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Synthesis and Properties of Thin-Film Polyvinyl Alcohol Composite Membranes

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A Thesis

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the University of Ottawa

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Abstract

Thin-film composite (TFC) membranes were developed with a polysulfone UF membrane used as the microporous substrate, polyvinyl alcohol as the material for skin layer formation and malic acid as the cross-linking agent. The cross-linking reactions of the membrane skin layer were carried out at high or ambient temperatures, and at the interface by using two miscible or immiscible solvents. Various parameters involved in the TFC membrane-making process have been investigated, and the flux change corresponding to individual steps in the membrane-making process was identified. The membrane transport properties and surface characteristics were studied by exposing membranes to chlorine test, by determining separations for various inorganic electrolyte and organic solutes, and by measuring ion-exchange-capacity. Separation experiments revealed the negatively charged feature of the PVA TFC membrane surface. Further, liquid chromatography was introduced to study the interfacial interaction forces working between membrane and solute in the membrane system. The TFC PVA membranes developed in this work can be classified into reverse osmosis membranes and nanofiltration membranes. The former class of membranes exhibits sodium chloride separation of 90% and product rate of 14 g/10 cm^2.h when the feed sodium chloride concentration and operating pressure are 2000 ppm and 1724 kPag, while the latter class of membranes exhibits sodium chloride separation of 70% and product rate of 45 g/10 cm^2.h at the operating pressure of 1550 kPag.

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I would like to thank Professor T. Matsuura and Professor S. Sourirajan for their assistance and guidance in the completion of this thesis.

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Nomenclature

PS:	Polysulfone
PES:	Polyethersulfone
PVA:	Polyvinyl alcohol
TFC:	Thin-film composite
UF:	Ultrafiltration
HGO1:	A type of UF membrane made from PS
HPO9:	A type of UF membrane made from PES
f:	Solute separation based on the feed concentration, %
PR:	Product rate through effective area of membrane surface, g/hr.
PWP:	Pure water permeation rate through effective area of membrane surface, g/hr.
R series:	R series TFC PVA membrane
N series:	N series TFC PVA membrane
N_1 series:	N_1 series TFC PVA membrane
N_2 series:	N_2 series TFC PVA membrane
IEC:	Ion exchange capacity, meq/g
V_1:	Volume of NaOH solution added, mL
C_1:	Equivalent conc. of NaOH solution, N
V_2:	Volume of HCl solution added, mL
C_2:	Equivalent conc. of HCl solution, N

W_2: Weight of composite membrane, g

W_1: Weight of substrate, g

Greek Letter

α: Separation factor o fpervaporation gas separation process

Chapter 1

1. Introduction

1.1 Membrane Separation Processes

In the last three decades, membrane processes have become a widely applicable technique of chemical engineering for the separation, concentration or fractionation of inorganic or organic substances in liquid or gaseous mixtures (Mulder, 1991). The advantages of the membrane separation processes are that no heating and phase change are involved. Their systems are compact, flexible and simple, and the processes are less energy intensive and more economical to operate. Membrane separation processes usually consist of letting a fluid mixture flow through an appropriate membrane, and withdrawing the membrane permeated product; the product is enriched in one or more constituents of the mixture. The heart of this separation technique is the membrane, which is a thin two-dimensional structure and mostly made from polymer materials and designed to pass preferentially certain components. Figure 1.1

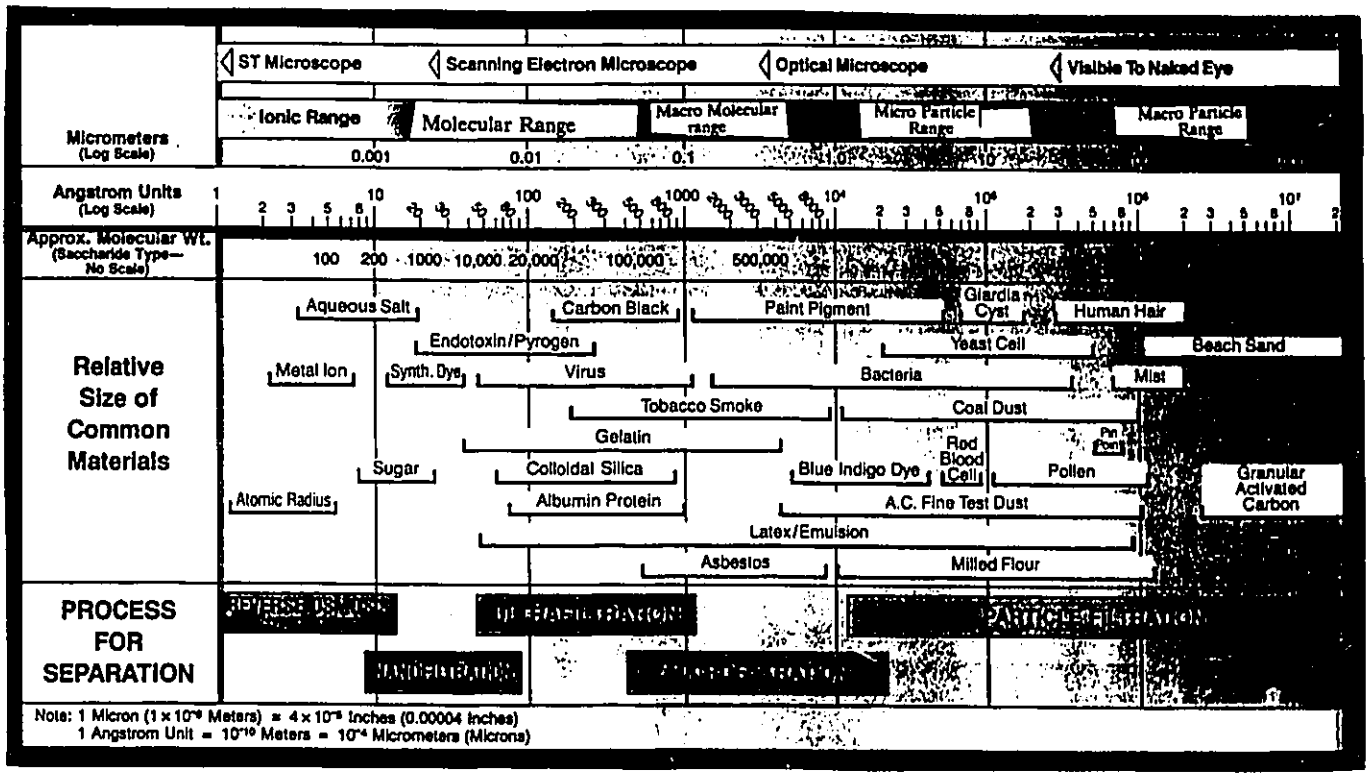


Figure 1.1: The classification of membranes based on separation process (Osmonics, 1990)

illustrates a newly updated synthetic polymer membrane classification concerned with liquid separation processes according to the membrane's structure (pore size) and application fields (Osmonics, 1990). It is needless to say that membrane development has played an important role in the study and application of membrane separation processes.

1.2 Thin-Film Composite Membranes

Thin-film composite membrane is a descendant of the Loeb-Sourirajan membrane--the first commercial reverse osmosis membrane (Sourirajan, 1981), and is composed of an ultrathin and dense polymer skin formed over a microporous support film (Cadotte, 1981). The Loeb-Sourirajan membrane was an asymmetric film having a dense surface layer about 2000 Angstroms thick integrally placed over a porous underlayer. The asymmetric membrane was made in one stage by casting a single polymer solution on a woven or nonwoven backing material, for instance, polyester fibres. The thin-film composite membrane, on the other hand, is made in two stages-casting of one kind of polymer solution on a backing material to produce a microporous support, followed by deposition of another polymer material to form a ultrathin skin layer on the previous microporous support (called substrate). The schematic diagrams of the Loeb-Sourirajan membrane and the thin-film composite membrane are shown in Figure 1.2 and Figure 1.3, respectively. The advantage gained by using the "composite" approach is that each material used

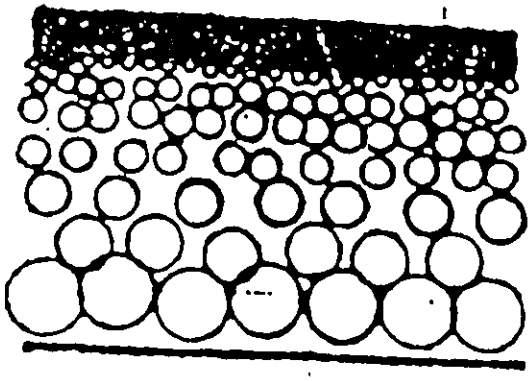


Figure 1.2: The schematic of the Loeb-Sourirajan membrane

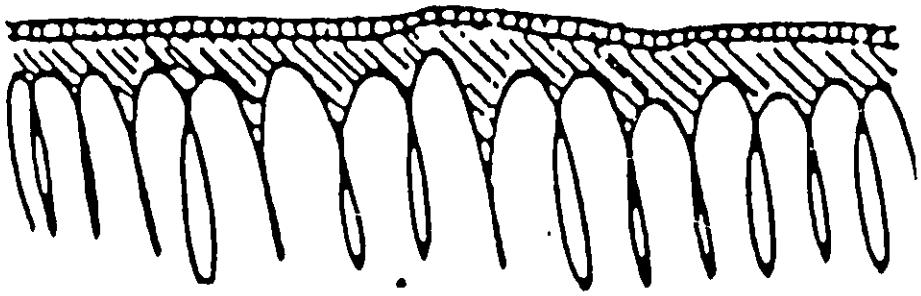


Figure 1.3: The schematic of Thin-film composite membrane

for the microporous support film and the skin layer can be optimized separately to provide improved membrane performance. In comparison with Lob-Sourirajan membrane, thin-film composite membrane could reach a relatively high level in terms of membrane stability, flux and solute separation.

1.3 Polysulfones and Polyvinyl alcohol

Aromatic polysulfones have proven useful as membrane materials (Sourirajan and Matsuura, 1986). Because of the highly oxidized state of the sulphur atom and the para position of sulfone group, polysulfones exhibit excellent oxidation resistance, thermal stability, mechanical strength and protection against degradation by extreme pH conditions. In fact, most widely used ultrafiltration (UF) membranes are prepared from the polysulfone materials. It is presently impossible, however, to prepare commercial reverse osmosis membranes from the materials. This is because the hydrophobic properties of the polysulfones make it difficult to prepare membranes which have small pore sizes and high water flux.

Being a material with high water permeability and very good film forming properties, polyvinyl alcohol always seemed an attractive material for reverse osmosis membranes, although it has been shown to have poor salt selectivity (Kaze and Wydeven, 1981). From the membrane application points of view, polyvinyl alcohol is generally unaffected by grease, hydrocarbons, and animal or vegetable oils; it has outstanding physical and chemical stability

against organic solvents. Polyvinyl alcohol may be used in many food contact applications. With respect to the membrane preparation, polyvinyl alcohol is readily soluble in water, and no specific solvent is needed. Polyvinyl alcohol molecules can cross-link with each other when reacting with diacids or dialdehydes under the certain conditions. Thus, by chemical cross-linking method, the selective permeability to water and salts of PVA membranes could be improved considerably.

In this work, polysulfone UF membranes were used as the microporous support (substrate), and polyvinyl alcohol was used as the material of skin layer for the composite membranes. The goal of the membrane development is to prepare thin-film composite reverse osmosis (RO) membranes with a separation of 90% for 2000 ppm NaCl solution, and nanofiltration membranes with a lower separation and higher product rate.

1.4 Liquid Chromatography and Membrane Studies

The liquid chromatography system is considered to be similar to the membrane-solution system in membrane studies (Taketani et al., 1982; Matsuura and Sourirajan, 1982; Tam, 1989; Fang, 1990). The chromatography system consists of a mobile liquid phase and a stationary liquid phase as well as packed polymer material. If the polymer from which the membranes are made is used as packing material in the chromatography column, there will be a direct relationship between the interaction forces at the membrane-

solution interface and the physicochemical process in the liquid chromatography system. The bulk solution and interfacial liquid layer of the membrane system are analogous to the mobile phase and stationary phase in LC system, respectively. Therefore the interactions on the membrane surface can be determined by relating the interfacial behaviour to the quantitative values of retention time obtained in the LC system.

Chapter 2

2. Literature Survey

2.1 Origin and Development of Thin-Film Composite (TFC) Membranes

In 1960 the discovery of the first practically useful reverse osmosis membrane was announced (Loeb and Sourirajan, 1960). This Loeb-Sourirajan membrane consisted of a single polymer cellulose acetate (CA), and had an asymmetric structure. Since then, considerable attempts have been made by many membrane researchers to form an ultrathin surface layer separately from the porous sublayer by using optimized polymer materials for each layer.

The earliest TFC reverse osmosis membrane was developed by Francis in 1964 (Francis, 1966). The ultrathin surface layer was formed by float-casting a liquid film of CA upon a water surface, and then the ultrathin layer was laminated onto a pre-prepared microporous CA support sheet to form the composite membrane. Almost at the same time, Riley et al. (1969) also made a composite membrane by coating a CA solution on a pre-formed cellulose nitrate microporous support sheet. In comparison with Loeb-Sourirajan membrane, the performance of these early composite membranes

provided no significant improvements. The problems associated with compaction and low surface porosity of the asymmetric support sheets appeared in long term and high pressure tests.

Cadotte made significant contributions to the development of TFC membranes by developing a type of new UF membrane from polysulfone material (Rozelle et al., 1967) and later using it as the support sheet of the NS-100 TFC membrane (Rozelle et al., 1977). The polysulfone film proved to have an excellent combination of compression-resistance and surface microporosity. The NS-100 composite membrane contained a cross-linked ultrathin aryl-alkyl polyurea skin on a microporous polysulfone (Udel P-3500) sheet. This TFC membrane, either in the surface layer zone or in the support layer zone, was fully noncellulosic. Since then, most TFC membranes have been made with noncellulosic polymer materials.

In the past twenty years, a wide variety of new achievements about TFC membrane development have been reported around the world, although only some of the TFC membranes, which are all generated by American or Japanese industrial companies, have reached commercial status. Polyamine and aromatic polyamine are considered as ideal synthetic ultrathin skin materials. On the other hand, many other new and modified polymer materials, for instance, polyvinyl alcohol (PVA) and sulfonated polyphenylene oxide (SPPO), have been examined as membrane application is spreading from its initial purpose of desalination to separation of not only inorganic substances but also organic substances. Since the phase inversion process used for fabricating the asymmetric CA membrane could not be used to produce

extremely thin membranes, several new routes have been utilized in making numerous TFC membranes. Table 2.1 and Table 2.2 present the reverse osmosis performance of some advanced TFC membranes and the structures of their ultrathin skin layer, respectively. The preparative methods for TFC membranes and the progress of PVA membranes will be evaluated in the following sections.

2.2 Evaluation of Preparative Methods for TFC Membranes

During the development of TFC membranes, attention had been focused on the formation of the ultrathin skin layer of the membranes. Generally, there are five different processes used for the preparation of TFC membranes. They are 1) casting a skin layer separately, then laminating to a support sheet, 2) gas-phase deposition of a skin layer from a glow discharge plasma, 3) dynamical formation of a thin film layer on the top of a porous substrate, 4) dip-coating a support sheet in a reactive monomer or a polymer solution followed by curing with heat or radiation and 5) interfacial polymerization of reactive monomer at the surface of a support sheet.

The first method was used in the preparation of TFC CA membrane in the early stage of the membrane development. This has been briefly discussed in section 2.1. The membrane made by this method never reached commercial viability, and the method was not reported in use for decades, although it is a general method which could be used with other polymers. There were several reports in

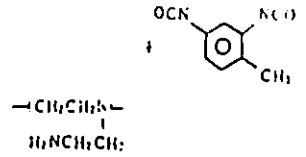
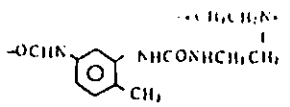
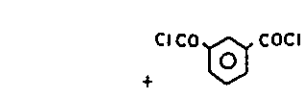
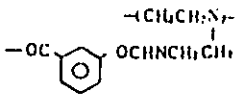
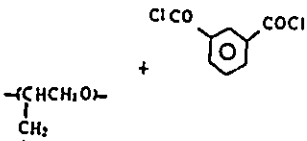
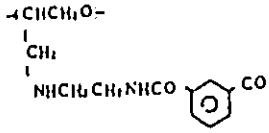
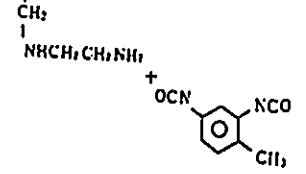
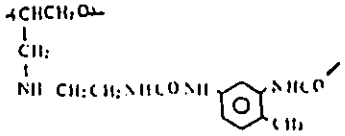
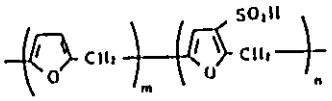
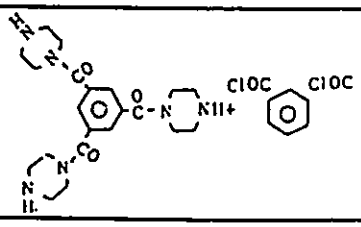
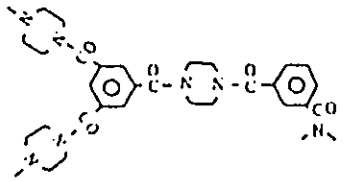
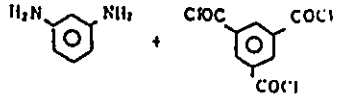
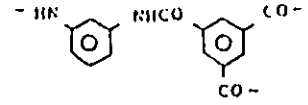
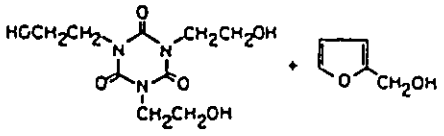
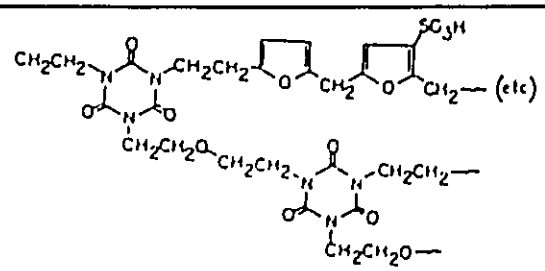
Table 2.1: The RO performance of some advanced TFC membranes *1

Membrane trade name and its (Manufacturer)	Properties		pH range	Reference
	Separation (%)	Product rate ($l/m^2.d.atm$)		
NS-100 (NSRI)	99.4	7.1	0.5-13	Rozelle et al., 1977
NS-200 (NSRI)	>99	10.8-12	1.5-13	Cadotte et al., 1974
NS-300 (Film-Tec.)	99.6	11.1	1.5-13	Cadotte et al., 1976
PA-300 (UOP)	98.5-99.4	12-15	2-12	Riley et al., 1976
RC-100 (UOP)	99.4	9.7-11.2	2-12	Riley et al., 1977
FT-30 (Film-Tec.)	98.7	17.7	3-11	Cadotte et al., 1985
NTR-7250 (Nitto Electric)	99.5 *2	24.6	5-11	Brady et al., 1984
PEC-1000 (Toray Industries)	99.8	5.36	1-13	Kurihara et al., 1982
Solcon-P (Sumitomo Chemical)	98	9.6	1-10	Sano et al., 1979

*1 feed: 3.5% NaCl solution.

*2 feed: 0.5% NaCl solution.

Table 2.2: The skin layers of some TFC membranes

Membrane trade name	Chemicals for skin layer	Skin layer structure
NS-100		
PA-100		
PA-300		
RC-100		
NS-200		
NS-300		
FT-30		
PEC-1000		

1970's about the formation of the skin layer of TFC membranes by plasma polymerization (Sano et al., 1979; Riley et al., 1967; Carnell, 1963; Petersen et al., 1975). A variety of organic gaseous phase monomers, for instance vinyl monomers, could be utilized in this technique to deposit a skin layer on a dry support sheet. But the gas phase deposit was quite heterogeneous, and it involved several reactions including polymerization, depolymerization and modification of functional groups. Dynamically formed membranes were among the earliest attempts to make very thin skin layer of synthetic membranes. Marcinkowsky et al. (1966) discovered that when colloidal particles in aqueous solution were passed under pressure across the surface of a finely porous solid a dynamic membrane was formed as the colloidal particles lodged in the surface pores. Many colloidal and non-colloidal particles, such as hydrous zirconium oxide, decaying leaves, and some polymers, were used over the years to make dynamic membranes (Johnson, 1972). Similarly, a variety of finely porous substances were tried as substrates, including stainless steel, carbons, and many ceramics. However, the dynamic membranes were difficult to form with good reproducibility and adequate salt rejection, and the membrane's application reached a very small industrial scale (Lonsdale, 1987).

An apparently versatile approach for TFC membranes seems the dip-coating method. One of the outstanding TFC membranes, named NS-200 membrane, was prepared by this method (Cadotte et al.,): a polysulfone support sheet was immersed in a 2 : 2 : 1 solution of

furfuryl alcohol : sulphuric acid : carbowax 20M in 80 : 20 mixture of water : isopropanol. The excess coating solution was allowed to drain off. After being cured in an oven at 125 to 140°C a sulfonated polyfuran skin layer was produced. Another excellent example of dip-coating fabrication is the PEC-1000 TFC membrane. The membrane is formed by acid-catalyzed condensation of the monomer 1,3,5-tris-(hydroxyethyl)isocyanuric acid (THEIC) on a microporous polysulfone and cured at 150°C for 15 minutes (Kurihara et al., 1982). The technical obstacle of the dip-coating method is the filling of surface pores of supporting polysulfone sheet with the coated chemical matters, which leads to a low flux across the membrane.

The first commercially interesting and noncellulosic TFC membrane, called NS-100, was the product of the interfacial polymerization method (Rozelle et al., 1977). The preparation of this membrane involved two steps. First a polysulfone support sheet was immersed in a water solution of a polymeric amine (0.5 to 1.0 per cent solution of polyethylenimine). After draining of the excess solution, the coated polymeric amine layer was brought in contact with a solution of 0.1% tolylene diisocyanate in hexane to form a very thin cross-linked polyurea zone by the interfacial reaction. In the second step, the film was heated in an oven at 110°C for 15 minutes to perform the crucial cross-linking of the residual unreacted polyethylenimine. Since the success of the NS-100 composite membrane, various polyamines have been synthesized and evaluated in the fabrication of this type of membrane. Perhaps

the crowning achievement of all efforts is the FT-30 membrane. The FT-30 was produced by the interfacial reaction of aromatic diamines (for example, m-phenylene diamine) in the aqueous phase with triacyl chlorides (for example, trimesoyl chloride) in the solvent phase (Cadotte, 1984). The FT-30 membrane showed excellent properties in terms of salt rejection, water productivity, chemical stability, and nonbiodegradability. From the commercial standpoint, the in situ interfacial polymerization is the most attractive method for preparation of TFC membranes.

In recent years, some new methods have been introduced into membrane preparation, such as photochemical reaction modification (Dickson and Tse-sheepy, 1989), the drying-leaching two-step method (Heinzelmann et al., 1991) and graft modification (Chiang and Hu, 1991). It still needs time to see the effects of these methods on TFC membrane development.

2.3 Development of Polyvinyl Alcohol (PVA) Membranes

PVA has been investigated in various membrane preparations and applications because the membranes made from PVA polymer could have high water permeability and excellent chemical stability. Table 2.3 shows an earlier experimental result of chemical stability of PVA membrane compared with polyvinyl butyral, polyvinyl acetate and cellulose acetate membranes. PVA material illustrated very reliable stability in all the experimental cases. Unlike the CA membrane and TFC membranes described previously in

section 2.1 and 2.2, PVA membranes were originated not only for desalination purposes but also for the separations of organic compounds by reverse osmosis and water/ethanol separation by pervaporation. Therefore, in addition to the PVA TFC membranes and their RO applications, the PVA asymmetric membranes as well as PVA membranes's other applications are covered in this brief review. The historic development of PVA membranes and their experimental performance are listed in Table 2.4.

Table 2.3: Chemical stability of PVA membrane at 20°C (Peter et al., 1976)*

Reagent	Concentration (weight %)	pH	Membrane material			
			PVA	PVB	PVAc	CA
HNO_3	12	0	3	0	0	0
H_2SO_4	48	0	3	0	0	0
HCl	7	0	3	0	0	0
NH_4OH	25	13	3	0	0	0
NaOH	10	14	3	0	0	0
Phenol	0.1	3	3	0	0	0
Phenol	1.0	3	3	0	0	0
Phenol	2.0	3	3	0	0	0
Ethanol	100	7	3	0	0	0
DMF	100	7	3	0	0	0
DMSO	100	7	3	0	0	0
Formamide	100	7	3	0	0	0

Stability degrees:
0=Destruction of membrane
1=Strong swelling, decrease of membrane properties
2=Little swelling, membrane still usable
3=Stable, no alteration of membrane properties

* The stability degrees were defined by Peter et al..

PVA: Polyvinyl alcohol
PVB: Polyvinyl butyral
PVAc: Polyvinyl acetate
CA: Cellulose acetate

Table 2.4: PVA Membrane Development Riview

Researcher	Method	Experiment (1) or (2)	f(%) or α	PR g/10 cm^2.h
Binning et al., (1961)	PVAc-PVA-dense film	water/ethanol (2)	99.5 (2)	low
Michelson and Harriott (1969)	No treatment	1000ppm NaCl 4200 kpag (1)	10 (1)	high
Huang and Jarvis (1970)	biaxialy oriented PVA film	water/alcohol (2)	50-250 (2)	0.75
Peter et al., (1971)	Bicarboxylic acid, heating	2000ppm phenol, 5000 bar (1)	74 (1)	1.23
Chen and Chang (1973)	Formalization	1000ppm NaCl, 4200 kapgr (1)	92 (1)	4.1
Dick et al., (1975)	Tolylene Diisocyanate crosslinking	1000ppm NaCl 5000 kpag (1)	98 (1)	2.1
Peter et al.,(1976)	Calcium-ion crosslinking	2000ppm phenol, 5000 kpag (1)	90-95 (1)	3
Peter et al.,(1978)	Cr^{3-}, Fe^{3-} Organic compounds	2000ppm phenol, 5000 kpag (1)	95 (1)	3
Peter et al., (1981)	Dicarbonyl, heating	2000ppm phenol, 5000 kpag (1)	97 (1)	9.5
Katz et al., (1981).	PVA Radiation crosslinking	2000ppm NaCl 7000 kpag (1)	35 (1)	high

(1): reverse osmosis experiments, f: separation (%)

(2): pervaporation or gas separation, α: separation factor.

Table 2.4: PVA Membrane Development Riview (continued)

Researcher	Method	Experiment (1) or (2)	f(%) or α	PR g/10cm^2.h
Katz and Wydeven (1982)	PVA Heating	2000ppm NaCl 7000 kpag (1)	90 (1)	10
Koyama et al., (1982)	PVA/PSSA heating	0.5% NaCl 4000 kpag (1)	85 (1)	1
Wang et al., (1983)	Dynamic	3000 ppm phenol 4000 kpag (1)	90 (1)	5000
Kakuse et al., (1986)	PVA-amino compound-trimesic chloride	2000ppm NaCl 1000 kpag (1)	97 (1)	40
Brannon et al., (1987)	drying/ precipitation/ crosslinking	Vitamin B12 diffusion		
Nobrega et al., (1987)	Heating	Water/ethanol (2)	87.5 (2)	1.5
She and shen, (1987)	Bicarboxylic acid crosslinking	2000ppm NaCl 4000 kpag (1)	85 (1)	10.5
Lemuel et al., (1988)	Formaldehyde crosslinking	Controlled release drug		
Yan et al., (1988)	Co^{60}-γ ray heating	Water/alcohol (2)		

(1): reverse osmosis experiments, f: separation (%)

(2): pervaporation or gas separation, α: separation factor.

Table 2.4: PVA Membrane Development Riview (continued)

Researcher	Method	Experiment (1) or (2)	f(%) or α	PR g/10 cm^2.h
Zhang et al., (1988)	Glutaraldehyde crosslinking	Gas O_2/N_2 (2)	4-14 (2)	
Nakanishi et al., (1989)	Haloacetalization-amination	Membrane potential and salt permeability		
Hirai et al., (1989)	Freezing-thawing	1.0 % PEG-400, 2000 kpag (1)	70 (1)	4.1
Hanaoka et al., (1990)	Freezing-thawing	Anisotropy in contraction behavior		
Huang and Yeom, (1990)	Amic acid crosslinking # 1	Water/ethanol (2)	70-380 (2)	1.6
Huang and Yeom, (1991)	Amic acid crosslinking # 2	Water / acetic acid (2)	34-176 (2)	0.7
Chiang and Hu (1991)	Graft modified	Water/ alcohol (2)		
Sanderson et al., (1992)	$K_2S_2O_8$ Insolubilization	1000ppm $MgSO_4$ 2.0 MPa (1)	90 (1)	20-65

(1): reverse osmosis experiments, f: separation (%)

(2): pervaporation or gas separation, α: separation factor.

Chapter 3

3 Experimental Methods

3.1 Membrane Preparation

3.1.1 Materials frequently used in the experiment

Polyvinyl alcohol: BDH prod. 66303, Molecular weight=65,000, Degree of hydrolysis=98%.

The molecular structure of PVA polymer is shown in Figure 3.1.

Cross-linking reagent: Malic acid, Fisher Scientific, Molecular weight=134.09;
or glutaraldhyde, Fisher Scientific, Molecular weight=100.02.

The molecular structure of malic acid is shown in Figure 3.2.

Cross-linking catalyst: acetic acid for malic acid,
or sulphuric acid for glutaraldhyde.

Solvent for PVA and cross-linking reagent: Distilled water and others.

Substrate: Polysulfone UF membrane, Type HGO1,
Polyethersulfone UF membrane, Type HPO9.

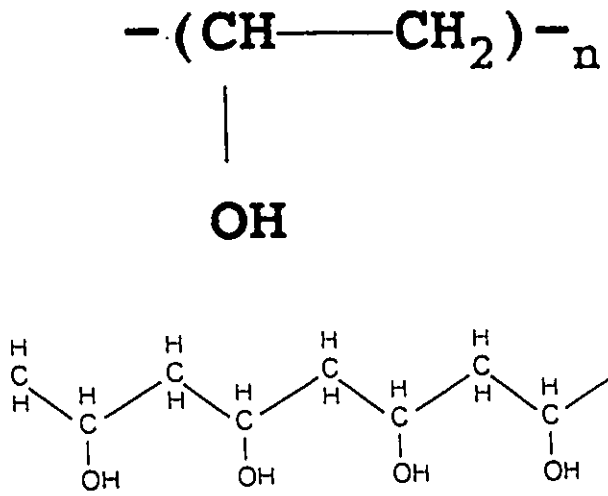


Figure 3.1: The molecular structure of PVA polymer

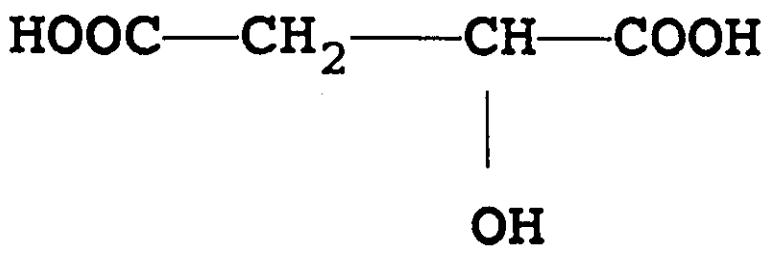


Figure 3.2: The molecular structure of malic acid

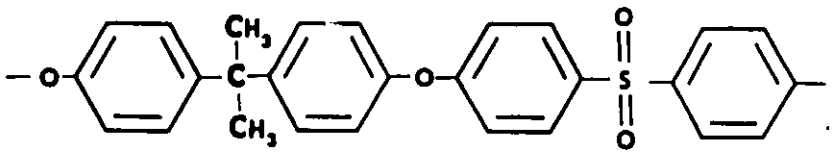


Figure 3.3: The chemical structure of polysulfone

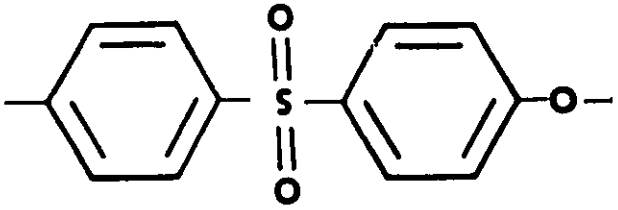


Figure 3.4 The chemical structure of polyethersulfone

The HGO1 and HPO9 UF membranes were provided by Osmonics Inc. U.S.A. The chemical structures of polysulfone and polyethersulfone are shown in Figures 3.3 and 3.4.

3.1.2 Membrane preparation procedure

The composition of the PVA polymer solution was as follows (weight%):

Polyvinyl alcohol:	*1 - 5*
Distilled water:	*99 - 95*

The cross-linking solution had the following composition (weight%):

Malic acid:	*0.5 - 6.0*
acetic acid:	*2.5*
Distilled water:	*97 - 92.5*

The preparation of the thin film composite membrane in this work was mainly concentrated on the formation of a cross-linked PVA skin layer on the UF membrane substrate. The procedure consisted of five main steps: 1) preparation of the PVA polymer solution, 2)coating of PVA polymer solution on the substrate and 3) drying of the cast film, 4) immersion of the film in a solution of cross-linking reagent and 5) heating of the membrane. A casting solution containing polyvinyl alcohol, distilled water and sometimes an additive (see chapter 4 for details) was stirred with a magnetic stirrer in a sealed glass bottle at 90 ^{o}C for 5 hours. The above solution was then coated on an ultrafiltration membrane which acted

as a microporous support. The coating method was either casting or dip-coating. After allowing to dry for several hours, the coated film was immersed into the cross-linking solution, which contained malic acid as cross-linking reagent (or glutaraldhyde) and acetic acid (or sulphuric acid) as catalyst, for a few seconds. Then the membrane was withdrawn from the cross-linking solution and heated in an oven at a predetermined temperature for a predetermined period. While being heated, malic acid reacted with polyvinyl alcohol polymer to form an ultrathin cross-linked layer on the surface of the polyvinyl alcohol film. The whole procedure is represented schematically in Figure 3.5. All details relating to the PVA solution composition, the composition of the cross-linking solution, the drying period, and the heating temperature and period are important variables in developing successful composite membranes. The membranes made by the above procedure had a dense fine pore structure (pore size, less than 20 Å) of an extremely thin layer on the membrane surface, where cross-linking reaction occurred. The remainder of the PVA film underneath this thin layer had relatively large pores. In addition, the ultrafiltration membrane as a supporting material to the PVA film, had even larger pores (pore size, more than 1000 Å). The membrane of the above structure is hereafter called TFC PVA membrane. Figure 3.6 schematically gives the cross-section of the PVA TFC membrane. It is the dense ultrathin surface structure which governs the level of solute separation, and hence is held in contact with the feed solution during separation operation.

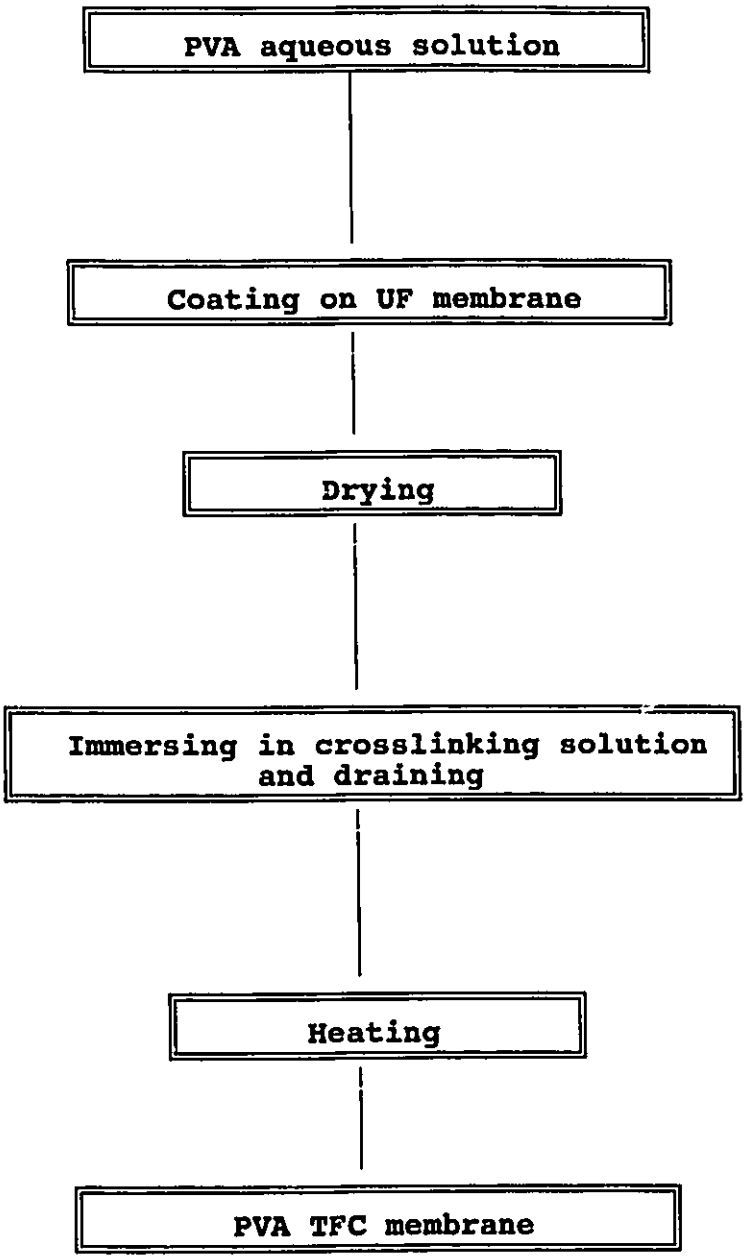


Figure 3.5: Schematic diagram for the preparation of PVA TFC membrane

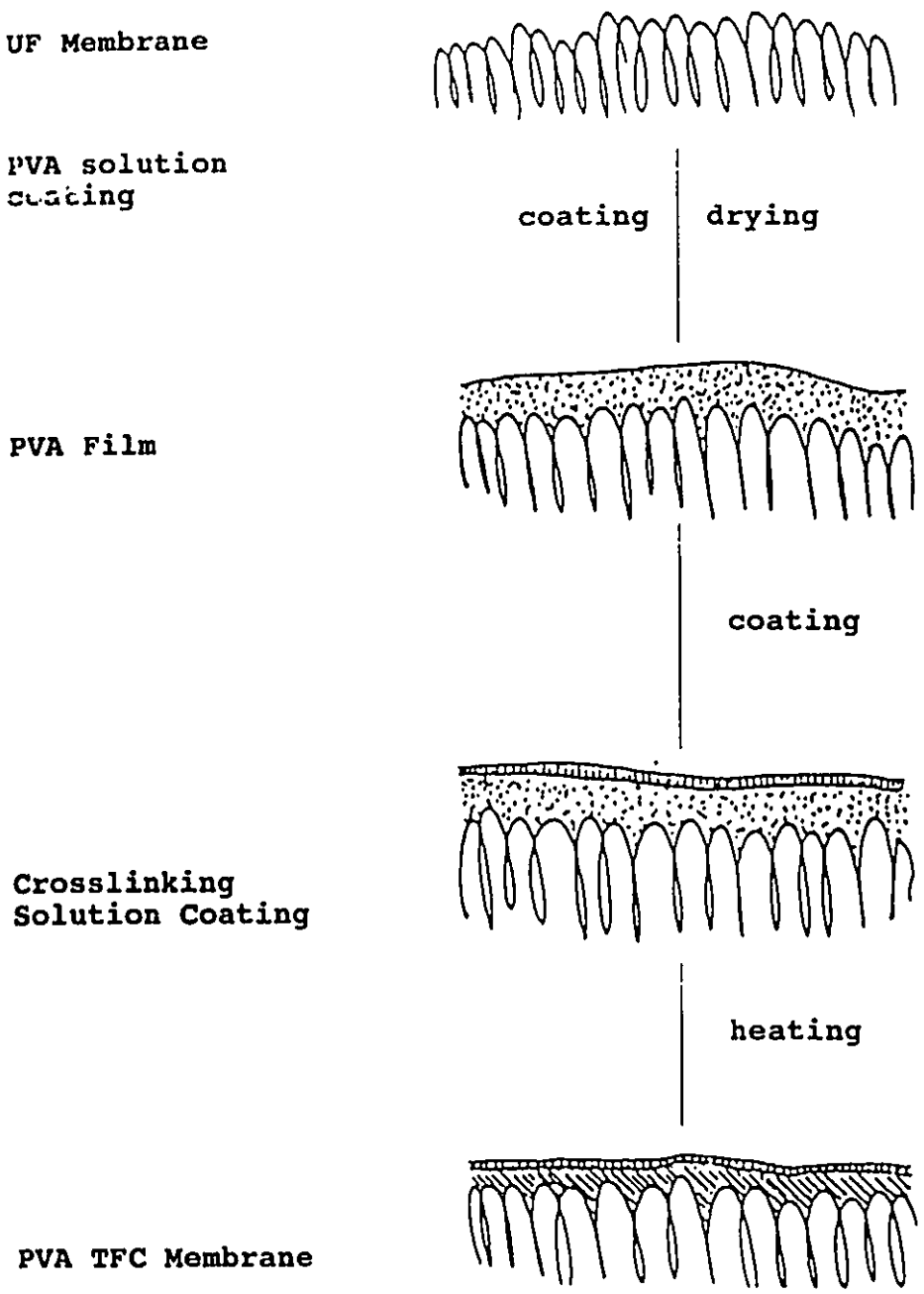


Figure 3.6: Schematic representation of the structure of the PVA TFC membrane

3.2 TFC Membrane Testing Procedure

The reverse osmosis cell, shown in Figure 3.7, was used to test the performance of the TFC PVA membranes. The cell consists of two detachable parts. The upper part is a high pressure chamber provided with inlet and outlet openings for the flow of the feed under pressure. The lower part is the membrane stand provided with an outlet opening for the withdrawal of the membrane permeated product solution. The membrane was mounted on a stainless steel porous plate embedded in the lower part of the cell. The upper and lower parts of the cell are set in proper alignment with rubber O-ring contacts between the high pressure chamber and the membrane. The effective area of the membrane in the cell is 10.2 sq. cm.

Six cells were used in series so that six different membranes could be tested at the same time. Since the ratio of retentate of feed solution to permeate is very large (at least 500 : 1), the concentration of feed solution entering each of six cells is practically the same. A schematic flow diagram of the experimental arrangement is shown in Figure 3.8 (only one cell illustrated). A positive diaphragm pump was used to pump the feed solution under pressure through the cell. The surge tank, a stainless steel high pressure cylinder, was used to minimize the pressure fluctuations in the cells. Under the operating conditions the fluid pressure in the cell was indicated by a liquid sealed pressure gauge. All membranes were subjected to a prepressurization of 2412 kPag for

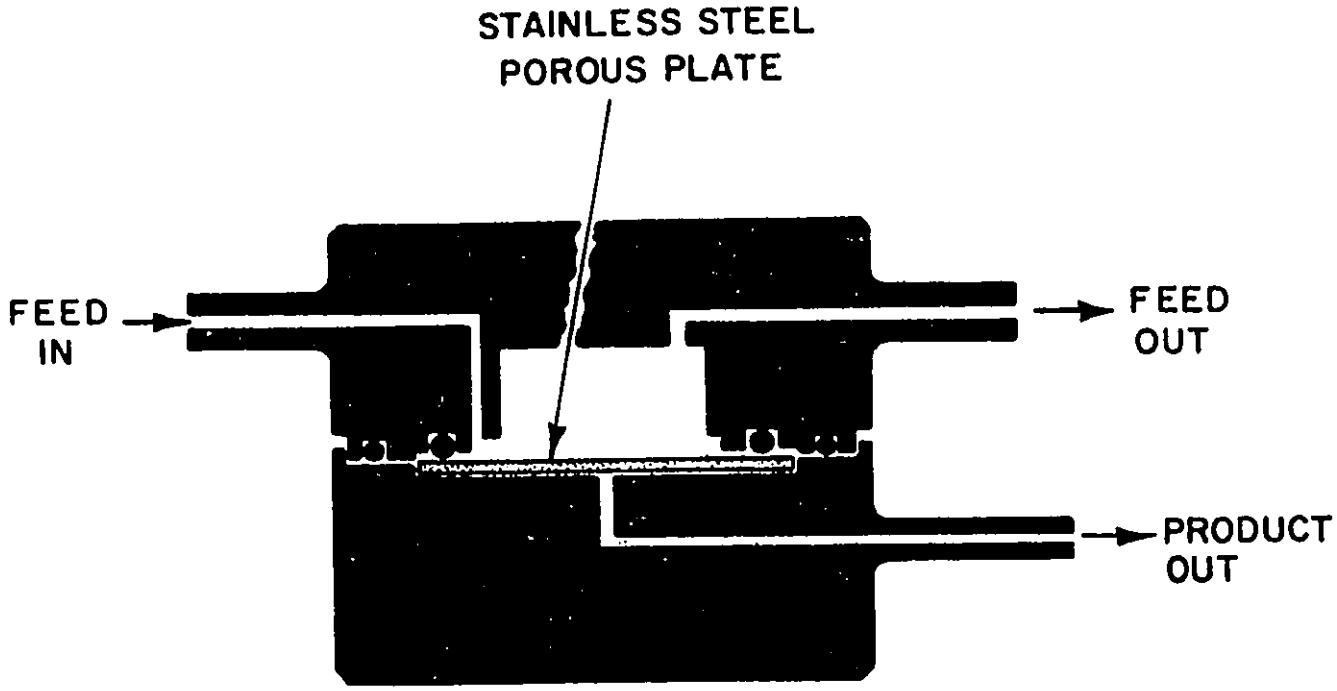


Figure 3.7: Cell for reverse osmosis membranes (Sourirajan, 1983)

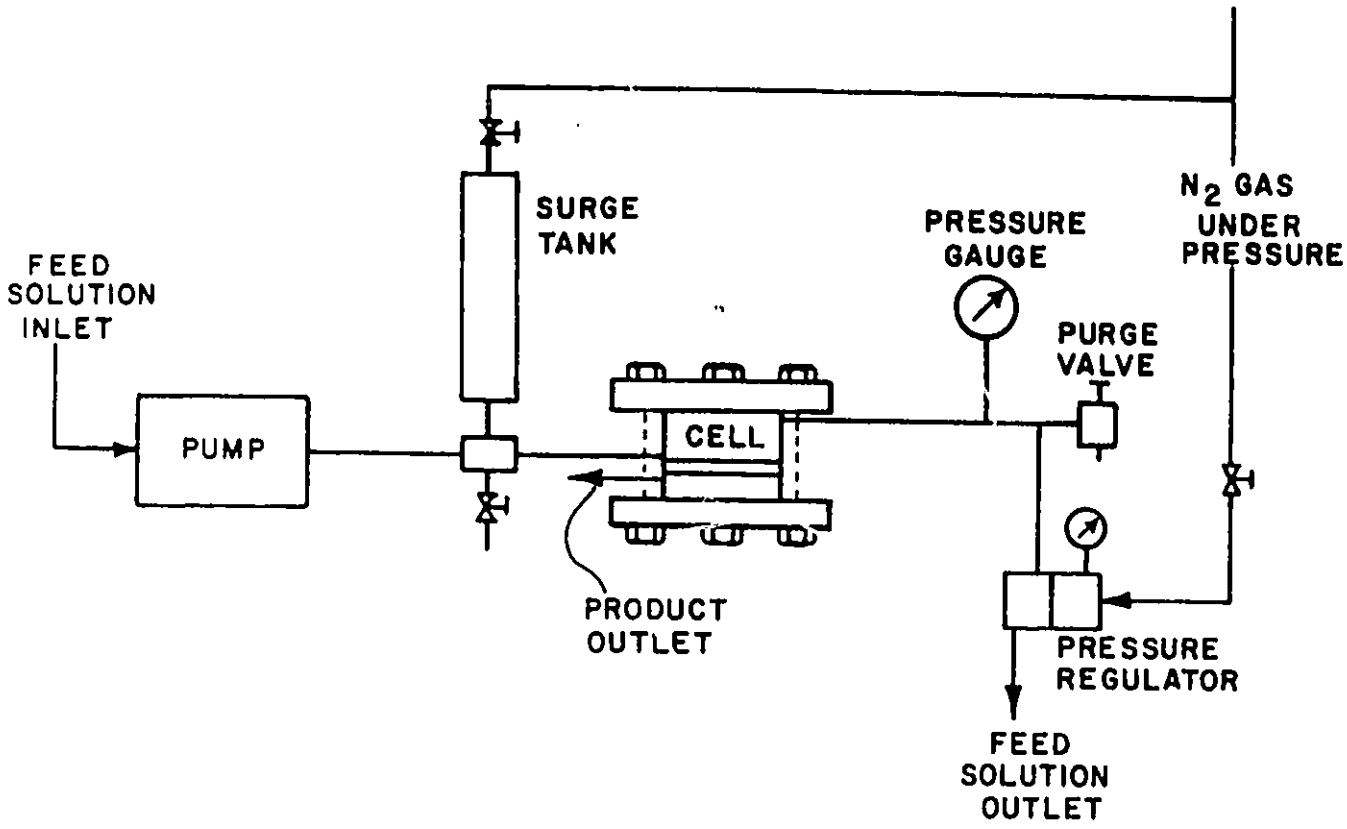


Figure 3.8: Schematic flow diagram of apparatus for reverse osmosis operation (Sourirajan, 1983)

an hour. The experiments were of the short-run type, each lasting for several hours, depending on the product rate of the permeated solution. They were carried out at room temperature, usually using an aqueous feed solution containing 2000 ppm of NaCl and a feed rate of 450 cc per minute at the operating pressure of 1724 kPag.

Some of the substrates and the PVA films were also tested in the reverse osmosis system following the same way as THC PVA membranes being tested.

The membrane performance was expressed in terms of separation (%) and product rate (PR), which are defined as follows:

$$Separation\ (\%) = \frac{(feed\ conc.) - (product\ conc.)}{(feed\ conc.)} * 100\ \%$$

$$PR\ (g/h) = \frac{permeated\ solution\ (g)}{time\ (hour)}$$

Sometimes, a pure water permeation rate (PWP) was also determined to characterize the membranes. The PWP was obtained in the absence of solute in the feed solution.

3.3 Ultrafiltration Performance of Substrate Membranes

The ultrafiltration performance of the two substrate membranes, HGO1 and HPO9, were investigated in the above reverse osmosis system following the TFC membrane testing procedure, except that aqueous solution of 100 ppm polyethylene glycol (PEG) was used

as feed and the operating pressure was 414 kPag. The concentrations of the feed and permeated solutions were determined by using a Total Organic Carbon Analyzer (Beckman Model 915B).

3.4 Separation of Various Inorganic Electrolyte Solutes and Organic Solutes

The separation experiments for various inorganic salts and organic samples were conducted in order to find out the resulting TFC PVA membrane's selectivities and the surface physical properties. The experiments followed the TFC membrane testing procedure except that the operating pressure was 1550 kPag. Immediately after the experiment for each sample was finished, the reverse osmosis testing system was cleaned by running distilled water at 1724 kPag for at least one hour.

3.5 Determination of Ion Exchange Capacity of the PVA TFC Membrane

The Ion Exchange Capacity (IEC) is defined as the ratio of milliequivalent value of the free acid form (H-form) in the polymer to unit weight of the dry cross-linked polyvinyl alcohol polymer. To determine the IEC value, the PVA polymer weight on the membrane must be known first. A piece of the ultrafiltration membrane used as the substrate to the PVA TFC membrane was heated in an oven at 100 ^{0}C for 10 minutes until it was dried, and then it was weighed (W1). The PVA membrane was made according to the membrane

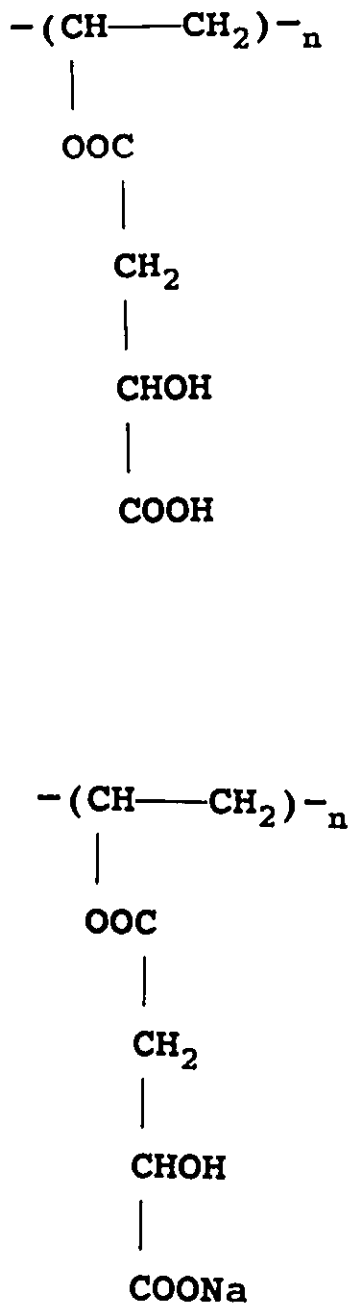


Figure 3.9: The chemical structure of the acidic form and the sodium ion form of the PVA polymer

preparation steps in section 3.1.1, dried and then weighed (W2). The weight of the cross-linked PVA polymer depends on the amount of PVA layer consumed in the reaction. Since high separation value was achieved for the TFC PVA membranes, we assume that the half of PVA polymer was cross-linked, therefore the weight of the cross-linked PVA polymer equals $(W_2 - W_1)/2$.

The weighed PVA membrane coupon was placed into an aqueous solution containing an excessive amount of sodium hydroxide and shaken for 5 hours. The proton in the acidic form of the polymer was exchanged with sodium ion and the resulting H^+ ions consumed a stoichiometric amount of hydroxide. The acidic form and the sodium ion forms of the PVA polymer are shown in Figure 3.9. The excess hydroxide in the above solution was then titrated with hydrochloric acid, using phenolphthalein (BDH Inc.) as a colour indicator. On the basis of above assumption, the IEC value was calculated as

$$IEC = \frac{(V_1\ C_1) - (V_2\ C_2)}{(W_2 - W_1)/2}$$

where: V_1 = volume of NaOH solution added, (ml),

C_1 = equivalent conc. of NaOH solution, (N),

V_2 = volume of HCl solution added, (ml),

C_2 = equivalent conc. of HCl solution, (N),

W_2 = weight of composite membrane, (g),

W_1 = weight of substrate, (g).

3.6 Liquid Chromatography Experiments

3.6.1 Packed polymer material

When the liquid chromatography method is used for membrane separation studies, the material packed in the column usually is the polymer from which the membrane is made. In this experiment, however, the surface of the finished membrane is not polyvinyl alcohol itself but the cross-linked polyvinyl alcohol polymer. For the similarities between the membrane separation system and the liquid chromatography system to be guaranteed, the packed polymer material should be the same as the surface material of PVA composite membrane. The method of the column packing employed in this experiment is as follows.

An aqueous solution of polyvinyl alcohol (10 wt-%) was mixed with an aqueous cross-linking solution containing malic acid (25 wt-%) and acetic acid (25 wt-%) in an open petri dish. The solution mixture was then heated in an oven at the temperature of 100 °C to form a sheet of solid cross-linked polymer, whose structure is considered similar to that of the surface of PVA composite membrane. The above polymer sheet was cut into pieces by using scissors, and crushed into powder in a mortar. The polymer powder so prepared was then sieved with 400 Mesh and 270 Mesh Tyler sieves to obtain the desired packing powder size of 38-53 μm diameter.

3.6.2 Column packing

The liquid chromatography column was a stainless steel pipe

with length of 12 cm and inside diameter of 0.1575 cm. Since the particles of the cross-linked polymer were electrically charged and could not be packed tightly in a dry state, the column was packed by a wet packing method under vacuum. The initial and remaining particles were weighed in their dry form. The weight of the polymer packed in the column was 0.1440 g.

3.6.3 Liquid chromatography

The liquid chromatography experiment was carried out with a Liquid Chromatograph (Waters Associate, Model 501) which was fitted with a R401 Refractometer. The refractometer signal was supplied to a Waters 745 Integrator. The solvent (water) was obtained from a Zenon Ultrapure Water System which ensured water purity of 18 MΩ of resistance. The solvent was degassed by boiling the water for 5 minutes. The water flow rate in the chromatograph system was 0.3 cm^3/min. An aqueous solution of one weight percent was made for each sample that includes a solute to be tested. Then, 10 μl of each sample solution was injected into the chromatograph by using a 50 μl Hamilton syringe. A certain period is required for a chromatography peak to appear on the recorder chart after the solute injection. The time which elapses between the solute injection and the peak maximum is defined as the retention time. The liquid chromatography system setup is given in Figure 3.10.

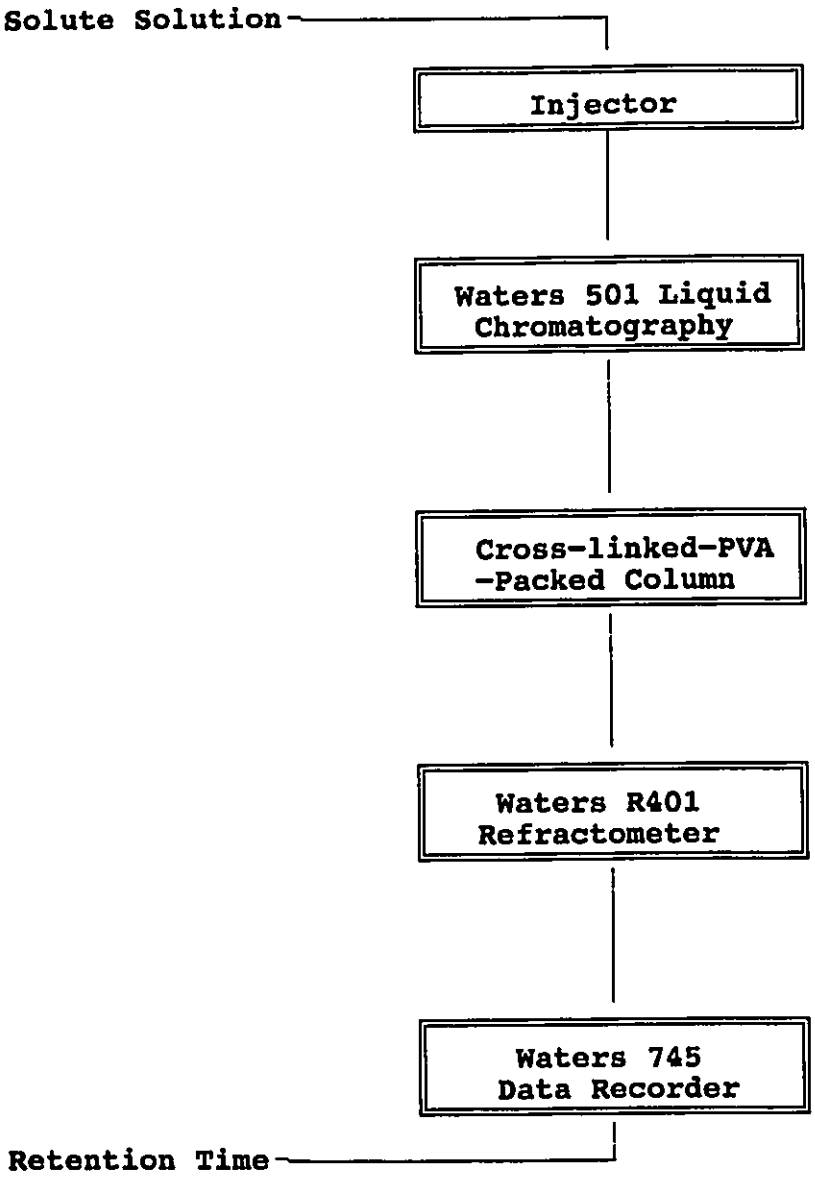


Figure 3.10: The liquid chromatography system setup

Chapter 4

4 Results and Discussion

The results are presented and discussed in the following manner. The experimental test conditions and variables are given. Except where mentioned, for each experiment, average results of three repeated tests of one experimental point are shown, and a error bar representing the maximum error range for each set of the experiment appears nearby the corresponding point in the figure.

4.1 Membrane Preparation Process and Parameters Affecting the Performance of the Membrane

The preparation of TFC PVA membranes followed basically the procedure presented in Section 3.1. There are various process parameters controlling the resultant membrane performance in the TFC membrane making process. Important process parameters are the cross-linking heat treatment temperature and period, the nature and concentration of cross-linking agents, the concentration of PVA polymer solution, substrate material types and many others. The effects of these process parameters on the TFC membrane performance

have been investigated. In the following studies, one parameter was varied while maintaining others unchanged, unless otherwise stated. Two ultrafiltration membranes were investigated in the beginning for choice of the substrate membrane.

The characteristics of the substrate membrane The office of Water Research and Technology, U.S.A., conducted a specific project to investigate the effect of the porous substrate membrane on the performance of the thin-film composite membrane (Cadotte et al., 1981). Kakuse et al. (1986) also characterized porous substrate membranes that were used to prepare one of the best TFC PVA membranes achieved by them. According to the above researchers, asymmetric membranes with surface pore diameters of 50 to 5000 Å and with pure water permeabilities of 10^{-4} to 10^{-1} g/cm^2.s.atm were considered most preferable for the substrate membrane. The substrate membranes used in this work were polysulfone ultrafiltration membrane HGO1 and polyethersulfone ultrafiltration membrane HPO9 provided by Osmonics Inc.. The ultrafiltration performance of the substrate membranes was investigated with polyethylene glycol solutes of different molecular weights. The results are listed in Tables 4.1 and 4.2. The pure water permeability obtained by converting the pure water permeation rate data in the table was in the range of 10^{-3} to 10^{-2} g/cm^2.s.atm. Therefore, the pure water permeabilities of these membranes are in the most preferable range. On the basis of the obtained separation, PR, and PWP values, the pore size and the pore size distribution of substrate UF membranes could be numerically

Table 4.1 HPO9 membrane performance data*

	cell No.1	cell No.3	cell No.5	cell No.2	cell No.4	cell No.6
PWP	148.7	161.2	195.5	413.2	599.1	281.3
PR	146.0	163.1	198.9	409.4	601.3	284.7
Sep. of PEG-400	12.3	14.5	6.3	10.9	12.5	10.6
PWP	140.	153.9	187.0	415.6	600.4	290.8
PR	137.3	145.3	179.8	433.8	596.7	286.1
Sep. of PEG-600	35.1	32.8	23.4	12.8	10.2	7.4
PWP	124.6	150.0	194.6	361.8	549.1	283.7
PR	122.0	148.8	189.1	343.9	526.8	293.8
Sep. of PEG-1000	56.6	54.4	41.6	19.0	21.4	11.0
PWP	115.0	135.2	160.8	361.8	530.6	271.2
PR	115.0	132.4	156.4	370.8	545.6	273.4
Sep. of PEG-3000	77.0	80.4	68.6	24.0	26.0	25.6
PWP	142.1	156.3	191.4	387.0	557.	281.1
PR	144.6	159.6	193.9	389.3	564.8	267.1
Sep. of PEG-4000	78.o	78.0	72.4	41.4	41.7	35.3
PWP	143.8	160.7	191.8	382.5	561.7	273.4
PR	136.1	152.9	180.6	368.0	524.9	255.9
Sep. of PEG-6000	85.4	85.3	80.0	35.9	41.2	45.1
PWP	150.5	165.0	197.2	400.9	581.3	284.2
PR	140.2	153.6	178.3	335.0	490.2	232.4
Sep. of PEG-9000	88.7	87.9	84.4	38.3	45.0	64.5
PWP	152.5	163.8	193.9	408.2	608.7	261.6
PR	150.3	140.4	193.1	351.1	518.7	234.3
Sep. of PEG-15000	89.3	89.6	84.5	47.2	50.3	71.9
PWP	151.4	141.8	194.5	394.1	570.5	255.6
PR	100.1	109.4	132.3	200.0	286.8	143.0
Sep. of g PEG-20000	94.6	94.0	95.0	94.0	95.0	94.2

*The UF membrane was provided by Osmonics Inc.. Feed: 100 ppm Polyethylene glycol aqueous solution, operating pressure: 414 kPag (60 psig). The concentrations of feed and permeate solution were determined by Total Organic Carbon Analyzer.

Table 4.2 HGO1 Ultrafiltration Membrane Performance Data*

	cell No.1	cell No.2	cell No.3	cell No.4	cell No.5	cell No.6
PWP	526.2	361.4	336.1	576.8	481.3	391.4
PR	495.1	288.8	292.3	486.9	443.3	374.67
Sep. of PEG-1000	13.5	10.3	8.0	10.6	11.5	11.0
PWP	692.1	470.1	337.5	723.4	638.2	438.0
PR	638.0	435.4	333.8	688.1	500.7	394.4
Sep. of PEG-1500	12.8	5.5	13.1	7.9	12.8	10.7
PWP	706.2	484.2	340.2	708.6	637.1	395.5
PR	658.3	471.8	344.1	700.3	614.6	378.4
Sep. of PEG-3000	22.9	8.0	35.6	21.0	22.9	30.0
PWP	672.8	466.3	352.5	711.6	580.1	397.5
PR	610.8	442.4	343.5	663.5	554.2	357.2
Sep. of PEG-6000	33.8	14.9	65.2	34.4	38.1	59.0
PWP	615.1	460.5	308.1	693.1	543.1	370.1
PR	494.6	438.9	302.4	689.0	415.2	335.2
Sep. of PEG-9000	57.1	18.2	81.8	50.5	56.4	78.4
PWP	663.8	425.3	341.5	625.2	590.5	373.8
PR	627.5	325.3	318.5	525.4	467.3	355.9
Sep. of PEG-12000	67.2	32.2	84.1	59.4	62.8	85.2
PWP	631.5	437.2	354.6	652.7	564.2	384.2
PR	497.6	323.8	278.3	532.0	397.3	335.2
Sep. of PEG-15000	67.1	32.9	86.6	62.9	64.7	87.8
PWP	618.2	479.5	363.6	716.8	599.1	379.0
PR	274.2	256.6	139.7	300.0	212.5	208.2
Sep. of PEG-20000	94.9	90.0	95.3	93.7	94.7	94.2

*The UF membrane was provided by Osmonics Inc.. Feed: 100 ppm Polyethylene glycol aqueous solution, operating pressure: 414 kPag (60 psig). The concentrations of feed and permeate solution were determined by Total Organic Carbon Analyzer.

calculated by applying the surface force-pore flow model (Sourirajan and Matsuura, 1985; Chan et al., 1982) to UF performance data. The calculations, however are beyond the scope of this work, and will be reported elsewhere.

Effect of aldehyde cross-linking agents on the membrane performance Dialdehydes are commonly used in the cross-linking reaction with PVA. In this experiment, both dialdehydes and aldehyde were used as cross-linking agents, and the cross-linking of PVA polymer was performed at 100°C for 10 minutes. Figure 4.1 shows that with glutaraldehyde the product rate was very low. Probably, cross-linking of PVA with glutaraldehyde proceeded to an excessive degree at 100°C. There is a possibility that the cross-linking at a lower temperature may lead to a high product rate. As shown in Figure 4.1, a higher product rate also could be obtained by using glyoxal as cross-linking agent. Although glutaraldehyde was used as the cross-linking agent in many other experiments, the results of those are not reported in this thesis.

Effect of malic acid concentration on the membrane performance As indicated in Chapter 3, malic acid was used as a cross-linking agent in many of the experiments. Therefore, the range of malic acid concentration where cross-linking reaction seems to proceed was searched for. Figure 4.2 shows that the product rate decreased and the separation of NaCl increased with an increase in malic acid concentration. From the above results, taking account of both separation and product rate, 3.0 wt% of malic acid was considered the best and chosen to be used throughout this work.

Effect of PVA concentration on the membrane performance Figure 4.3 shows that the sodium chloride separation did not change significantly , while the product rate was decreased greatly with an increase in PVA concentration. From the above results 1.0 wt% PVA solution was considered the best and was used in further experiments.

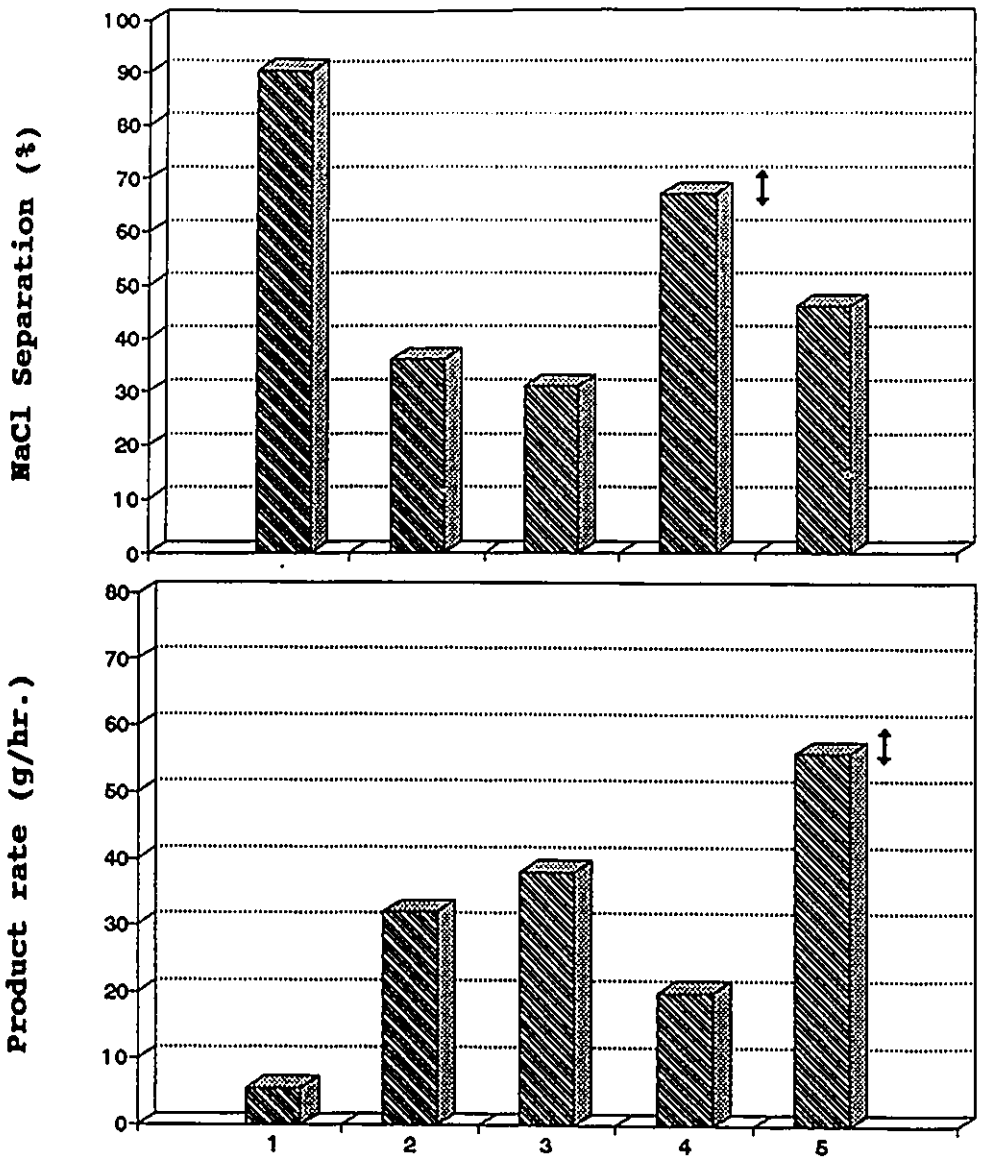
Effect of additives in PVA solution on the membrane performance In order to improve the membrane flux some organic and inorganic additives were added to the PVA solution. The concentration of the additives depended on the additive and was in the range from 0.1 to 0.2 wt%. The results are shown in Figure 4.4. Some improvement in the product rate was observed when ethyl alcohol was added to the polymer solution. On the other hand, there was practically no effect of additives on the solute separation. It was decided not to use any additive in the polymer solution in further experiments.

Effect of solvent for PVA on the membrane performance Methyl alcohol, ethyl alcohol, iso-propyl alcohol and tetrahydrofuran were compared with water as the solvent for PVA. Figure 4.5 shows that the solute separation and the product rate were different for different solvents. However, a decision was made to use water as solvent for PVA since water is readily available.

Effect of heat treatment on the membrane performance Subjecting the membrane to heat treatment in an oven is a decisive step in the process of making TFC PVA membranes. In this step, the

cross-linking structure is formed in the membrane, and hence the membrane performance does not change hereafter. Therefore, the effects of cross-linking temperature and cross-linking period on the membrane performance were studied. It is evident in Figure 4.6 that the cross-linking of PVA becomes more effective at a higher temperature. The figure shows that the solute separation increases and the product rate decreases with an increase in the cross-linking temperature. The effect of the cross-linking period was also studied at the cross-linking temperature of 100°C (Figure 4.7). The cross-linking temperature of 100°C and the cross-linking period of 10 minutes were optimum conditions and were used in further experiments.

Effect of alcohol solution manipulation on the membrane performance Kakuse et al. (1986) reported that the flux across TFC membranes increased when they were treated with alcohols. In order to test the effect of the alcohol treatment, the PVA membranes cross-linked at 100°C for 10 minutes were tested before and after they were immersed into 20 wt% aqueous solutions of different alcohols for two hours. Figure 4.8 shows that the product rate could be improved as much as 50% by the alcohol solution manipulation, while the solute separation remained unchanged.



1. glutaraldehyde 2. PVA-glutaraldehyde mixture*
3. paraformaldehyde 4. formaldehyde 5. glyoxal

Figure 4.1: Effect of aldehyde cross-linking agents on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt %, cross-linking agent conc. 3.0 wt %, cross-linking temperature 100 °C and cross-linking period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.
* glutaraldehyde was added to PVA solution before coating PVA solution on the substrate.

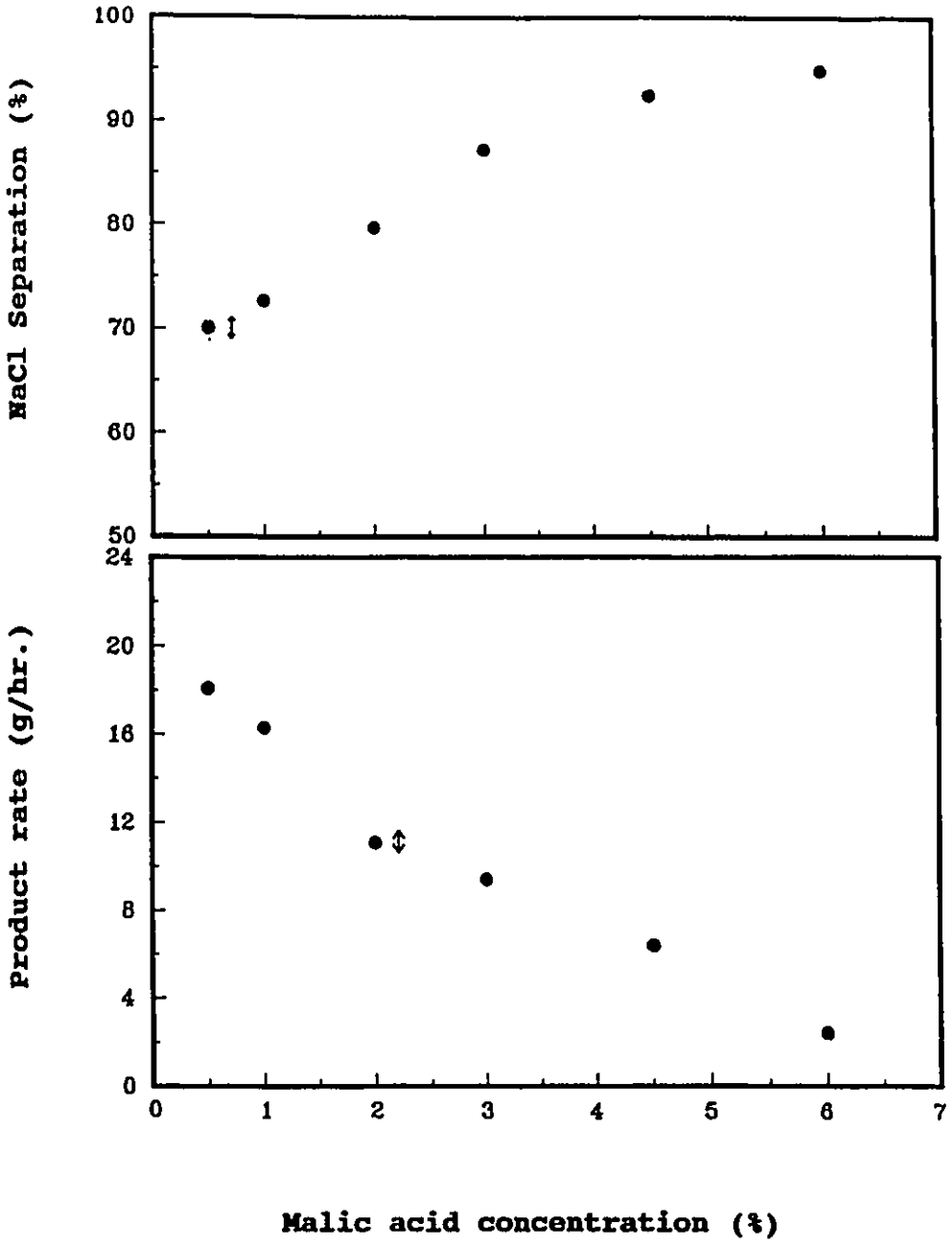


Figure 4.2 Effect of malic acid concentration on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt%, cross-linking temperature 100 °C and cross-linking period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.

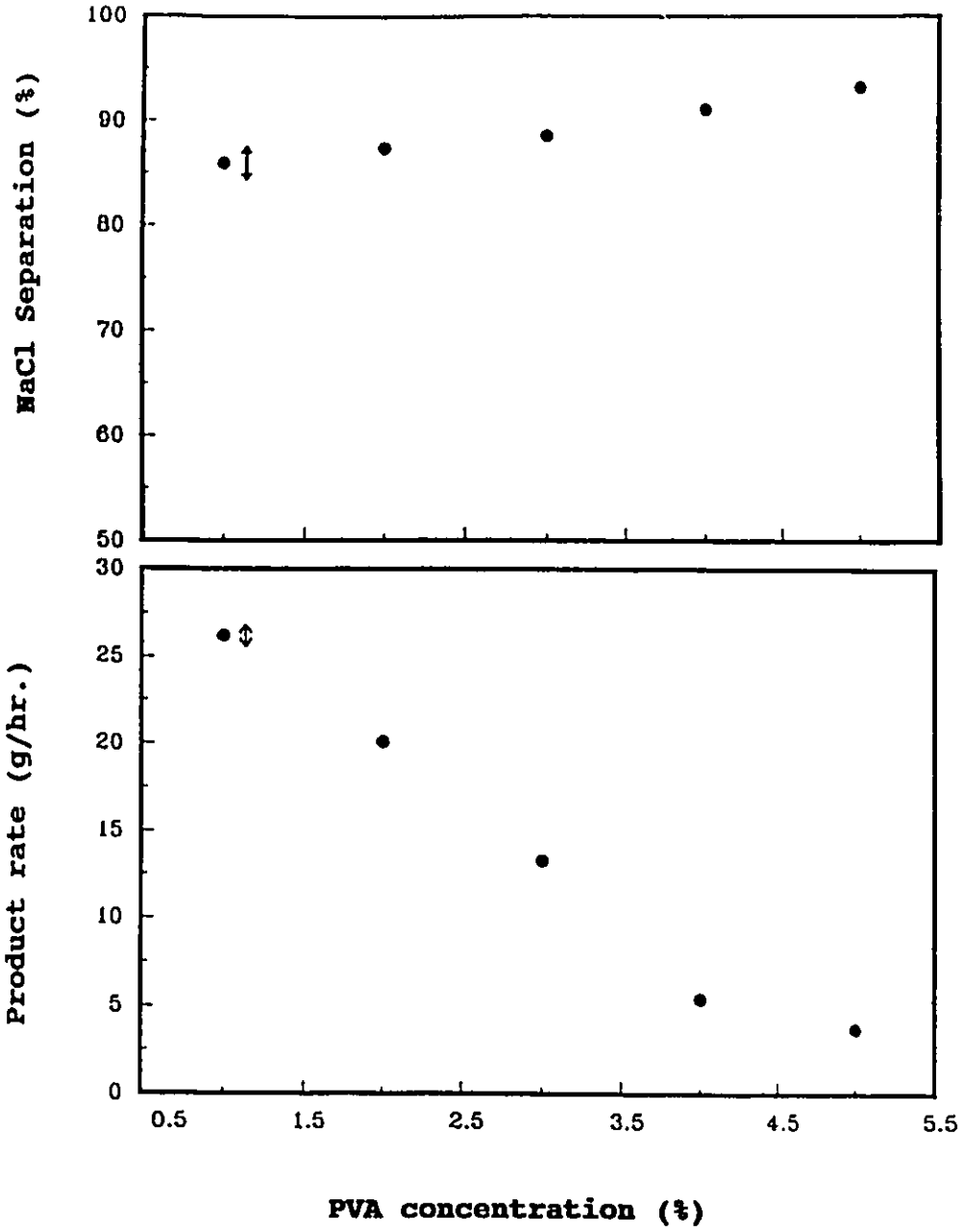
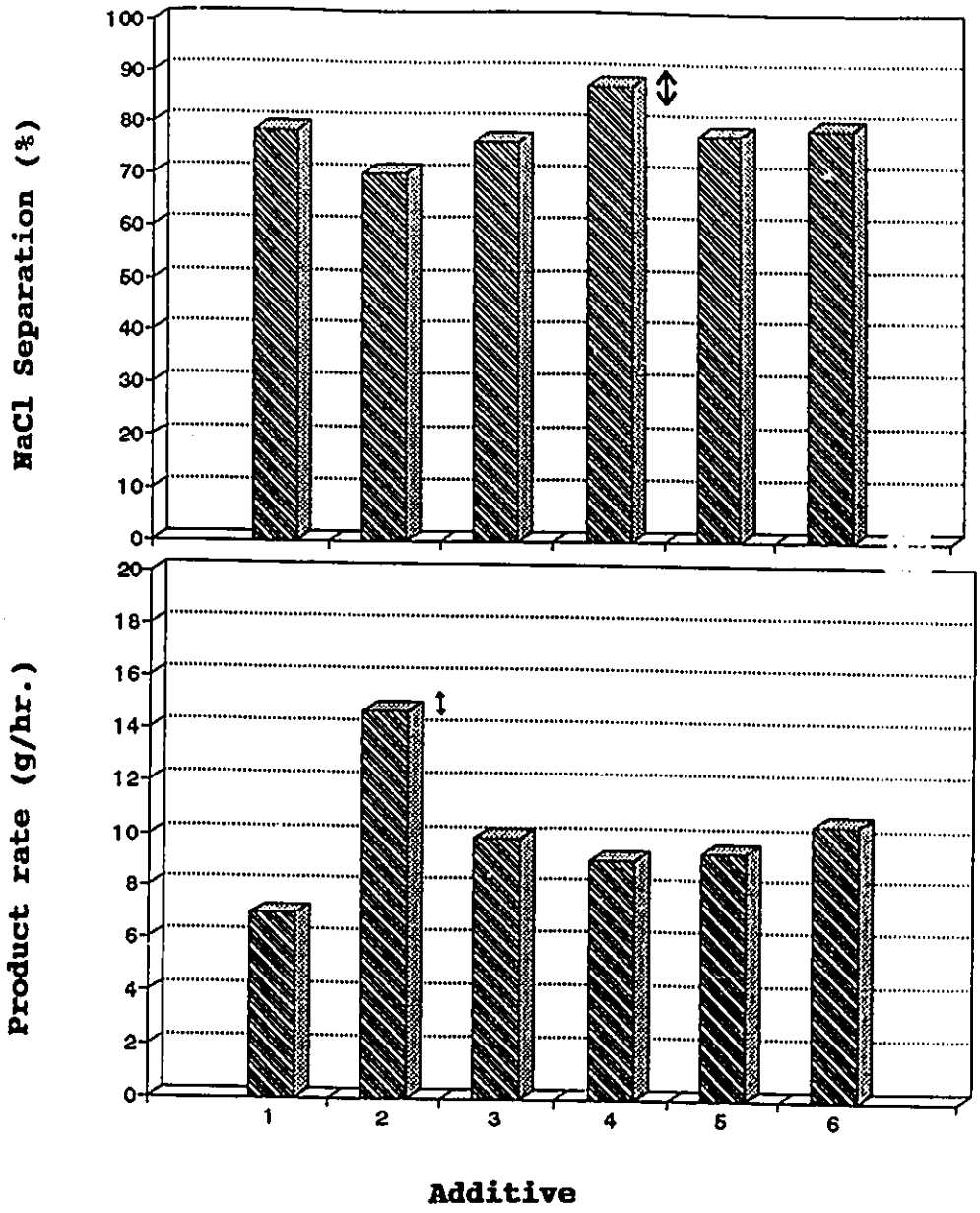
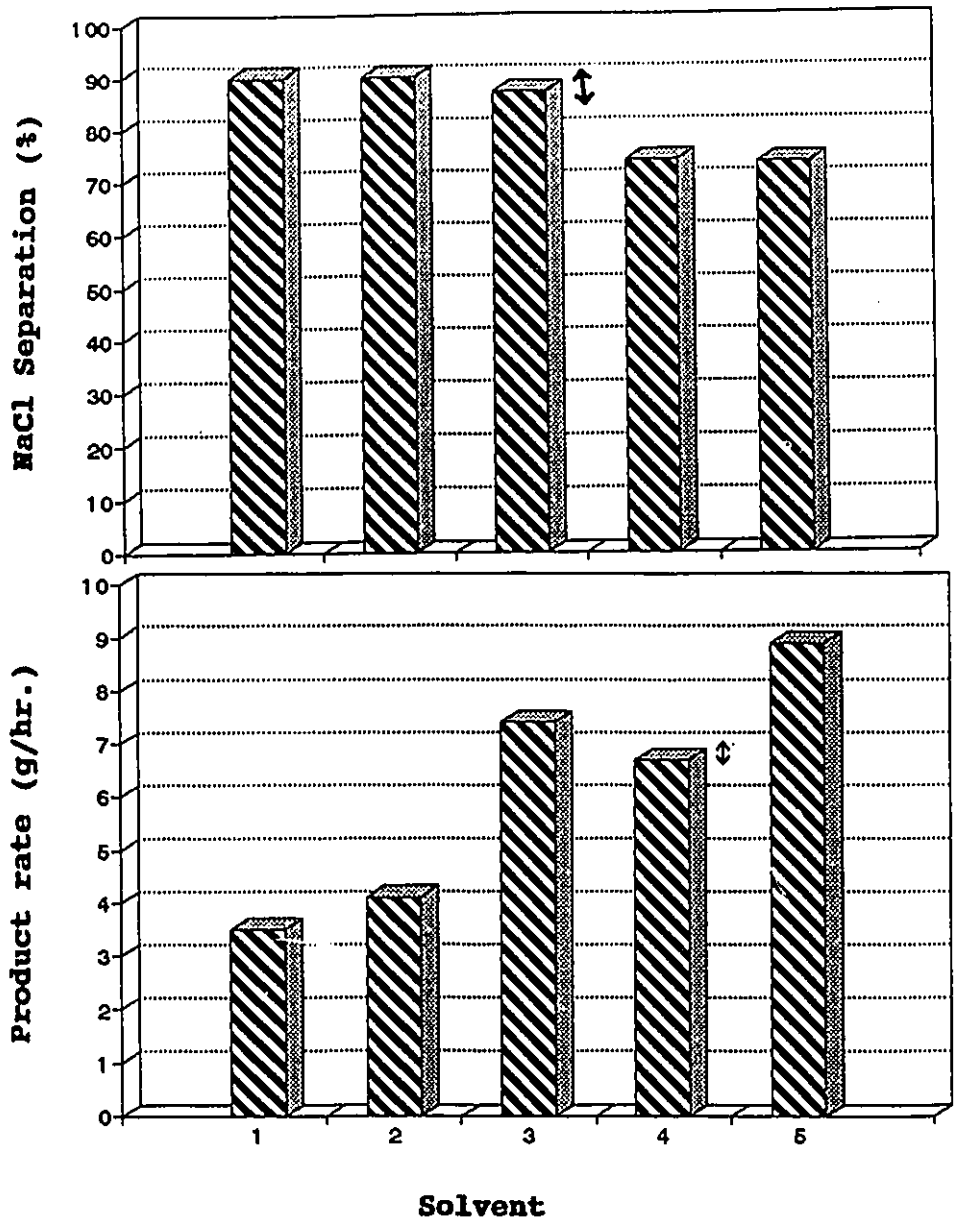


Figure 4.3 Effect of PVA concentration on the membrane performance. Membrane making conditions: Malic acid conc. 3.0 wt%, cross-linking temperature 100 °C and crosslinking period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution,operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.



1. formamide 2. ethyl alcohol 3. tetrahydrofuran
4. none 5.manganese chloride 6. cyclohexane

Figure 4.4 Effect of the additive in PVA solution on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt%, malic acid conc. 3.0 wt%, additive conc. 0.1 - 0.2 wt%, cross-linking temperature 100 °C and cross-linking period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.



1. methyl alcohol 2. ethyl alcohol 3. water
4. 2-propyl alcohol 5. tetrahydrofuran

Figure 4.5 Effect of the solvent of PVA on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt%, malic acid conc. 3.0 wt%, cross-linking temperature 100 °C and cross-linking period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.

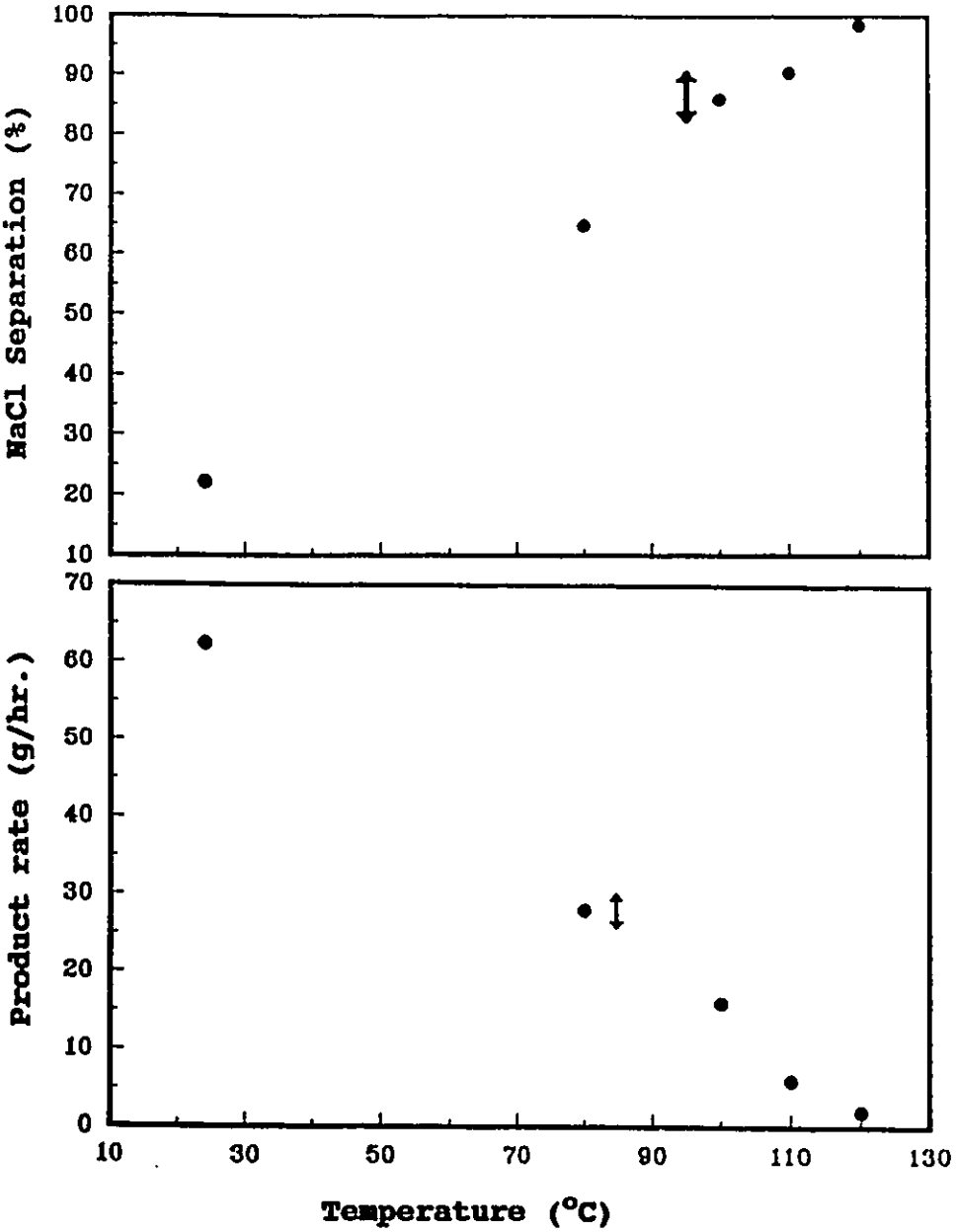


Figure 4.6 Effect of cross-linking temperature on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt%, malic acid conc. 3.0 wt% and cross-linking period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.

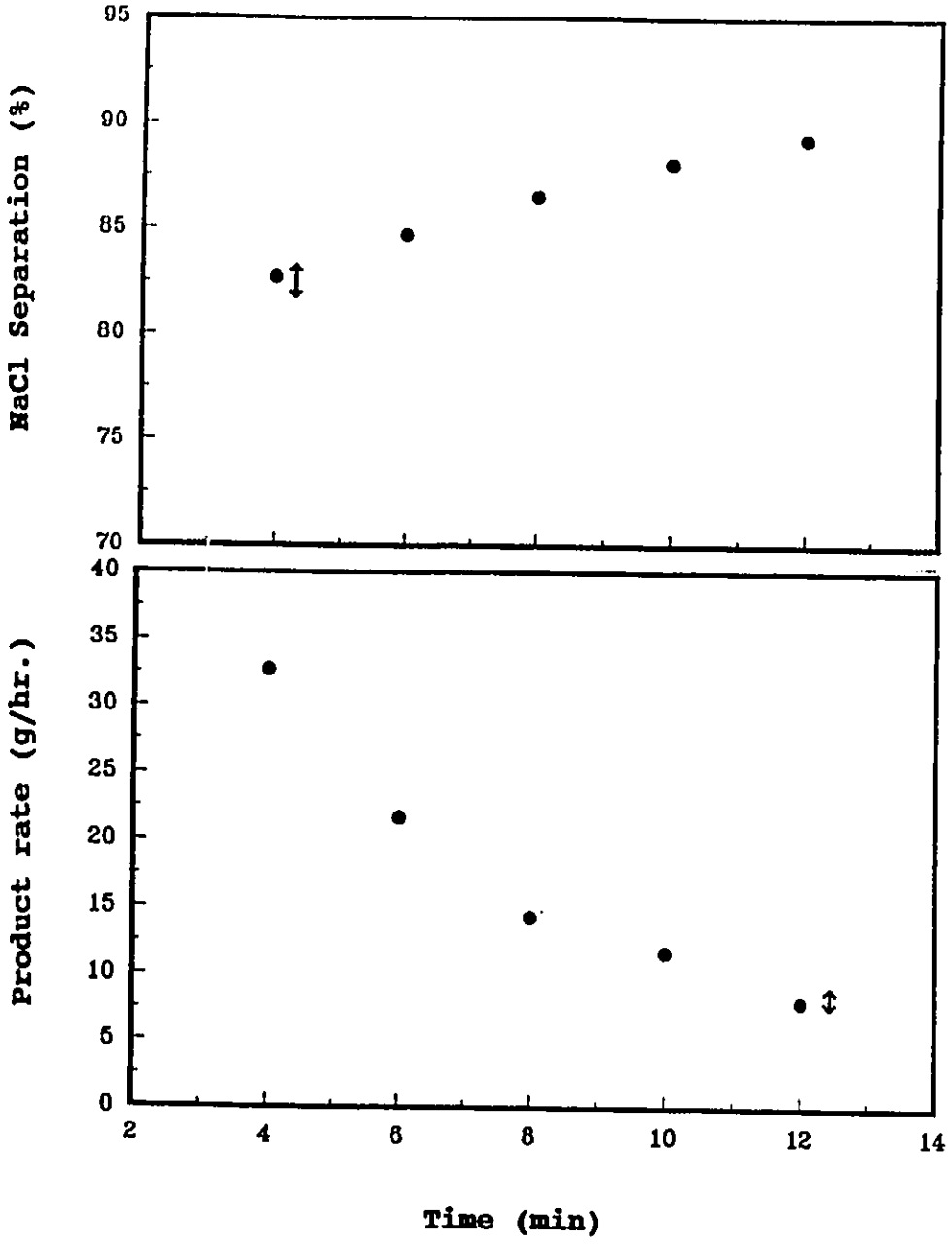
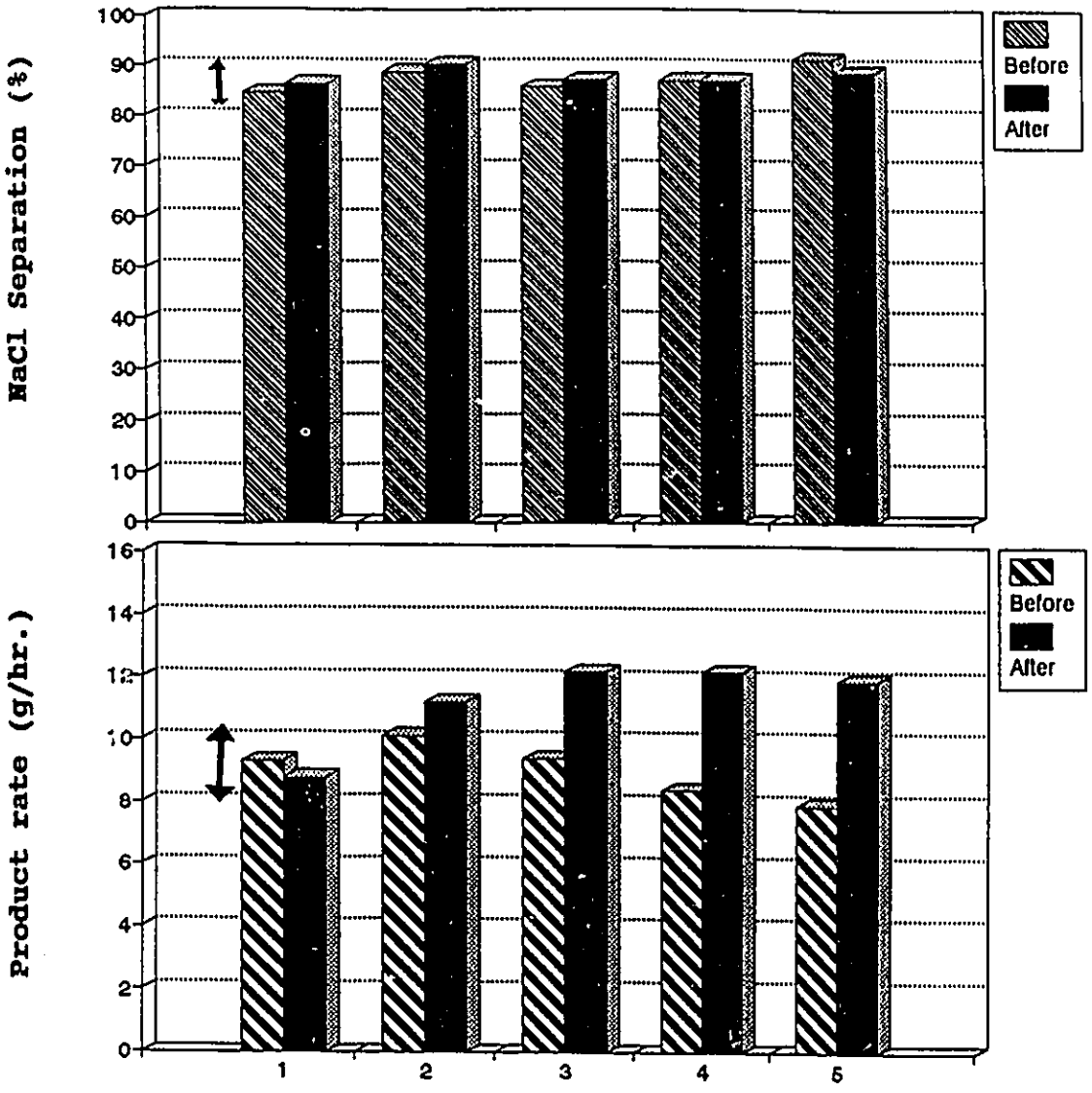


Figure 4.7 Effect of cross-linking period on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt%, Malic acid conc. 3.0 wt% and crosslinking temperature 100 °C. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.



1. methyl alcohol 2. glycerol 3. ethyl alcohol
4. n-propyl alcohol 5. n-butanol

Figure 4.8 Effect of immersion in alcohol solution on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt %, malic acid conc. 3.0 wt%, cross-linking temperature 100 °C and crosslinking period 10 min. Alcohol conc. 20 wt%, immersion time two hours. Testing conditions: feed 2000 ppm NaCl aqueous solution, operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.

4.2 A Study on the Flux Change of the Membrane during the Membrane Fabrication Process

Our earlier studies (Section 4.1) showed that a new TFC PVA membrane can be produced by using the materials mentioned in Section 4.1 and controlling the process parameters involved. The TFC PVA membrane so-produced had an acceptable range of sodium chloride separation, although the product rate of the TFC-PVA membrane was not high enough for practical purposes. It was also concluded that the flux of PVA membranes developed by other researchers was low (see Table 2.4). Therefore, it was necessary for us to try improving the membrane's product rate by investigating the flux change of the membrane during the membrane fabrication process.

Like other composite membranes, PVA-TFC membranes developed in this study consist of three layers: a UF substrate layer, a PVA middle layer and cross-linked surface layer (Figure 1.3). In order to find the causes of the loss of the flux of the resultant membranes, the effect of various parameters involved in the membrane preparation on the rate of permeation through individual layers of the membrane was investigated separately. In this study each layer was treated individually under the same conditions as those in the PVA-TFC membrane-making process.

Effect of heating on the flux of Polyethersulfone (PES) HPO9 and polysulfone (PS) HGO1 substrates HPO9 UF membrane (made from

PES) and HGO1 (made from PS) UF membranes were chosen as substrates to support PVA-TFC membranes. After being washed in distilled water and dried in air, the two membranes were heated in an oven at 100°C for 10 minutes, since those were the conditions under which the cross-linking reaction was carried out. Figure 4.9 shows that HPO9 membrane lost most of its initial pure water permeation rate (PWP) by heat treatment. In contrast, under the same heating conditions, the PWP of HGO1 membrane remained nearly equal to its initial value (Figure 4.10). Therefore it was confirmed that HGO1 is a substrate suitable for preparation of TFC membranes, since it can withstand a high temperature during the cross-linking process.

Effect of drying on the flux of PES substrate To distinguish from "heat treatment", the term "drying" refers to the process in which membranes are dried at ambient temperature naturally. During the normal procedure of making PVA TFC membranes, the substrate membranes were washed with distilled water and dried at room temperature before being coated with PVA solution and cross-linked. This drying process may affect the membrane morphology. It had been found that HGO1 membrane could withstand a high temperature during heat treatment, but the HPO9 membrane could not; therefore, drying effect was studied for the PES HPO9 membrane only. Figure 4.11 shows the difference in pure water permeation rate between HPO9 membranes with and without drying. The PWP decreased greatly once the HPO9 membrane was dried. However, a high level of pure water permeation rate could be maintained after the HPO9 membrane was immersed in glycerol solution for a few hours before being

dried and heat-treated. As is obvious from Figure 4.12, the membrane flux was acceptable for the membrane to be used as a substrate even after heat treatment and an increase in PWP was noticed with an increase in glycerol concentration. However further reverse osmosis tests revealed that the solute separation of the glycerol-treated HPO9 substrate membrane was very low even after coating and cross-linking of the PVA layer. It is possible that glycerol, while staying in the pores of the PES membrane, can greatly decrease the membrane's susceptibility to drying and heating, but at the same time also decreases PVA cross-linking density.

Effect of pressure on the pure water permeation rate of dried PS substrate Figure 4.13 shows that there was no pure water permeation through the dried PS HGO1 membrane until the operating pressure was increased to 1380 kPag; but high fluxes could be achieved with the same membrane once a high pressure opened most of the pores on the membrane surface. This is because water does not enter the pores until a certain pressure is achieved due to the hydrophobic nature of the membrane material. Cadotte et al. (1981) came to the same conclusion.

Before the above experiment it was thought that the loss in product rate occurred during the PVA solution coating step. Large PVA molecules may enter the substrate's pores and block the pores partially during the coating step, resulting in the reduction of pore sizes. However, since the above experiment indicates that even small water molecules can not enter the pore of the dried PS

substrate unless a pressure is applied, penetration of PVA macromolecules into the pore during the coating step seems impossible.

Effect of the thickness of the PVA layer on the PS-PVA membrane The effect of the number of layers of PVA coating on the substrate membrane was investigated by coating the HGO1 membrane with 1 wt% PVA aqueous solution repeatedly. The PVA coated substrate membranes were dried and tested for reverse osmosis performance without cross-linking. Figure 4.14 shows that the product rate of the membrane decreased while sodium chloride separation increased with an increase in the number of coatings.

Effect of drying time on the flux of the PS-PVA membrane HGO1 membranes coated once with 1.0 wt% aqueous PVA solution were dried in air under ambient conditions for different periods. Then, the RO performance of the PS-PVA membranes so prepared was investigated. Figure 4.15 shows that the drying period did not affect the RO performance significantly.

Effect of heat treatment on the flux of the PS-PVA membrane PS-PVA membranes were prepared by coating the HGO1 substrate membrane once with 1.0% aqueous PVA solution and by drying at room temperature for six hours. The PS-PVA membranes so prepared were heated in an oven at different temperatures for 10 minutes. It was found that the product rate of the PS-PVA membranes decreased with an increase of the temperature when the temperature was lower than 80°C. The product rate became strongly temperature dependent when the temperature was above 80°C (Figure 4.16). In particular, both

the solute separation and the product rate changed drastically when the temperature rose from 80°C to 90°C. The above effect is probably due to the fact that the crystallinity of PVA increases when the temperature is above 80°C. It has to be noted that the heat treatment was adopted to enhance the water resistance by the promotion of crystallization (Finch, 1975). Hydrogen bonding between PVA chains could also be taking place, resulting in a tighter packing of the PVA macromolecules.

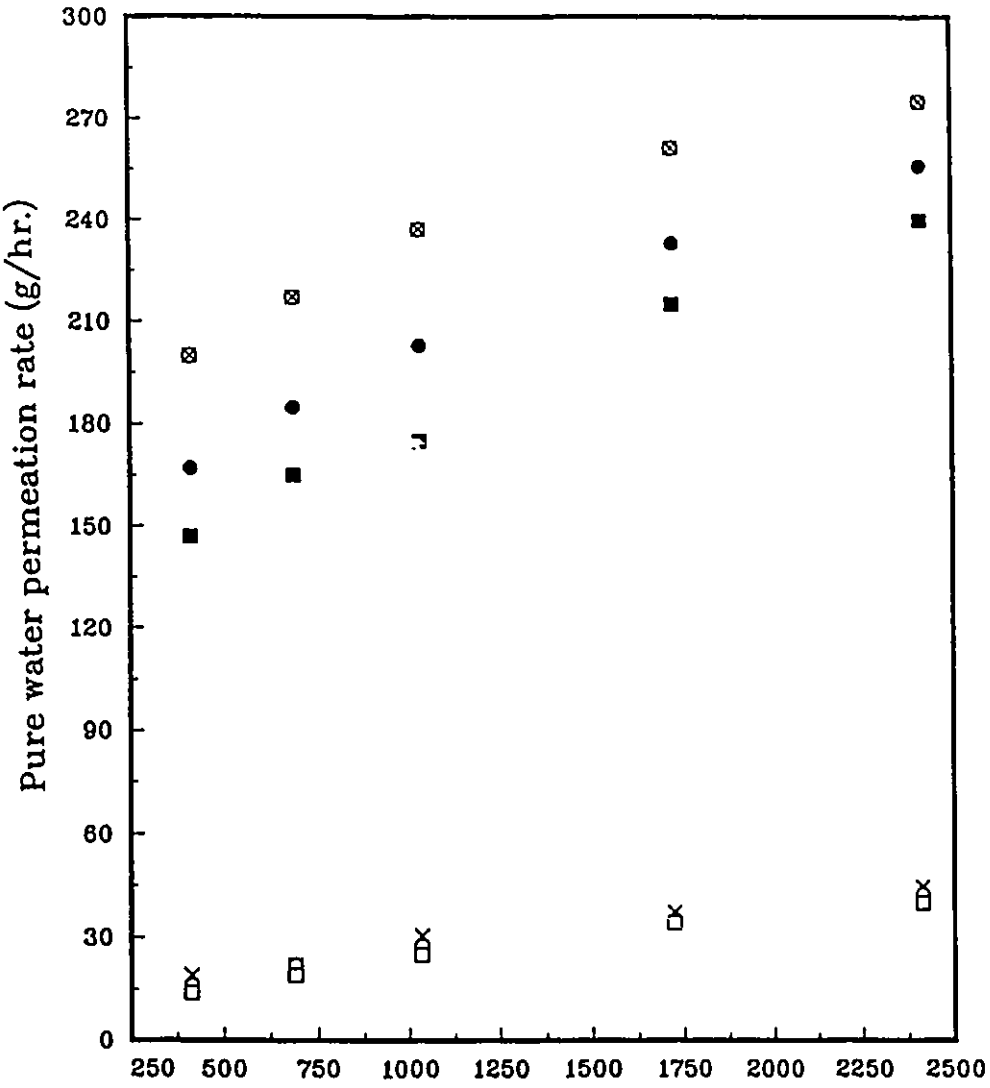


Figure 4.9: Effect of heat treatment on the pure water permeation rate of HPO9 membrane. (●, ■ and ⊗) membranes were tested before heat treatment, (O, □ and ×) membranes were tested after being treated at 100 °C for 10 min. Pure water was used as feed.

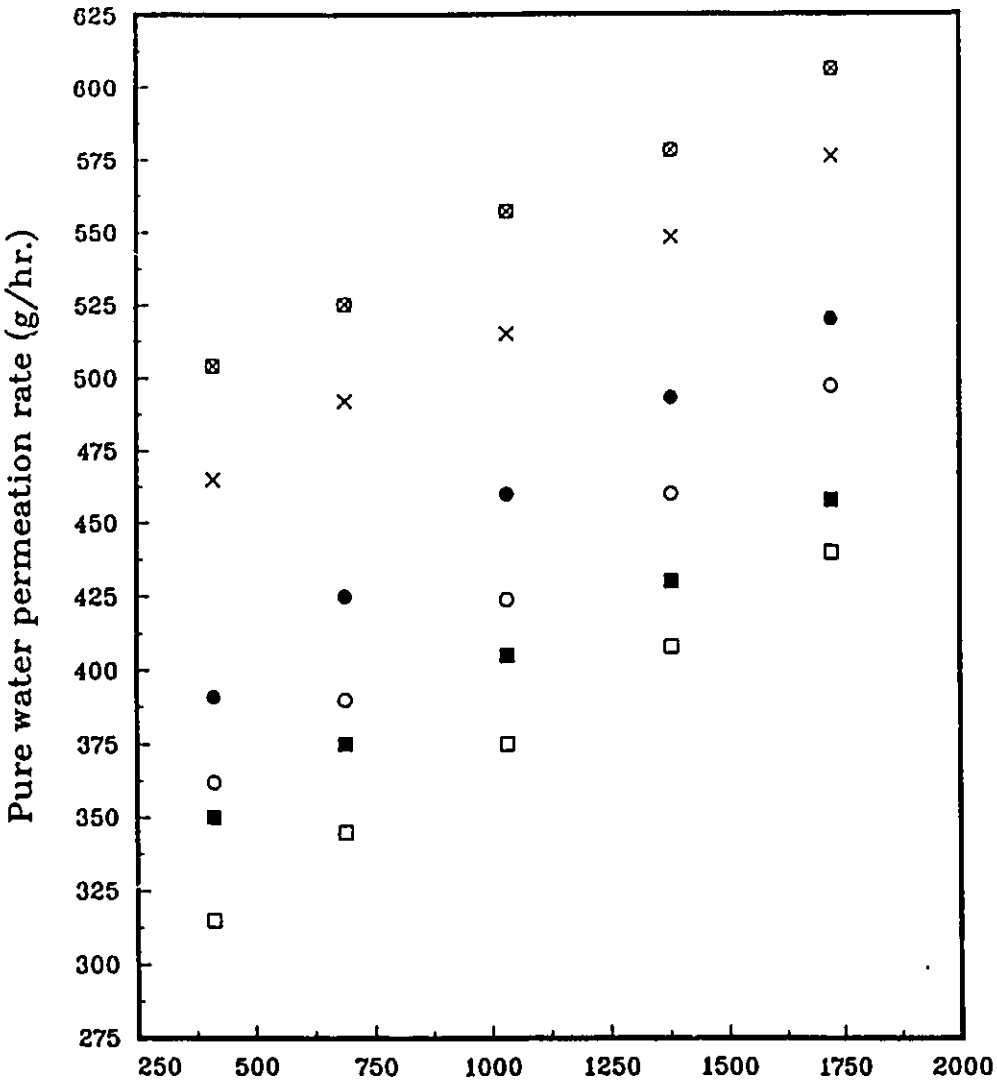


Figure 4.10: Effect of heat treatment on the pure water permeation rate of HG01 membrane. (●, ■ and ⊗) membranes were tested before heat treatment, (○, □ and ×) rembranes were tested after being treated at 100 °C for 10 min. Pure water was used as feed.

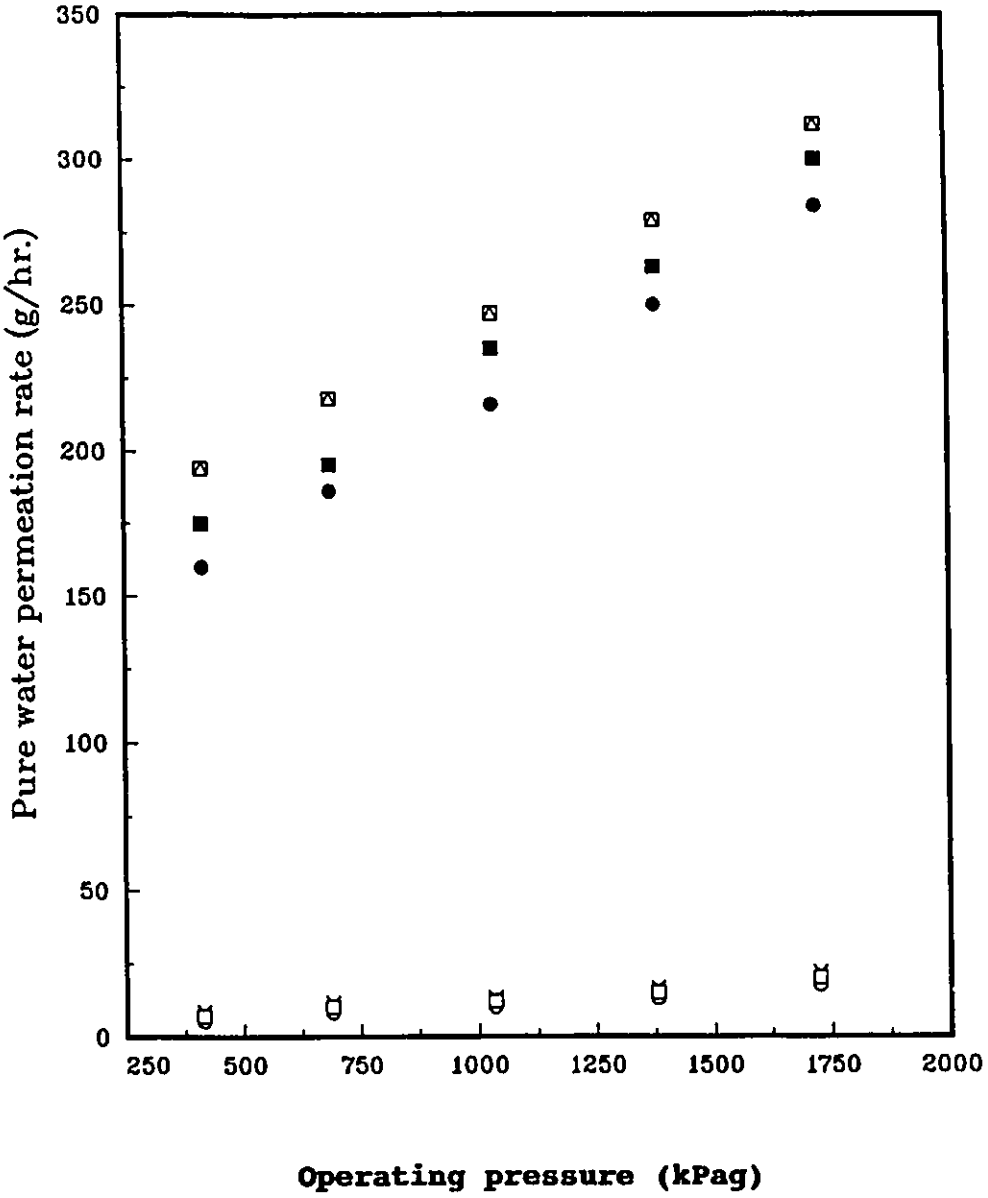


Figure 4.11: Effect of drying process on the pure water permeation rate of HPO9 membrane. (●, ■ and ⊠) membranes were tested before the drying process, (O, □ and ×) membranes were tested after the drying processg. Pure water was used as feed.

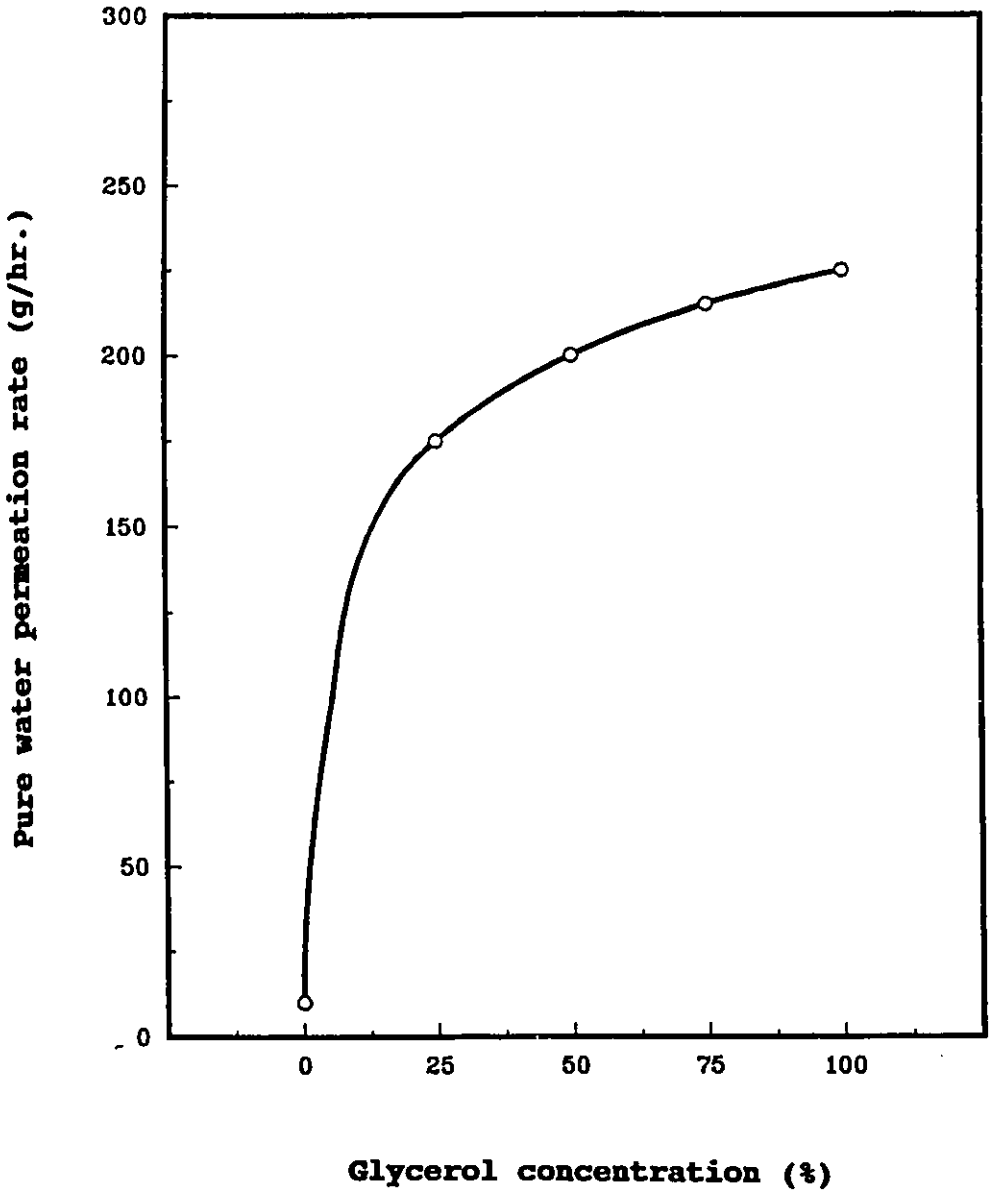


Figure. 4.12 Effect of concentration of glycerol on the pure water permation rate of the glycerol-treated HPO9 membrane. The UF membrane was provided by Osmonics Inc.. The membranes were immersed in glycerol solutions for 3 hours, and then heated at 100^{0}C for 10 min. Operating conditions: pure water as feed and operating pressure 414 kPag (60 psig).

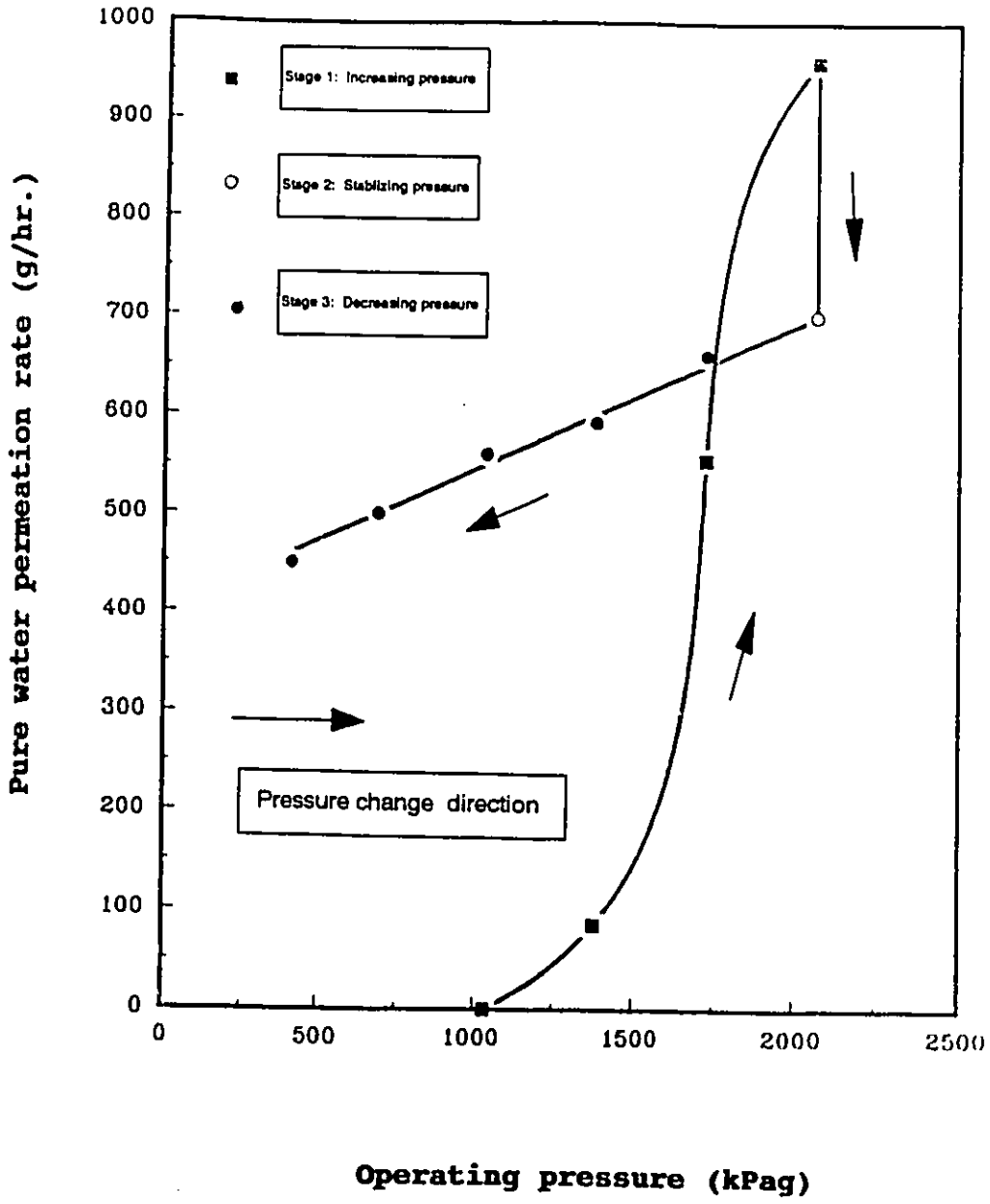


Figure 4.13: Effect of operating pressure on the pure water permeation rate of the dried HGO1 membrane. The UF membrane was provided by Osmonics Inc.. Pure water was used as feed. 3 coupons of HGO1 UF membranes were tested. The value of one coupon is represented in the Figure.

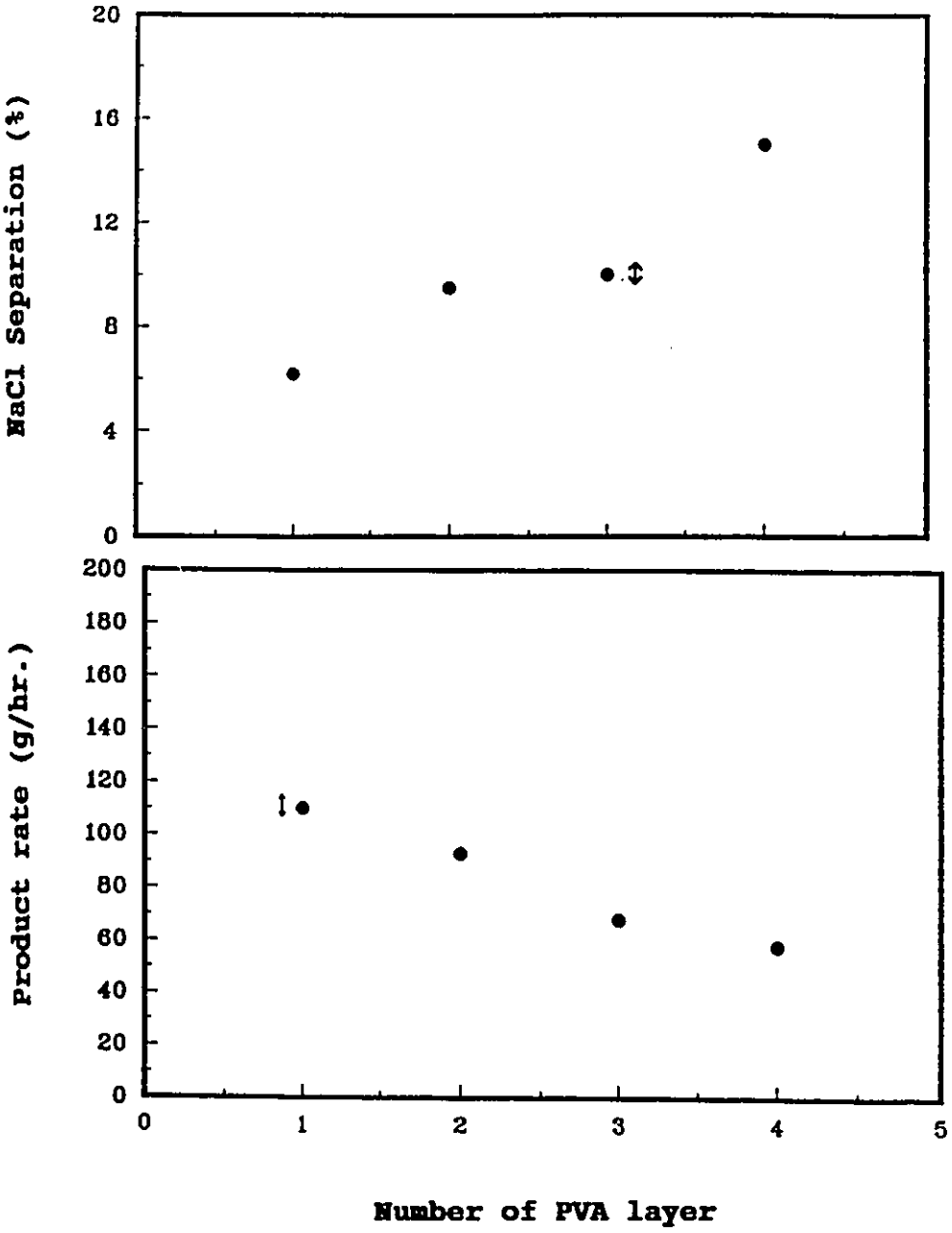


Figure 4.14 Effect of the number of PVA layer coatings on the performance of PVA-HGO1 film. Substrate: HGO1 UF membrane, coating solution: 1.0 wt% PVA aqueous solution; the membranes were dried at room temperature. Testing conditions: feed 2000 ppm NaCl solution and operating pressure 1724 kPag (250 psig).

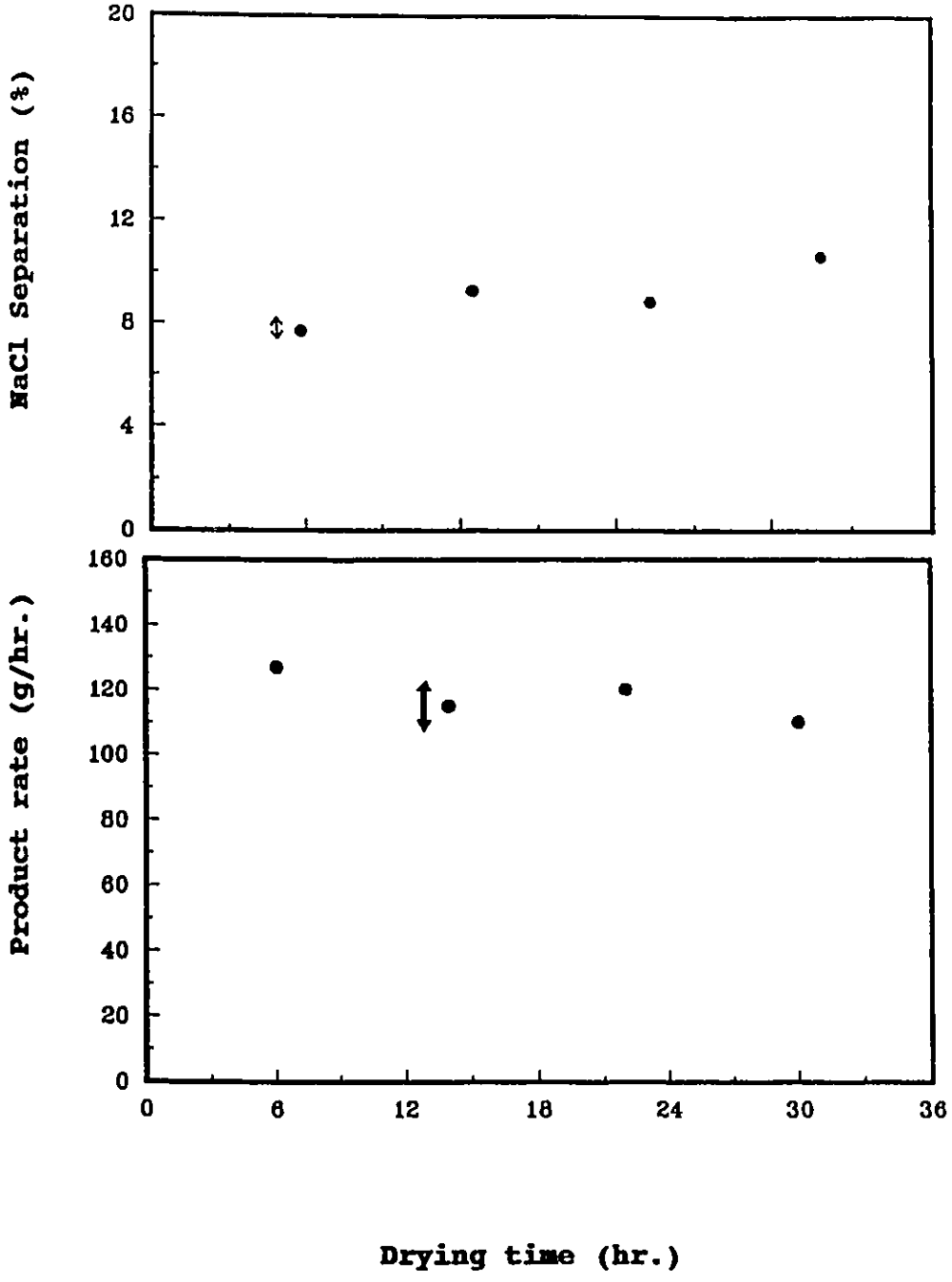


Figure 4.15 Effect of drying time on the performance of PVA-HGO1 film. Substrate: HGO1 UF membrane, coating solution: 1.0 wt% PVA aqueous solution; membranes were dried at room temperature. Testing conditions: feed 2000 ppm NaCl solution and operating pressure 1724 kPag (250 psig).

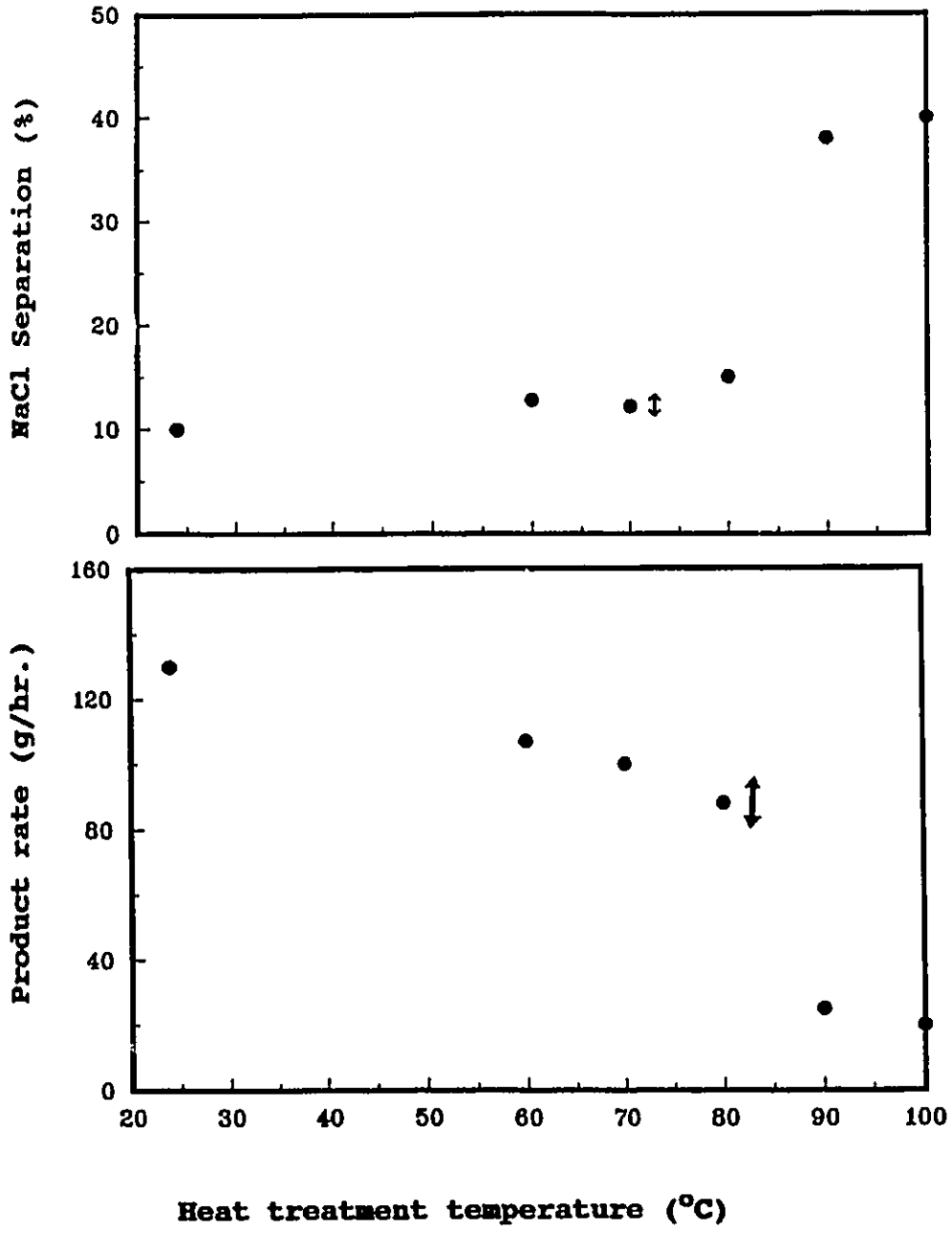


Figure 4.16 Effect of heat treatment on the performance of PVA-HGO1 film. Substrate: HGO1 UF membrane, coating solution: 1.0 wt % PVA aqueous solution; The films were dried and heated but without cross-linking. Heating period 10 minutes. Testing conditions: feed 2000 ppm NaCl solution and operating pressure 1724 kPag (250 psig).

4.3 Searches for New Method to Improve the Membrane Flux

The preceding investigations (Section 4.2) revealed that the low flux of the TFC PVA membrane resulted from the flux loss during the processes of coating, drying and heat treatment. Among those processes, it was heat treatment that caused the most significant loss of the membrane flux. Efforts were made therefore to reduce the effect of the heat treatment. Since practically no cross-linking reaction between the PVA and bicarboxylic groups can take place at ambient temperatures, some other cross-linking agents were searched for. Glutaraldehyde and methacrolein were considered as potential candidates for cross-linking agents at room temperature. Therefore, the PS-PVA membranes were cross-linked with glutaraldehyde and methacrolein and tested for RO performance.

Treatment with Glutaraldehyde One wt% aqueous PVA solutions were prepared using PVA polymers of different molecular weights and coated on HGO1 substrate membranes. Then, the membranes were dried and immersed into a 3 wt% glutaraldehyde solution and dried again at ambient temperature. The membranes so prepared were subjected to RO experiments. The results are summarized in Table 4.3 and Table 4.4.

Treatment with Methacrolein Methacrolein was used as a cross-linking agent to react with PVA at room temperature. The solvent for methacrolein was water. The membrane preparation procedure was, however, slightly modified for this system. Cross-linking

Table 4.3 RO performance of membranes cross-linked with glutaraldahyde at room temperature

PVA molecular weight	2,000	25,000	65,000
Reaction period	overnight	overnight	overnight
NaCl separation(%)	92.9-90.4	91.8	92.2-94.6
Product rate (g/hr.)	1.2-3.3	3.0	1.5-0.7

Table 4.4 Effect of reaction period at room temperature on the membrane performance

PVA molecular weight	65,000	65,000	65,000
Reaction period	2 hours	4 hours	6 hours
NaCl separation (%)	9.6-39.7	54.2-52.8	38.5
Product rate (g/hr.)	190-65.5	6.3-17.8	2.5

agent and surfactant (Na_2SO_3) were added to PVA solution before PVA solution was coated onto the HGO1 membrane. The purpose of adding a surfactant was to reduce the surface tension of the polymeric solution. Table 4.5 summarizes the membrane preparation procedure and the RO performance data of the resultant membrane.

The thickness of the cross-linked surface layer is another factor governing the membrane flux. When the cross-linking agent is dissolved in water, the aqueous cross-linking solution may penetrate deeply into the hydrophillic PVA layer, resulting in a thick cross-linked surface layer. This can be avoided when the cross-linking agent is dissolved in a hydrophobic solvent, since cross-linking takes place only at the solution-PVA layer interface. Hence, the experiments were performed with methcrolein and trimeric chloride as cross-linking agents dissolved in organic solvents.

Methacrolein dissolved in organic solvents Methacrolein in different organic solvents were allowed to react with the PVA layer. The experimental procedures and RO performance of resulting membranes are summarized in Table 4.6.

Water immiscible cross-linking reagent A 1 wt% aqueous solution of PVA containing 0.3 wt% phenylenediamine and 0.5 wt% sodium hydroxide was coated on the HGO1 substrate membrane and dried in air for 30 minutes. The PVA film, which was not completely dried, was brought into contact with water-immiscible hexane containing 2 wt% trimeric chloride as cross-linking agent and then heat-cured in an oven. Phenylenediamine has two primary amino groups in the molecule. Once heated in the oven, PVA and the

amino compound are supposed to be cross-linked with trimeric chloride. NaOH was used as a scavenger for the by-product of hydrochloric acid (HCl). The RO test results are shown in Table 4.7.

The attempts to let the cross-linking reaction take place at room temperature and/or at the cross-linking solution-PVA layer interface resulted in no significant improvement in the membrane performance, as shown in Tables 4.3-4.7. Therefore, no further attempts were made.

Table 4.5 Performance of the membrane cross-linked with methacrolein

PVA molecular weight	65,000	65,000	65,000	65,000
Composition and coating method	1.0% PVA + 0.1% Na_2SO_3 + 3.0% Methacrolein, coated on the HGO1		1.0% PVA + 0.1% Na_2SO_3 coated on HGO1, dried & treated with 3.0% Methacrolein	
Cross-linking conditions	overnight at room temperature	20 min at 60 °C	overnight at room temperature	20 min at 60 °C
NaCl separation(%)	14.6-13.7	13.2	12.7-17.6	12.2
Product rate (g/hr.)	68.0-83.0	123	151-98.2	45.9

Table 4.6 RO performance of the membrane cross-linked with methacrolein in organic solvents

PVA molecular weight	65,000	65,000	65,000
Solvent for methacrolein	Acetone	butanol	Hexane
Composition and coating method	1.0% PVA +0.1% Na_2SO_3, coated on HGO1 and dried, contacted with 3.0 % methacrolein organic solution for 10 sec.		
Cross-linking conditions	room temperature 16 hours		
NaCl Separation(%)	-	54.6	-
Product rate (g/hr.)	0	23.0	0

Table 4.7 Performance of the PVA membrane made with water immiscible cross-linker

Membrane	HGO1	HGO1-PVA	PVA TFC	PVA TFC	PVA TFC
Heating condition	100°C 18 min	100°C 18 min	100°C 4 min	100°C 10 min	100°C 18 min
Separation (%)	7.9	20.8	81.6	82.6	88.2
PR (g/hr.)	304	18.0	5.3	7.3	8.0

4.4 Membrane Transport Properties and Surface Characteristics

On the basis of the works presented in 4.1 - 4.3, some standard procedures were established for making TFC PVA membranes. The chosen parameters of the preparation procedure are listed in Table 4.8 together with the code given to the procedure. The membranes of R series are typical reverse osmosis membranes. The membranes of N series are nano-filtration membranes, which have the properties of lower salt separation and higher product rate in comparison with those of RO membranes. The membranes reported in Table 4.8 will be used in ongoing experiments to investigate the membrane transport properties and surface characteristics.

Table 4.8 Principlal process parameters for TFC PVA membrane making and the membranes so-prepared

	R series membranes*	N series membranes**	
		N1 series	N2 series
Substrate	Polysulfone UF membrane	Polysulfone UF membrane	Polysulfone UF membrane
PWP range of substrate	10^{-3} - 10^{-2} $g/cm^2.s.atm$	10^{-3} - 10^{-2} $g/cm^2.s.atm$	10^{-3} - 10^{-2} $g/cm^2.s.atm$
PVA concentration	1.0 wt%	1.0 wt%	1.0 wt%
Solvent	distilled water	distilled water	distilled water
Number of PVA solution coating	1	1	1
Drying period of PVA film in air	8 hr	8 hr	8 hr
Cross-linking solution conc.	3.0 wt%	2.5 wt%	2.5 wt%
Cross-linking temperature	100 °C	85 °C	80 °C
Cross-linking period	10 min	8 min	6 min

*: Priority given to higher separation,

**: Priority given to higher product rate.

Effects of operating pressure and feed concentration on the membrane performance The effects of the operating pressure and the feed concentration were investigated with respect to the R series membranes, which seem superior to any of the membranes listed in Table 2.4 in terms of salt separation and the product rate. The experimental results are illustrated in Figures 4.17 and 4.18. Figure 4.17 shows an increase in both flux and separation with increasing operation pressure. There was a slight decrease in separation and an increase in flux with an increase in feed concentration (Figure 4.18).

Chlorine sensitivity of the membrane Some reverse osmosis membranes, in particular polyamide membranes, are known to be susceptible to reaction with chlorine in water. This is a serious disadvantage for reverse osmosis membranes, since a high level of chlorine often exists in tap water, which is disinfected with chlorine, or in solutions to which chlorine is added in order to control the growth of micro-organisms. Preparation of membranes of high chlorine resistance has always been, therefore, an important goal for the membrane manufacturer. Among successful examples, the FT-30 TFC membrane was found to have appreciable resistance to degradation by 100 ppm chlorine as reported in the literature (Cadotte, 1981). The effect of chlorine on the TFC PVA membrane was therefore investigated and the results are summarized Table 4.9. The experiment was performed in the following way. Three membranes of N1 series were tested for RO performance with an aqueous NaCl feed solution of 2000 ppm under the operating pressure

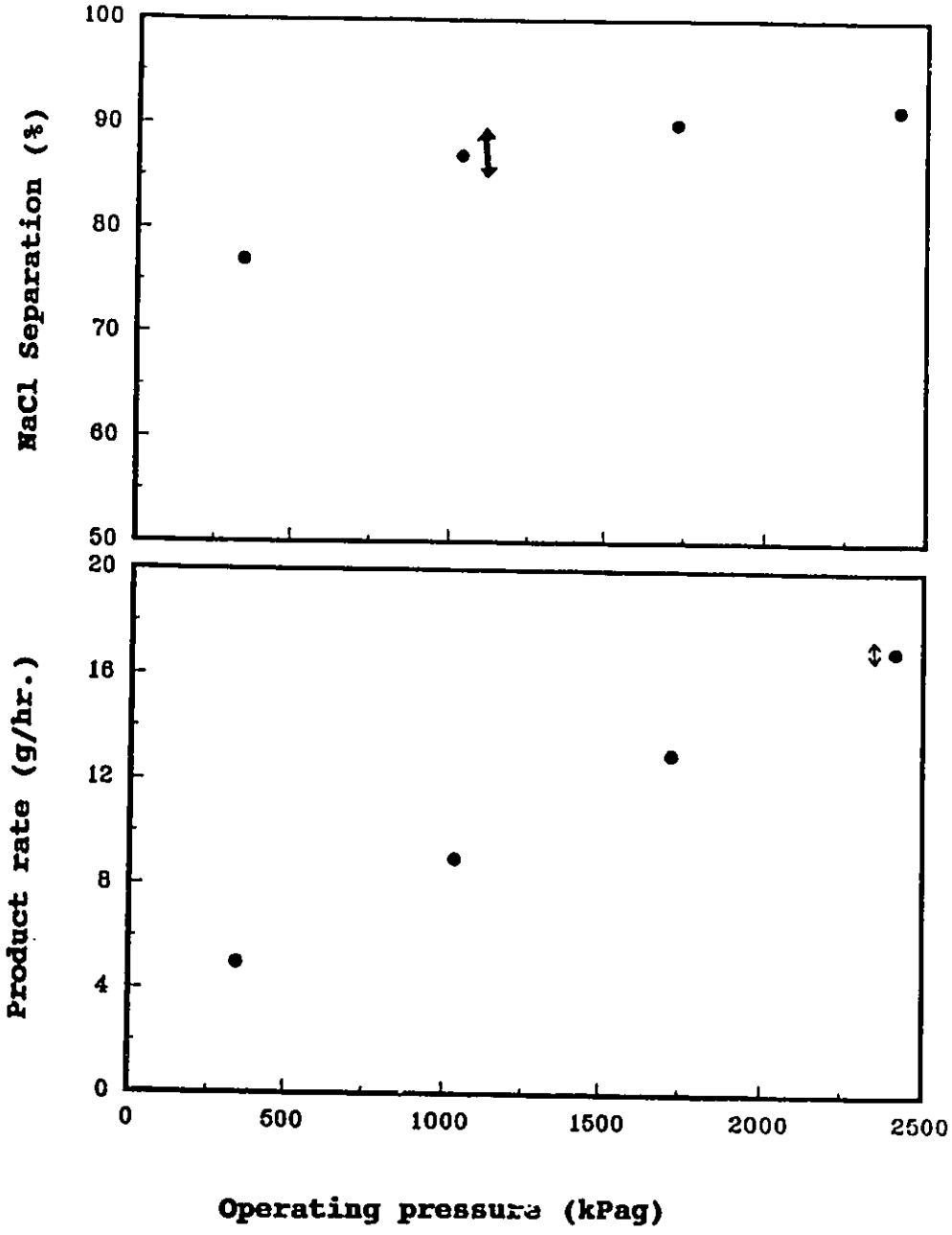


Figure 4.17 Effect of operating pressure on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt %, cross-linking agent 3.0 wt% of malic acid, heating temperature 100 °C and heating period 10 min. Testing conditions: feed 2000 ppm NaCl aqueous solution. The details of the membrane making and testing procedures are described in Chapter 3.

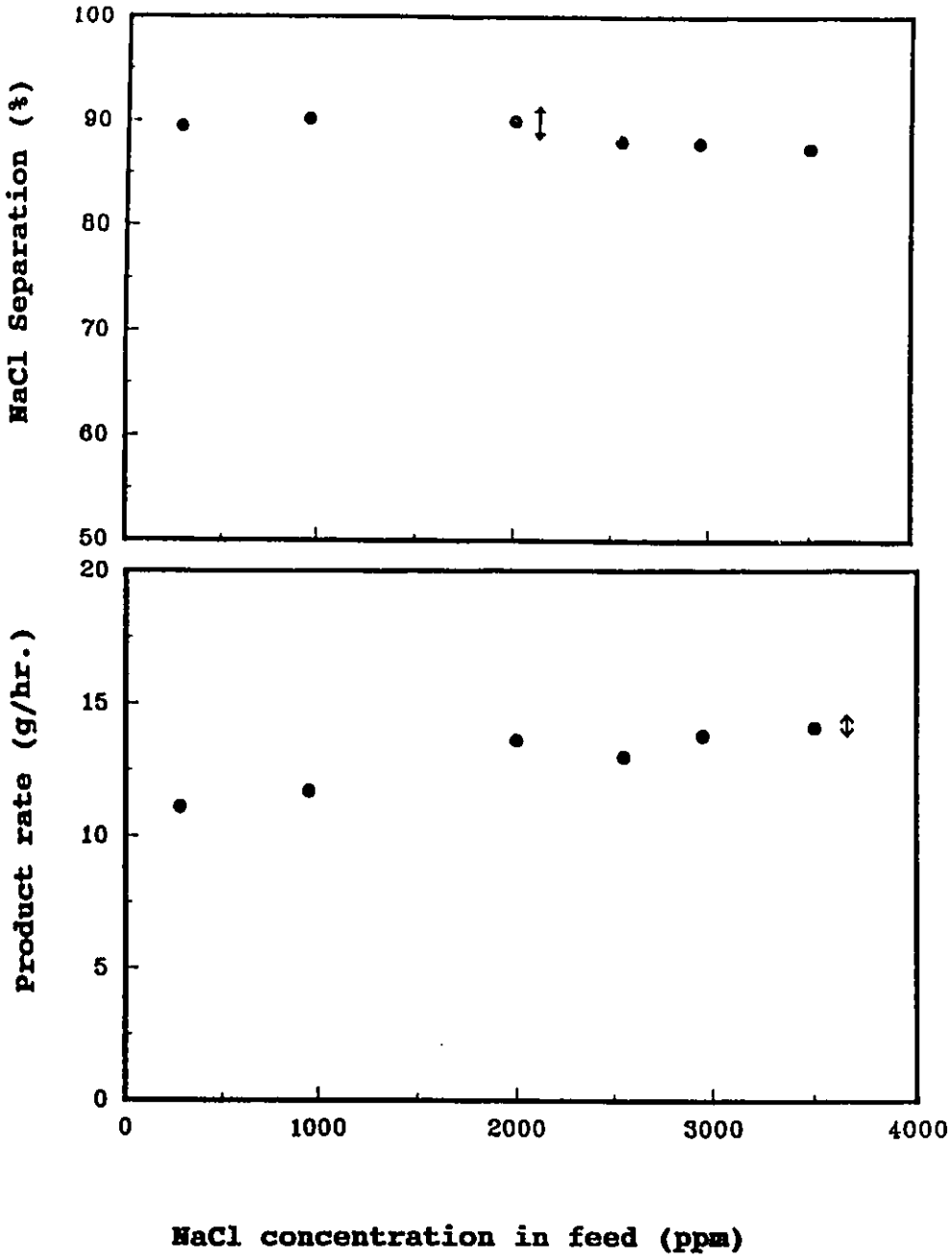


Figure 4.18 Effect of feed concentration on the membrane performance. Membrane making conditions: PVA conc. 1.0 wt%, cross-linking agent 3.0 wt% of malic acid, heating temperature 100 °C and heating period 10 min. Testing operating pressure 1724 kPag (250 psig). The details of the membrane making and testing procedures are described in Chapter 3.

of 1550 kPag. Then, the membranes were removed out of the RO system and immersed in an aqueous solution containing 225 ppm chlorine in the form of sodium hypochlorite for two days. Subsequently, the chlorine-exposed membranes were placed back into RO system and continued to be exposed to chlorine for one day under the RO conditions with 225 ppm chlorine aqueous solution as the feed. Finally, the RO experiment with a feed sodium chloride solution of 2000 ppm was repeated. Table 4.9 indicates that the sodium chloride separation remained unchanged while the product rate increased slightly following exposure to chlorine.

Table 4.9 Conditions & results of the chlorine resistance test

Time	Condition	Performance	N1 series Membrane		
			1	2	3
day 1	2000 ppm NaCl 1550 kPag	Separation (%)	58.5	75.8	71.7
		Product rate (g/hr.)	62.5	37.2	39.0
day 1 & day 2	225 ppm NaClO solution	Membranes were immersed for two days			
day 3	225 ppm NaClO 1550 kPag	Membranes remained in RO system under the operating conditions			
day 4	2000 ppm NaCl 1550 kPag	Separation (%)	58.6	72.9	71.3
		Product rate (g/hr.)	73.0	46.0	45.0

Separation of various inorganic electrolyte solutes and organic solutes The comparison of separation data with respect to various inorganic and organic solutes often indicates that the surface interaction forces govern the membrane separation of the solute. Several studies were conducted, in this respect, for the membranes of different materials by different authors (Sourirajan, 1983; Johnston, 1975; Kinjo and Sato, 1978; Matsuura et al., 1975; Chang, 1982). They have unanimously concluded that factors such as the ionic size, solute-solvent interaction and solute-membrane interaction are important in governing the separation of solutes. In particular, Chang (1982) obtained separation data for fifty four different salt samples with a formaldehyde-cross-linked PVA membrane, and concluded that the cross-linking reaction rendered the membrane surface negatively charged.

The separation of various inorganic electrolytes and organic solutes was conducted with respect to N series membranes in this study and the results are summarized in Table 4.10 together with the experimental conditions. Although there is a considerable amount of scatter in the product rate data, several rules can be found in the order of solute separations. The main features of Table 4.10 can be summarized as follows.

Among chloride salts the order in the rejection is,

KCl > NaCl > LiCl and $CaCl_2$ > $MgCl_2$

Comparing the cations of different valences when the anion is chloride, the order becomes

KCl, NaCl, LiCl > $CaCl_2$, $MgCl_2$ > $AlCl_3$

The observed orders in the solute separation indicate that the separation of the electrolyte solutes decreases with an increase in the cationic charge density.

Comparing the separation of different halide anions when the cation is sodium, the order in the separation is

$NaF > NaCl > NaBr$

Furthermore, comparing the separation of NaCl with Na_2SO_4, $MgCl_2$ with $MgSO_4$, LiCl with $LiNO_3$ and $AlCl_3$ with $Al(NO_3)_3$, we can conclude that the order of the separation among anions involved is

$SO_4^{2-} > Cl^- > NO_3^-$.

The above order indicates that the separation of the electrolyte decreases with a decrease in the charge density of anions.

The orders in the separation of both cations and anions suggest that the membrane surface is negatively charged, which is in agreement with the conclusion obtained by Chang (1982). The negative charge induced to the membrane surface is probably due to the unreacted carboxyl group of the diacid. The above experimental results also indicate that the separation of the electrolyte solutes depends largely on the coulombic interaction between solute ions and the charge on the membrane surface.

Unlike the inorganic electrolyte solutes, the order in the separation of the uncharged organic molecules listed in Table 4.11 is exactly the order of the increasing molecular weight, indicating the governing factor is the solute size. The separation of the dye molecule is exceptionally high since it is charged negatively by

dissociation.

Ion exchange capacity (IEC) of the TFC PVA membrane The ion exchange capacity of the PVA layer of the TFC PVA membrane was determined by the method described in Section 3.5. Some numerical values obtained by the intermediate steps involved in the procedure and the final IEC results are listed in Table 4.12. On the basis of the assumption presented in Section 3.5 that a half of the PVA film was cross-linked, the IEC values were evaluated to be 2.25 and 1.97 meq./g, respectively, for the two test samples. If assuming the whole PVA layer was cross-linked during the reaction, the IEC values were half of the above data. It should be noted that the theoretical maximum IEC value should be 5.78 meq./g assuming that the structure of the repeat-unit of the cross-linked PVA is as illustrated in Figure 3.9 with a molecular weight of 173.
These IEC values represent the negative charge.

Table 4.10 Separation of inorganic salts by TFC PVA membrane

Sample tested	Experiment conditions	Membrane performance	TFC PVA Membrane	
			N2 series	N1 series
LiCl	2000ppm 1550 kPag	Separation(%)	46.4	60.4
		PR (g/hr.)	54.8	40.6
NaCl	2000ppm 1550 kPag	Separation(%)	49.5	69.3
		PR (g/hr.)	63.6	42.0
KCl	2000ppm 1550 kPag	Separation(%)	51.8	70.3
		PR (g/hr.)	67.8	56.5
NaBr	2000ppm 1550 kPag	Separation(%)	55.2	66.4
		PR (g/hr.)	46.0	40.7
NaF	2000ppm 1550 kPag	Separation(%)	54.9	73.1
		PR (g/hr.)	56.4	40.8
$MnCl_2$	2000ppm 1550 kPag	Separation(%)	20.5	34.0
		PR (g/hr.)	42.4	41.2
$CaCl_2$	2000ppm 1550 kPag	Separation(%)	18.6	30.6
		PR (g/hr.)	42.0	33.4
$MgCl_2$	2000ppm 1550 kPag	Separation(%)	12.8	29.3
		PR (g/hr.)	49.2	34.6
$AlCl_3$	2000ppm 1550 kPag	Separation(%)	11.1	22.4
		PR (g/hr.)	38.8	38.4
Na_2SO_4	2000ppm 1550 kPag	Separation(%)	77.3	87.0
		PR (g/hr.)	67.5	45.2
$MgSO_4$	2000ppm 155 kPag	Separation(%)	60.9	76.9
		PR (g/hr.)	53.5	53.5
$LiNO_3$	2000ppm 1550 kPag	Separation(%)	43.6	65.0
		PR (g/hr.)	63.5	53.9
$Al(NO_3)_3$	2000ppm 1.550 kPag	Separation(%)	4.4	15.4
		PR (g/hr.)	43.7	40.9

Table 4.11 Separation of organic compounds by TFC PVA membrane

Organic & (MW)	Conditions	Membrane performance	TFC PVA membrane	
			N1 series	N2 series
Red dye*	200ppm 1550 kPag	Separation (%)	>99.5	>99.5
		Product rate (g/hr.)	38.0	57.6
PEG-400	2000ppm 1550 kPag	Separation (%)	53.4	39.0
		Product rate (g/hr.)	37.6	50.6
Sucrose (342.3)	2000ppm 1550 kPag	Separation (%)	44.5	30.9
		Product rate (g/hr.)	40.0	68.0
PEG-200	2000ppm 1550 kPag	Separation (%)	39.1	23.7
		Product rate (g/hr.)	31.7	40.3
Glucose (198.7)	2000ppm 1550 kPag	Separation (%)	38.7	22.3
		Product rate (g/hr.)	32.0	51.4

*provided by Osmonics Inc., and the name and formula are unknown. The molecular weight is about 500.

Table 4.12 Ion exchange capacity of TFC PVA membrane

	Titration test #1			Titration test #2		
HGO1 membrane	coupon #1	coupon #2	coupon #3	coupon #1	coupon #2	coupon #3
Weight of dried substrate (g)*	0.2400	0.2590	0.2840	0.2765	0.2590	0.2550
Weight of PVA membrane (g)**	0.2500	0.2695	0.2950	0.2880	0.2717	0.2650
Weight of PVA layer (g)	0.0120	0.0105	0.0110	0.0115	0.0127	0.0100
Total PVA weight (g)	0.0336			0.0342		
Cross-linked PVA (g)	0.0168			0.0171		
Conc. of NaOH solution (N)	0.01			0.01		
Added NaOH solution (ml)	30.0			30.0		
Conc. of HCl solution (N)	0.01			0.01		
Consumed HCl solution (ml)	26.23			26.64		
IEC value (meq./g)	2.25			1.97		

* The substrates were dried in oven at 100°C for 10 minutes.

** The membranes were R series.

4.5 Liquid Chromatography for the Study of Interfacial Interaction

Retention time (volume) data obtained from the liquid chromatography experiment reflects the interaction forces working in the system polymer(packing material)-solvent (mobile phase)-solute. Namely, a longer retention time means a stronger attractive force working between the solute and the polymeric material. Furthermore, the above system simulates the interaction forces working between polymer(membrane)-solvent-solute in the reverse osmosis system. The liquid chromatography is therefore a useful tool to study the interfacial interaction forces and to have an insight into the mechanism of the reverse osmosis separation. The retention time was determined for various solutes when water is used as a solvent and pumped through a column packed with cross-linked PVA powder. The solutes are inorganic electrolytes, PEG of different molecular weights and other organic solutes. The details of the experiment are described in the liquid chromatography experiment. The results of the experiments are listed in Tables 4.13 to 4.15.

Regarding the retention time of the electrolyte solutes, although all the data are found in a very narrow range, some distinct tendencies are observed.

Comparing the chlorides of alkali metal cations, the order in the retention time is

KCl < NaCl < LiCl

Comparing the chlorides of alkaline earth cations, the order in the retention time is

$BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2$

Comparing the chlorides of metal ions with different valences, the order of retention time is

monovalent < divalent < trivalent

The above data indicate that the retention time increases with an increase in the cationic charge density.

For different halide anions, when the cation is fixed to sodium ion, no correlation was found between the anionic charge density and the retention time. However, for anions of different valences, the retention time of Na_2SO_4 is less than that of NaCl, indicating that the retention time increases when the anionic charge density is decreased. The above results are again consistent with the assumption of a negative charge on the polymer particle packed in the chromatography column. The retention volumes of the electrolyte solutes are smaller than that of D_2O without exception, indicating that water is preferentially adsorbed to the polymeric material.

As for the organic solutes without charge, the primary interaction force is due to van der Waals interactions and steric interaction. While the van der Waals attractive force increases with molecular weight, particularly when the molecule is a straight chain molecule, the steric repulsive force also increases with an increase in the molecular weight (Sourirajan, 1983). Therefore, a maximum in the retention time is expected when these two opposing

effects are superimposed. The maximum is observed at the molecular weight of 6000 in the homologous group of polyethylene glycol.

A similar tendency is observed also for alcohol solutes. Comparing the straight chain alcohols, the retention time increases monotonically from methyl to n-hexyl alcohol. However, the retention time of isopropyl alcohol is smaller than that of n-propyl alcohol, and the retention time of t-butyl alcohol is smaller than that of n-butyl alcohol, indicating that the branching of the molecule increases the steric repulsion.

It should also be noted that the molecules that have more than one hydrophillic functional group such as glycerol and sucrose demonstrated retention volumes smaller than D_2O. On the other hand, the retention time of benzene solute is the largest, indicating a hydrophobic interaction between the hydrocarbon solute and the polymer. Similar tendencies were observed with respect to other polymeric materials including cellulose acetate and aromatic polyamide (Sourirajan and Matsuura, 1985; Tam, 1989). The retention times of hydrocarbon and phenol relative to other organic solutes are, however, much smaller for cross-linked polyvinyl alcohol than cellulose acetate and aromatic polyamide, reflecting the stronger hydrophilicity of polyvinyl alcohol. The chromatography retention volume data suggest that the separation of phenol should be high by the reverse osmosis membrane made of cross-linked polyvinyl alcohol. This prediction has to be confirmed experimentally.

Table 4.13 Retention time for inorganic salts

Sample	Molecular weight	Retention time (minute)	
D_2O	18.02	3.69	3.69
LiCl	42.39	3.36	3.36
NaCl	58.45	3.20	3.20
KCl	74.55	3.20	
NaI	149.9	3.36	3.31
NaBr	102.9	3.10	3.10
NaF	42.0	3.32	3.42
$MgCl_2$	95.21	3.42	3.42
$CaCl_2$	110.99	3.36	3.42
$SrCl_2$	158.53	3.31	3.26
$BaCl_2$	208.24	3.20	3.10
$MgSO_4$	120.37	3.26	3.20
Na_2SO_4	142.06	3.15	3.10
$AlCl_3$	133.34	3.42	3.42

Table 4.14 Retention time for polyethylene glycols

PEG Sample	Retention Time (minute)	
PEG-200	3.52	3.52
PEG-400	3.63	3.74
PEG-600	3.68	3.58
PEG-1000	3.79	3.84
PEG-1500	4.0	4.06
PEG-3000	3.79	3.84
PEG-6000	5.18	5.34
PEG-9000	4.75	4.86
PEG-12000	4.16	4.06
PEG-15000	3.63	3.63
PEG-20000	4.22	4.27
PEG-35000	4.16	4.16

Table 4.15 Retention time for organic compounds

Sample	Molecular weight	Retention time (minute)	
D_2O	18.02	3.69	3.69
Methyl alcohol	32.04	4.43	4.43
Ethyl alcohol	46.07	4.48	4.48
n-Propyl alcohol	60.09	4.59	4.54
Isopropyl alcohol	60.09	4.54	4.54
n-Butyl alcohol	74.12	5.18	5.18
t-butyl alcohol	74.12	4.87	4.87
n-Hexyl alcohol	102.12	6.51	6.67
Phenol	94.11	5.10	5.08
Acetone	58.08	4.48	4.54
Methyl ethyl ketone	72.11	4.54	4.54
Glycerol	92.1	3.61	3.68
Sucrose	342.3	3.49	3.65
Ethyl acetate	88.11	4.85	4.05
Benzene	78.11	10.41	10.68

Chapter 5

5. Conclusions

1. Thin-film composite (TFC) membranes can be prepared by coating a PS UF membrane with a PVA polymer and cross-linking the resulting polymer layer with malic acid or glutaraldehyde.

2. The important process parameters are the composition of PVA polymer solution, concentration of cross-linking solution, as well as cross-linking temperature and period.

3. The PVA coating and the process of heat treatment to promote cross-linking are the major steps which cause low water permeation of the resulting TFC PVA membranes.

4. The TFC PVA membrane prepared in this work has excellent chlorine resistance and can be used for reverse osmosis processes at low operating pressure.

5. The product rate of the TFC PVA membrane can also be increased by adding an additive (ethyl alcohol) into PVA solution, by immersing the membrane in alcohol solutions and by exposing the membrane to a chlorine solution.

6. The separation of the TFC PVA membranes for inorganic electrolyte solutes increases with an increase in the negative charge density and with a decrease in positive charge density of

the ions involved in the electrolyte solute. The separation for uncharged organic solutes is in the order of the molecular size.

7. Because of the existence of unreacted carboxylic groups in the cross-linked PVA, the surface layer of the TFC PVA membranes is negatively charged.

8. The retention time in liquid chromatography experiments can serve as an effective measure of determining the interaction force working in the membrane-solute-solution system.

Chapter 6

6. Recommendations

1. Use of a factorial design would be desirable to determine the significance of some important process parameters discussed in Section 4.2, such as PVA concentration, cross-linking reagent concentration, cross-linking temperature and time.

2. Further investigations are necessary with all cross-linking reagents shown in Figure 4.1 and Section 4.3. For all the above cross-linking reagents, high and low temperature cross-linking as well as other techniques, such as ultraviolet and Co^{60}-γ ray irradiation, should be tried.

3. To reduce the thickness of TFC PVA membranes, water-immiscible solvents should be introduced as the solvent for cross-linking regents.

4. The potential application in pervaporation of the TFC PVA membrane prepared in this work should be attempted.

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Appendix

A Calculation of the theoretical maximum IEC value of TFC PVA membranes

Assuming all hydroxyl groups of PVA molecules are esterified with a carboxyl group of malic acid molecules, while the other carboxyl group of the latter acid molecules is left free, one equivalent of free acid is formed from one repeat unit of the PVA molecule. The molecular weight of the repeat unit is 173 g/repeat unit (see Figure 3.9 as a reference). Therefore, the theoretical maximum IEC value can be calculated by:

$$(IEC)_{max} = \frac{1}{173} = 5.79 \ (meq/g)$$