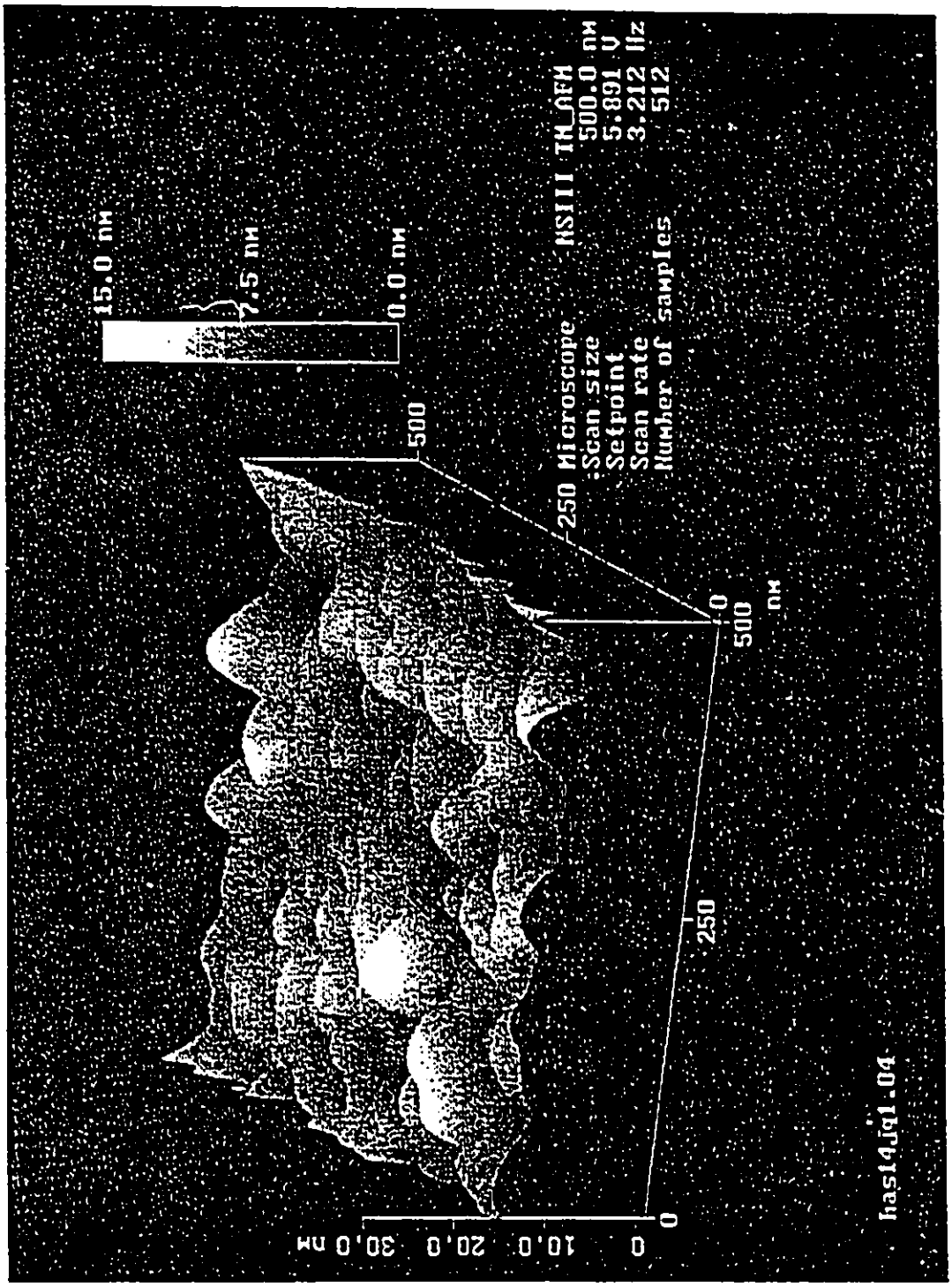
APPENDIX A-8

AFM MICROGRAPH OF THE SKIN LAYER OF THE MEMBRANE AT 0 HOUR



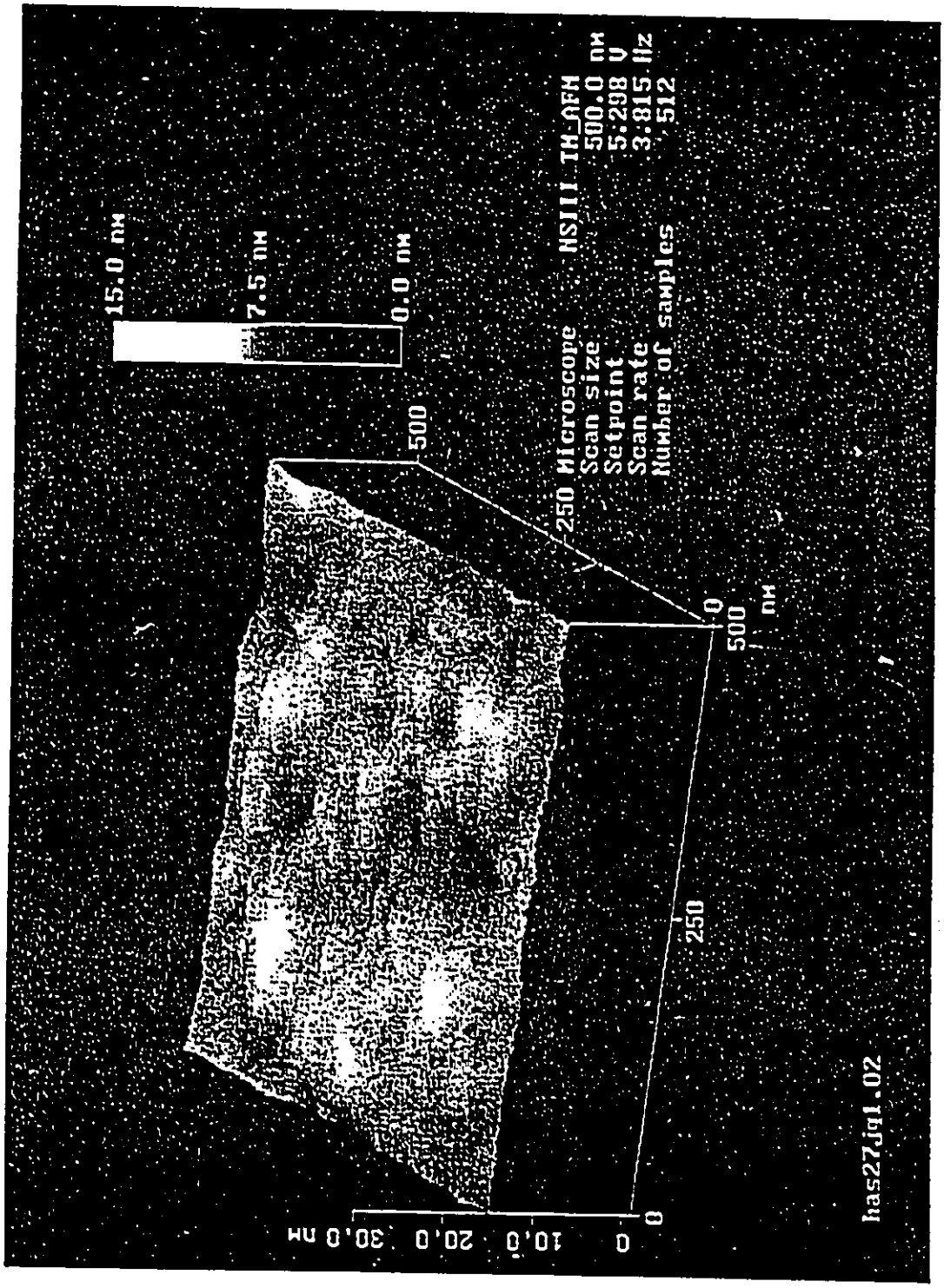
APPENDIX A-9

AFM MICROGRAPH OF THE SKIN LAYER OF THE MEMBRANE AT 24 HOURS



APPENDIX A-10

AFM MICROGRAPH OF THE SKIN LAYER OF THE MEMBRANE AT 240 HOURS



APPENDIX B

CALIBRATION DATA AND CURVE FOR GC (P&T)

Calibration Data	
Area x 10^-6	Conc ppm
0	0
4.6	1.3
4	1.1
11.7	3.8
13.2	3.8
50	10
52.3	10
51.4	10
51.8	10
50.5	10
55	10
48.9	10
46.9	10
48	10
46.4	10
54.2	10
54.4	10
36.9	11.3
33.2	11.4
67.5	16
67.7	16
70.5	16
65.6	16
93.7	20
90.6	20
130	30
131	30
173	40