MEMBRANE DEVELOPMENT AND FABRICATION FOR REVERSE OSMOSIS AND ULTRAFILTRATION

PART 3

Report to the
Water Research Commission

by

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FINAL REPORT TO THE
WATER RESEARCH COMMISSION

BY THE
INSTITUTE FOR POLYMER SCIENCE
UNIVERSITY OF STELLENBOSCH

PART 3:
THE CHEMISTRY OF POLY-2-VINYLIMIDAZOLINE REVERSE OSMOSIS MEMBRANES

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THE REPORT IS PRESENTED IN FOUR PARTS:

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EP JACOBS and RD SANDERSON

PART 2: STATISTICAL AND NUMERICAL TECHNIQUES IN THE OPTIMIZATION OF MEMBRANE FABRICATION VARIABLES
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(CLASSIFIED - NOT AVAILABLE FOR DISTRIBUTION)
NKH STROHWALD, EP JACOBS and RD SANDERSON

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EXECUTIVE SUMMARY

This investigation forms part of a research programme designed to contribute to the development of reverse osmosis (RO) technology. More specifically, it contributes to knowledge of the preparation, characterization and use of poly-2-vinylimidazoline-type polymeric precursors and of sulphonic acid chloride crosslinking agents for the fabrication of ultrathin-film (UTF) membranes for RO desalination.

The technique of using membranes in pressure-driven separation operations is gaining ever-increasing acceptance, both in research and in various industrial applications. The first major breakthrough in the field of RO came in the late 1950s when a method for the making of effective and very thin CA membranes was discovered. This area of research then expanded rapidly into the field of UTF composite membranes. The use of these membranes in industry has become very important; much of the knowledge and many of the concepts regarding this young science are disclosed in patent literature and in government reports. Many materials have been screened for possible use as RO membrane materials. Of the numerous chemical systems used to create successful UTF membranes, those generally used have been the interfacially formed polymeric desalting barriers prepared from derivatives of polyethyleneimine (PEI), phenylenediamine or piperazine precursors, reacted with either a di- and/or tri-functional benzenecarboxylic acid chloride as crosslinking agent.

Only during the last few years have sound scientific studies been directed at ascertaining why membranes perform the way they do and why they fail chemically. Much of this recent activity resulted from the availibility of sufficiently sophisticated analytical techniques, such as electron scanning calorimetric analysis (ESCA), which are suitable for the analysis of thin crosslinked polymeric networks(3).

This followed from the premise that poly-2-vinylimidazoline (PVAM) can be synthesized inexpensively and simply from available reagents. A second reason for using such a chemical compound as a UTF membrane precursor was that the nitrogen atoms are not part of the main polymer chain. Upon reaction of homopolymeric PVAM with an acid chloride crosslinking agent, tertiary amide groups should be formed. Having any nitrogen-containing unreacted groups which might be susceptible to chlorination, causing subsequent deterioration of the membrane, in the polymer side chain, was thought to offer a possible way of increasing resistance of a membrane to degradation by chlorine.

In the event of this study leading to the obtaining of efficient RO membranes, the novel chemical system was to be optimized in order to achieve formation of an ultrathin-film structure with high membrane performance.

The goals of the investigation was:

i) to study the chemistry of PVAM;

ii) to obtain insight into the reactions which this compound undergoes with aromatic acid chloride crosslinking agents in the fabrication of UTF-RO membranes and into the chemical composition of a final PVAM/SCl deslating barrier;

iii) to study certain selected membrane fabrication conditions and the effect of variations on the membrane performance;

iv) to ascertain what the effect of various operating conditions may have a PVAM UTF membrane.

The work proved the following:

1. Poly-2-vinylimidazoline (PVAM) can be used as precursor material in interfacial reactions to make efficient RO membranes. These could be made in flat-sheet and tubular forms. Two different polymer products, termed PVAM-OD and PVAM-FD, were obtained by using two different sets of reaction conditions. PVAM was characterized by ^{13}C nmr spectroscopy and found to be a copolymer, comprising ring-closed (imidazoline) and its hydrolysed form of ring-opened (amide) repeat units. PVAM-CFD was obtained after partial purification of PVAM-FD.

   The use of PVAM, with its nitrogen atoms having one reactive hydrogen and being pendent to the hydrocarbon chain, resulted in some increase in chlorine-tolerance of the membranes. This chlorine-tolerance was greater than that of membranes made with aliphatic polymeric precursors, e.g. PEI (NS-100/1 membranes), but not as great as that of membranes made from aromatic precursors, e.g. phenylenediamine (FT-30 membranes).

2. The use of aromatic crosslinking agents containing sulphonylhloride groups, in addition to carboxylic acid chloride groups, illustrated the importance of the chemical nature of the reactive groups and of the effect which the structure of the reactants has on membrane structure, as reflected in the RO performance of the membranes. In terms of membrane performance, the use of the crosslinking agents 3-chlorosulphonylbenzoyl chloride (SCl) and 3,5-dichlorosulphonylbenzoyl chloride (Cl2S) gave flat-sheet membrane RO performances better than those of membranes prepared with the more generally used reagent, isophthaloyl chloride (IPC). For example:

   a) Use of SCl instead of IPC gave PEI UTF membranes which gave higher flux and rejection, as illustrated by the following RO performances:

PEI/IPC membranes	98,4% rejection; 600 lmd flux
PEI/SCl membranes	98,7% rejection; 835 lmd flux

(Membranes were tested with 5 000 ppm NaCl solution at 4 MPa)

(b) Use of SCl instead of IPC gave early PVAM UTF membranes which gave higher rejection, as illustrated by the following RO performances by flat-sheet membranes:
PVAM/IPC membranes 72,7% rejection; 1 760 lmd flux
PAM/SCl membranes 84,6% rejection, 680 lmd flux
(Membranes were tested with a 5 000 ppm NaCl solution at 4 MPa)

(c) Use of the trifunctional reagent Cl2S gave PVAM UTF membranes which gave higher rejection and flux than those of membranes prepared with SCl, as illustrated by the following results:
PVAM/SCl membranes 84,6% rejection; 680 lmd flux
PVAM/Cl2S membranes 96,4% rejection; 800 lmd flux
(Membranes were tested with a 5 000 ppm NaCl solution at 4 MPa)

3. Numerous fabrication variables were found to be important in the preparation of efficient PVAM UTF membranes; slight variations led, in some cases, to large variations in membrane performance. Of the variables studied, those considered most important were: polysulphone (PS) substrate, chemistry of the crosslinking agent, concentration of crosslinking agent and of precursor, addition of acid acceptor to the precursor solution and heat-cure temperature.

   The best RO performance results obtained for PVAM-OD/SCl membranes in flat-sheet form were:

   94,3 ± 1,2% rejection; 1 096 ± 50 lmd
   (tested for 5 000 ppm NaCl at 4 MPa)

   97,4 ± 1,4% rejection; 400 ± 22 lmd
   (tested for 2 000 ppm NaCl at 2 MPa)

   The optimum RO performances of PVAM-OD/SCl tubular membranes (developed during a parallel study) were:

   97,1 ± 0,1% rejection; 730 ± 24,1 lmd
   (tested for 2 000 ppm NaCl at 2 MPa)

   The optimum RO performances of PVAM-FD/SCl tubular membranes (developed during a parallel study) were:

   98,2 ± 0,7 rejection; 560 ± 150 lmd
   (tested for 2 000 ppm NaCl at 2 MPa)

4. Exposure of PVAM UTF membranes to chlorine is not advisable. It is, however, proposed that exposure of PVAM-FD/SCl membranes to 5 ppm chlorine at pH 6 to 7 for a short period of time would be tolerated. Prolonged exposure to chlorine results in irreversible decline in rejection.

Maximum performance of PVAM-FD/SCl tubular membranes has been recorded in the pH 6,5 to 7 range. These membranes can be safely used over a pH range of 4,5 to 8,5.

Exposure of membranes to solutions of pH 3 over a period of one month under dynamic conditions, led to a drop in baseline rejection performance and increase in flux. Under similar conditions at pH 11, the membranes showed only a slight drop in rejection but an almost doubling in flux.

After static storage of membranes at pH 3 there was a rapid and irreversible decline in membrane performance. Similar storage of membranes at pH 11 caused no decrease in salt rejection but an almost doubling in flux.

Flat-sheet PVAM/SCl membranes may be operated at temperatures of up to 40°C. Compared with the performance of membranes operated at 25°C, the salt rejection by membranes operated at 40°C was unaffected, but fluxes were almost doubled.

5. The use of model compounds to study the effect of external variables on groupings typical of those found in a PVAM/SCl ultrathin films revealed the problems associated with hydrolytic stability which could arise in the UTF membrane: during synthesis of the PVAM precursor, during formation of the PVAM UTF membrane and during operation of the membrane. Model-compound studies proved to be very valuable in characterizing batches of PVAM by ^{13}C nmr spectroscopy and determining the chemical composition of PVAM-FD/SCl membranes. However, the results of the studies of the reactions of the PVAM/SCl membranes model compounds could not adequately explain changes, at the molecular level, in the membrane's performance under harsh operating conditions. It is nonetheless suggested that model-compound studies should be carried out in parallel with chemical studies on any future novel UTF membrane system development.

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ABSTRACT

This study concerns the preparation of poly-2-vinylimidazoline (PVAM) and 3-chlorosulphonylbenzoyl chloride (SCl) and their use for making ultrathin-film composite reverse osmosis membranes.

PVAM was prepared by two synthetic routes, leading to two products, termed here, PVAM-OD and PVAM-FD. PVAM was characterized by ^{13}C nmr spectroscopy and found to be a copolymer of ring-closed (amidine) repeat units and hydrolysed or ring-opened (linear amide) repeat units. The model compounds of these functional groups were synthesized.

Using different combinations of membrane fabrication conditions, numerous PVAM/SCl membranes were made and tested for salt rejection and permeate flux. Good RO performances were achieved. Flat-sheet PVAM-OD/SCl membranes gave 97,4% rejection and 400 lmd flux (tested at 2 000 ppm NaCl feed, 2 MPa and 25°C). The performances of PVAM/SCl membranes were improved when membranes were made in tubular form. In an optimum case PVAM-FD/SCl tubular membranes gave 99,1% NaCl rejection and 860 lmd flux (tested at 2 000 ppm NaCl feed, 2 MPa, 20°C).

The model compounds representing the functional groups present in the PVAM/SCl desalting barrier were prepared, characterized and then exposed to solutions of high and low pH and chlorinated solutions. Reactions were followed and products analysed by high-pressure liquid chromatography.

The PVAM/SCl membranes were also tested to determine whether they were stable in feedwaters of low and high pH and in feedwaters containing chlorine.

OPSOMMING

Hierdie studie behels die bereiding van poli-2-vinielimidasolien (PVAM) en 3-chlorosulfoniel bensoielchloried (SCl) en die gebruik daarvan vir die maak van ultradun-film saamgestelde tru-osmose membrane.

PVAM is berei volgens twee sintetiese metodes wat tot twee produkte gelei het, naamlik PVAM-OD en PVAM-FD. PVAM is met behulp van ^{13}C kmr-spektroskopie gekarakteriseer en daar is gevind dat dit 'n kopolimeer met geslote-ring (amidien) herhaaleenhede en gehidroliseerde of oop-ring (lineêre amied) herhaaleenhede is. Modelverbindings van hierdie funksionele groepe is berei.

Deur verskillende kombinasies membraanvervaardigingstoestande te gebruik, is 'n groot aantal PVAM/SCl-membrane gemaak en vir soutverwerping en permeaatvloed getoets.. Goeie resultate is verkry. Plat-vel PVAM-OD/SCl-membrane het 97,4% soutverwerping en 400 lmd vloed getoon (getoets vir 2 000 dpm NaCl, by 2 MPa en 25°C). Die resultate van die PVAM/SCl-membrane is verbeter toe membrane in buisvorm gemaak is. In 'n optimum geval het PVAM-FD/SCl-buismembrane 99,1% NaCl soutverwerping en 860 lmd vloed getoon (getoets vir 2 000 dpm NaCl, by 2 MPa en 20°C).

Die modelverbindings, wat die funksionele groepe van die PVAM/SCl-ontsoutingslaag verteenwoordig, is berei, gekarakteriseer en toe aan oplossings van hoë en lae pH en chloor-bevattende oplossings blootgestel. Reaksies is gevolg en produkte met behulp van hoë-druk vloeistofchromatografie geanaliseer.

Die PVAM/SCl-membrane is ook in water met lae en hoë pH en chloor-bevattende water vir hulle stabiliteit getoets.

LIST OF ABBREVIATIONS

CA	Cellulose acetate
CL2S	3,5-Dichlorosulphonylbenzoyl chloride
DMF	N,N-Dimethylformamide
EDA	Ethylenediamine
ESCA	*Elecron spectroscopy for chemical analysis*
AHEA-1	Poly(acrylic acid-co-hydroxyethyl acrylate), 10% acrylic acid in copolymer (Batch 1)
AHEA-2	Poly(acrylic acid-co-hydroxyethyl acrylate), 10% acrylic acid in copolymer (Batch 2)
DBEI	1,3-dibenzoyl-2-ethylideneimidazolidine
HMC	N-Propionylethylenediamine
HMC 1	1-Benzoyl-2-propionylethylenediamine
HMC 2	1-Benzenesulphonyl-2-propionylethylenediamine
HPLC	High-pressure liquid chromatography
IPC	Isophthaloyl chloride
MC	2-Ethylimidazoline
MC 1	1-Benzoyl-2-ethylimidazoline
MC 2	1-Benzenesulphonyl-2-ethylimidazoline
Nmr	Nuclear magnetic resonance spectroscopy
PAN	Polyacrylonitrile
PEI	Polyethyleneimine
PS	Poly(bisphenol A sulphone)
PVA	Polyvinylamine
PVAM	Poly-2-vinylimidazoline (polyvinylamidine)
PVAM-OD	PVAM prepared by the oven-drying method
PVAM-FD	PVAM prepared by the freeze-drying method
PVAM-CFD	PVAM-FD, partially purified by extraction of ethylenediamine
PVAM-AR	Poly-2-vinylbenzimidazoline

PVAM-HY	Poly-N-aminoethylacrylamide (hydrolysed form of PVAM)
PVOH	Polyvinyl alcohol
ppm.h	Product of chlorine concentration and exposure time
RO	Reverse Osmosis
2S	1,3-Benzenedisulphonyl chloride
SCL	3-Chlorosulphonylbenzoyl chloride
SLS	Sodium lauryl sulphate
TEA	Triethylamine
TDS	Total dissolved solids content
TFC	Thin Film Composite, trademark of membranes made by Fluid Systems Division, UOP.
TLC	Thin-layer chromatography
TMC	1,3,5-Benzenetricarboxylic acid chloride
UF	Ultrafiltration
UTF	Ultrathin film

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CHAPTER 1

INTRODUCTION

This investigation forms part of a research project to contribute to the development of reverse osmosis (RO) technology. More specifically, it contributes to knowledge of the preparation, characterization and use of poly-2-vinylimidazoline-type polymeric precursors and of sulphonic acid chloride crosslinking agents for the fabrication of ultrathin-film (UTF) membranes for RO desalination.

1.1 REVERSE OSMOSIS MEMBRANES

The technique of using membranes in pressure-driven separation operations is gaining ever-increasing acceptance, both in research and in various industrial applications. The first major breakthrough in the field of RO came in the late 1950s when a method for the making of effective and very thin CA membranes was discovered(1). This area of research then expanded rapidly into the field of UTF composite membranes. The use of these membranes in industry has become very important; much of the knowledge and many of the concepts regarding this young science are disclosed in patent literature and in government reports. Many materials have been screened for possible use as RO membrane materials. Of the numerous chemical systems used to create successful UTF membranes, those generally used have been the interfacially formed polymeric desalting barriers prepared from derivatives of polyethyleneimine (PEI), phenylenediamine or piperazine precursors, reacted with either a di- and/or tri-functional benzenecarboxylic acid chloride as crosslinking agent(2).

Only during the last few years have sound scientific studies been directed at ascertaining why membranes perform the way they do and why they fail chemically. Much of this recent activity resulted from the availibility of sufficiently sophisticated analytical techniques, such as electron spectroscopy for chemical analysis (ESCA), which are suitable for the analysis of thin crosslinked polymeric networks(3).

1.2 OBJECTIVES

The goal of the present study was to investigate the use of polymeric precursor compounds with 2-imidazoline structure in the fabrication of UTF RO membranes. This followed from the premise that poly-2-vinylimidazoline (PVAM) can be synthesized inexpensively and simply from available reagents. A second reason for using such a chemical compound as a UTF membrane precursor was that the nitrogen atoms have only one reactive site and are not part of the main polymer chain. Upon reaction of homopolymeric PVAM with an acid chloride crosslinking agent, tertiary amide groups should be formed. Having any nitrogen containing groups which might be susceptible to chlorination, causing subsequent deterioration of the membrane, in the polymer side chain, was thought to offer a possible way of increasing resistance of a membrane to degradation by chlorine.

It was, furthermore, desirable to use novel aromatic chemical crosslinking components which contained sulphonyl chloride groups and which varied in functionality. Incorporation of sulphonate groups in membrane structures could result in increases in rejection, flux and fouling resistance of the membrane(4).

The chemical reactions which occur during the creation of UTF RO membranes by interfacial polycondensation reactions are only partially understood. The crosslinked interfacial film is often less than 300 nm thick and because there are indications that such a thin-film desalting barrier is not homogeneous but varies in both chemical structure and degree of crosslinking through its thickness, techniques must be found to shed more light on the membrane chemistry. Further objectives were to create some of the model structures expected to be formed in the ultrathin film and to study the chemical behaviour of the different functional groups under conditions similar to those under which membranes were used. This would, unfortunately, be limited to the study of reactions in solution and not in an ultrathin crosslinked film.

In the event of this study leading to the obtaining of efficient RO membranes, the novel chemical system was to be optimized in order to achieve formation of an ultrathin-film structure with high membrane performance(5).

The objectives of this research would be:

(i) to study the chemistry of PVAM;

(ii) to obtain insight into the reactions which this compound undergoes with aromatic acid chloride crosslinking agents in the fabrication of UTF RO membranes and into the chemical composition of a final PVAM/SCl desalting barrier;

(iii) to study certain selected membrane fabrication conditions and the effect of variations on the membrane performance;

(iv) to ascertain what the effect of various operating conditions may have on a PVAM UTF membrane.

1.3 SCOPE

To meet the objectives of the research, a number of tasks was undertaken, as given below.

1.3.1 SYNTHESIS AND CHARACTERIZATION OF PVAM

As very little was known of PVAM, various synthesis routes were to be studied and attempts made to characterize the products. If, after synthesis, more than one functional group was found to be present in the product, it would be of interest to study the effect of such chemical variations on the chemistry and performance of the ultrathin film. The synthesis and characterization of PVAM are described in Section 4.3.

1.3.2 SYNTHESIS AND USE OF AROMATIC CROSSLINKING AGENTS CONTAINING SULPHONYL CHLORIDE GROUPS

The compounds to be synthesized were:

3-Chlorosulphonylbenzoyl chloride (SCl)
3,5-Dichlorosulphonylbenzoyl chloride (Cl2S)

Membranes were to be fabricated using the PVAM precursor and the different crosslinking agents and then tested for their RO performance. Early indications were that SCl and Cl2S were promising crosslinking agents. The synthesis and use of the crosslinking agents is described in Section 4.2.

1.3.3 CREATION OF NOVEL PVAM/SCL AND PVAM/CL2S UTF MEMBRANES, USING VARIOUS FABRICATION CONDITIONS, AND DETERMINATION OF THEIR RO PERFORMANCES

The formation of any membrane system involves a multitude of fabrication variables, such as concentration of reagents, contact time and conditions of heat-curing, all of which are, furthermore, interrelated. A number of combinations of these variables was to be used in the fabrication of UTF RO membranes from PVAM as polymeric precursor and a sulphonate-group-containing compound as the crosslinking agent. The objectives of this operation were to:

(a) obtain indications as to the salt rejection and water permeability capability of the PVAM UTF RO membranes;

(b) attempt to determine, by changing one variable at a time, which fabrication variables appeared to have the most significant effects on RO membrane performance;

(c) arrive, by this approach, at a set or sets of fabrication conditions under which PVAM UTF RO membranes of high baseline RO performance could be fabricated.

The results are described in Section 4.4.

(Information obtained during this phase of the research was used later as the basis for the choice of levels for fabrication conditions during the development of a method for the mathematical optimization of PVAM/SCl membranes, during a parallel project(5).)

1.3.4 EVALUATION OF THE STABILITY OF PVAM/SCL MEMBRANES AT LOW AND HIGH pH, AND IN A CHLORINE ENVIRONMENT

PVAM/SCl membranes were to be prepared and evaluated for their RO performance after they had been exposed to harsh operating conditions imposed by feedwaters containing chlorine and by feedwaters of high and low pH. Results are given and discussed in Section 4.5.

1.3.5 PREPARATION OF THE MONOMERIC MODEL COMPOUNDS REPRESENTING THE FUNCTIONAL GROUPS HYPOTHESIZED TO BE PRESENT IN THE PVAM/SCL MEMBRANE AND STUDY OF THEIR REACTIONS IN LOW AND HIGH pH MEDIA AND IN A CHLORINE ENVIRONMENT

Model-compound studies were carried out on the monomeric forms of the repeat units of the effective PVAM/SCl UTF RO membrane. To this end, model compounds were selected, synthesized and

1.3.5 PREPARATION OF THE MONOMERIC MODEL COMPOUNDS REPRESENTING THE FUNCTIONAL GROUPS HYPOTHESIZED TO BE PRESENT IN THE PVAM/SCL MEMBRANE AND STUDY OF THEIR REACTIONS IN LOW AND HIGH pH MEDIA AND IN A CHLORINE ENVIRONMENT

Model-compound studies were carried out on the monomeric forms of the repeat units of the effective PVAM/SCI UTF RO membrane. To this end, model compounds were selected, synthesized and characterized. They were then exposed to chlorine-containing solutions and solutions of high and low pH, and their stability or reactivity under such conditions determined. Results are described in Section 3.9.

The aim of this study was basically to investigate the usefulness of the results obtained from the model compound studies in explaining any change in membrane performance which occurred, at the molecular level, after exposure of the membranes to chlorine-containing feedwater and to low and high pH media. The relationships between model-compound-study results and the PVAM precursor, PVAM/SCI membranes and their behaviour under harsh operating conditions are discussed in Section 4.7.

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CHAPTER 2

HISTORICAL AND THEORETICAL BACKGROUND

2.1 WATER PURIFICATION

The rapidly expanding population of the world is placing a great strain on available water supplies. As in some other parts of the world, South Africa has arid regions and is faced with the additional hardship of periodic droughts.

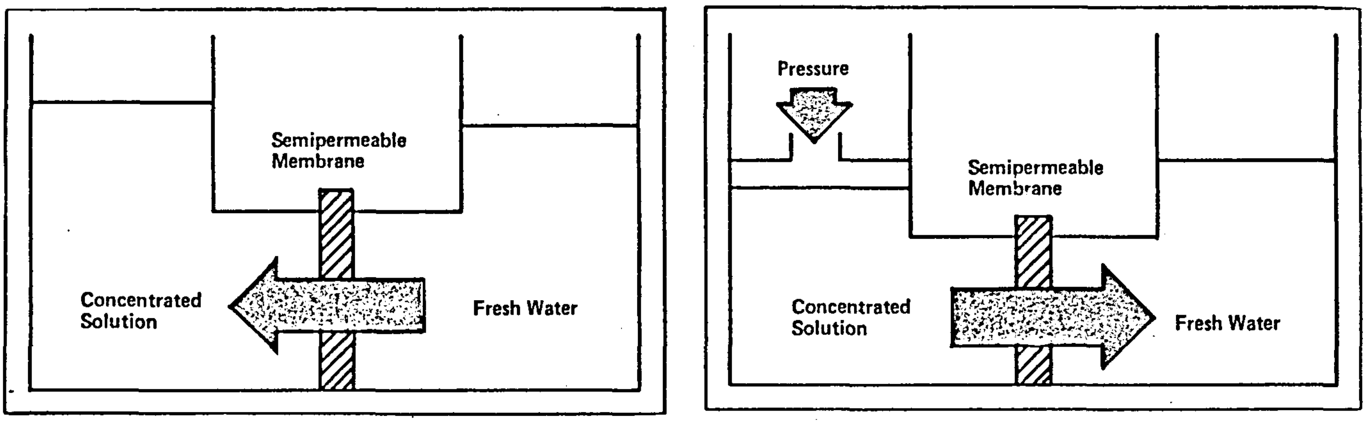
Present groundwater resources in the Republic are estimated to be adequate for only the next 30 years, whereafter the demand will exceed supply(1). The time has therefore come for conventional sources of water supply in selected areas to be supplemented by means of advanced techniques applied to wastewater purification to meet the future increase in demands for water of both adequate quality and quantity.

A number of processes has been developed, worldwide, for obtaining usable or potable water by desalination of seawater and brackish water(2). These processes include: distillation, freezing, ion-exchange and the membrane-based operation of reverse osmosis (RO).

Since the early 1970s, desalination by the pressure-driven membrane process of RO has developed into a commercially viable process(3,4). RO has become increasingly favoured as a separation process because it consumes far less energy than other processes do(5,6).

2.2 REVERSE OSMOSIS

Reverse Osmosis (RO) is a process for the separation of substances in a solution(7). It is the process whereby water is forced by pressure through a semipermeable membrane, counter to the normal direction of osmotic flow, as shown in Figure 2.1



Osmosis - normal flow from low-concentration solution to high-concentration solution.

Reverse osmosis - flow reversed by application of pressure to high-concentration solution.

FIG. 2.1: SCHEMATIC REPRESENTATION OF THE PROCESSES OF OSMOSIS AND REVERSE OSMOSIS(8)

By this process, nearly salt-free water is forced out of a salt-containing solution by the application of pressure to the salt-containing solution; this pressure must obviously be higher than the osmotic pressure of the salt solution. The RO process enables ions in solution and small molecules of 1 nm and less particle size to be concentrated, leaving a permeate of much-reduced concentration of such dissolved solids. The permeate from the membrane is generally withdrawn at atmospheric pressure and ambient temperature. RO can take place at any operating pressure at which fluid flow through the membrane can be established, i.e. the osmotic pressure of the solution must be overcome(9). The heart of the RO process is the semipermeable membrane which must allow passage of the water but not of the dissolved solids(10). Both the chemical nature and porous substructure of the membrane surface together govern the mechanism of RO separation(9,10). The technique of separation by RO depends on the property of certain porous membranes to hold water in the "ice-like" state(11) and thus act as a barrier which is more permeable to water but less permeable to most solutes(12). The molecular size cut-off for RO is usually from 0,4 - 0,8 nm. Water permeability of a membrane is inversely (although not linearly) related to the salt rejection. Single-stage desalination of seawater by RO requires a membrane which approaches theoretical semipermeability and which is sufficiently thin to permit rapid transport of water at practical pressures and recovery rates. The product flux through a membrane is inversely proportional to the thickness of the separating layer(13).

The principles of pressure-driven membrane processes have been discussed by Belfort(14). Aspects of RO, including free-energy requirements, transport relations and mechanisms of salt rejection, have been reviewed by Dresner and Johnson(15) and are the subject of many books(16,17) and review articles(5,7,18,19 20). The economics of RO have been discussed by Reed(21), Belfort(14) and others(22). Economic considerations of seawater and brackish water desalination by RO under South African conditions has been discussed by Schutte(1).

According to Sourirajan(9) the science of RO is based on the following:

(i) the physicochemical basis for RO separations;
(ii) the materials science of RO membranes;
(iii) the engineering science of RO transport.

The overriding objective of the materials science of RO membranes is to establish scientific criteria for the creation of new and more useful membranes for specific applications. This aspect of the subject is concerned with the identification of precise physicochemical factors governing choice of membrane material, choice of film-casting conditions for the chosen membrane material, and the correlation of such physicochemical factors with data on membrane performance under various conditions of RO operation.

Relatively speaking, the science of RO is still in the early stages of development.

2.2.1 REVERSE OSMOSIS MEMBRANES

A practical reverse osmosis (RO) membrane for treatment of water should possess several characteristics:(14,23)

(i) *the membrane should be permeable to water in preference to all other* components in the feed stream;

(ii) the rate of permeation of water per unit surface area (water flux) must be high enough to produce reasonable product volumes per unit time;

(iii) the membrane must be durable both physically and chemically and have a reasonably long life (the lifetime of a commercial RO membrane being used with a brackish water feed should be about 1-3 years);

(iv) the membrane must withstand substantial pressure gradients, either alone or together with some prior backing or support material;

(v) the membrane should be easily cast into the configuration needed for use (preferably with a high surface-to-volume ratio).

The choice of barrier materials for membranes and the control of their morphology are important in the pursuit of useful permselective membranes. All present commercial RO membranes are polymeric. The choice of the barrier polymer is governed by the film-forming properties and by the permselectivity of the polymer. It has been said(24) that no parameters exist which enable a precise choice to be made of a particular polymer structure for improved membrane materials for RO. In practice, only a few empirical rules are applied, and the choice of membrane materials is based largely on the results of numerous experiments. Generally speaking, a higher ratio of hydrophilicity to hydrophobicity in the molecular chain will lead to an increase in water flux of membranes prepared from that material(25). The choice of suitable candidate polymers for the fabrication of synthetic membranes has been discussed by Strathmann(26) and Blais(27). Cellulose derivatives, polyhydrazide, polyimide and polyamide compounds emerged early as suitable membrane materials. Comparisons have been drawn between these compounds for their suitability as RO membranes(23,28).

The preparation of RO membranes has been discussed by Pusch and Walch(29). A review of modified cellulose acetate (CA) membranes, polymer film membranes, ultrathin and composite membranes and other types of RO membranes, and the related topics of water transport, salt rejection, concentration polarization, compaction, diffusion, degradation and fouling has been presented by Delyannis(30). Electron microscopic investigations into the pore structure and configuration of synthetic membranes have been described by Pusch and Walch(29,31) and others(26).

Some factors affecting the life of a RO membrane ("life" being defined as the time taken for RO performance to fall below a chosen value) include:(32)

(i) feed solution - chemical constituents and temperature;
(ii) operating conditions - pressure;
(iii) membrane type - chemical composition;
(iv) membrane form - asymmetric, composite or hollow-fine fibre;
(v) plant geometry - flat-sheet, tubular, spiral-wrap or hollow-fine fibre.

Chemical factors governing membrane life are the interactions between the membrane material and species to which it is exposed. Two main types of chemical reactions can occur:

(i) severing of the polymer chain, resulting in lower mean membrane-polymer molecular mass, leading to a loss of strength;

(ii) chemical alteration of units on the membrane polymer chain; because salt rejection is dependent on the chemical nature of the polymer, chemical changes in the polymer can have either a beneficial or a detrimental effect on membrane performance.

Both chain scission and chemical change are permanent effects in that they remain when the agent which caused them is removed.

2.2.1.1 RO Membrane Configurations (Module types)

Several types of membranes are available in a variety of commercial modules(5,10,28,33): tubular, plate-and-frame, spiral-wound and hollow-fine fibre. The spiral-wound module (made from flat-sheet membranes) and the hollow-fibre module have emerged as probably the industrially most important types of membrane configurations. The requirements for successful osmotic modules including the requirements for each of the four commercial module types, their advantages and disadvantages, have been discussed in various papers(33,34).

2.2.2 HISTORY

Aspects pertaining to the early history of membrane processes and synthetic membranes have been reviewed by Michaels(35) and Gelman(36), amongst others, and have been referred to by Lonsdale(5) and Strathmann(26).

In the mid-1950s the United States (US) Department of the Interior established the Office of Saline Water (OSW) to develop and evaluate methods for the purification of water. RO emerged as an attractive operation because of its simplicity and low energy requirements. The search then began for strong, reliable, economic and selective membranes.

Early research on the use of RO for desalination was done by Reid and Breton. In 1958 they demonstrated that cellulose acetate (CA) membranes were capable of rejecting 98% of salts from solutions of concentrations up to those of sea water, although these membranes had a very low permeation rate(37). In the early 1960s Loeb and Sourirajan(38) developed a method for the preparation of asymmetric cellulose acetate (CA) membranes which comprised a very thin surface layer and a supporting thicker and more porous layer, both layers of the same composition. These exhibited enhanced water fluxes of up to two orders of magnitude greater than those shown by earlier membranes. The higher flux of these membranes is attributable to the extreme thinness of the skin layer(39). This work signalled that the technology necessary to purify water by RO was at hand and these were the membranes upon which the RO industry came to be founded. (The RO performances of the early CA membranes has been summarized by Lonsdale(40).)

The chemical and physical structures of asymmetric CA membranes have best been described by Kesting(41). Once the nature of the asymmetric membrane was understood, after work done by Riley(42), the logical further step was the concept of composite membranes. Francis speculated that membrane performance could be improved if the ultrathin dense barrier layer and porous substructure of the asymmetric membrane were fabricated separately and then laminated together. Each of these layers could then be individually optimized for best performance. In 1964 Francis and Cadotte of North Star Research Institute fabricated the first thin-film composite CA membrane(43). Microporous CA films were used as porous supports for these new membranes. Riley and co-workers of UOP were also active in the development of similar composite membranes at about the same time(44).

In 1966 Cadotte(45) developed a method for casting microporous support films from polysulphone, polycarbonate and polyphenylene-oxide polymers. Of these, polysulphone (PS) proved to have the best combination of compaction resistance and surface microporosity. Use of polysulphone as the support membrane for ultrathin CA membranes resulted in such CA membranes having fluxes of 400-600 lmd and salt-removal efficiencies of 95-98% at about 5-7 MPa (750-1000 psi) pressure. Although these composite CA membranes showed definite improvements in desalination performance, they showed several significant disadvantages(10):

(a) susceptibility to biological attack (biodegradability);
(b) loss of flux due to compaction at high pressure ("creep" phenomenon);
(c) damage at high and low operating pH (hydrolytic vulnerability) and
(d) *difficulty in obtaining simultaneously high membrane flux and high rejection.*

These problems stemmed from the intrinsic nature of the macromolecule and were not easily solved without chemically modifying the polymer or replacing it altogether(27).

In the 1960s, after the Du Pont group started investigating selective polymers for membrane desalination, aromatic amides and polyhydrazides were found to have useful properties. In 1960 Du Pont used aromatic polyamide materials to develop commercial hollow-fibre membranes(27,46,47). These membranes were less susceptible to biological and chemical attack than the CA membranes, but were degraded by chlorine. Early membranes and the hollow-fibre membranes were of the asymmetric type.

A significant advance in the art of thin-film composite membrane fabrication was made by Cadotte(48,49) in 1970 when he developed the NS-1 (NS-100) membrane: a nitrogen-containing aryl-(alkyl polyurea) *formed in-situ on a microporus polysulphone support by the method of interfacial polymerization*(50). This membrane had good single-pass seawater desalination qualities and the characteristics of non-biodegradability and resistance to compaction. It was this latter development which intensified the widespread interest into thin-film composite membrane technology. Since that time, significant advances have been made in thin-film composite membrane technology for both seawater and brack-water desalination. New membranes and their RO performances will be tabulated and discussed in Section 2.3.3.

The primary emphasis in composite membrane research and development was focused on a series of nitrogen-containing aromatic-backbone polymers which exhibited water and salt permeability characteristics, as well as thermal, biological and chemical properties superior to those of CA. Microporous polysulphone and analogous polymers have been widely adopted as the materials for the support film in composite membrane preparation(51,52). Polysulphone is well suited to the interfacial polymerization method of membrane preparation (described in Section 2.3.2.1) as it tolerates the alkaline conditions of the reaction as well as the drying and/or heat-curing steps in the process(53). Properties of PS support films which affect UTF composite membranes have been described(54).

In the mid-1970s the Office of Saline Water was replaced by the Office of Water Research and Technology (OWRT). Government funding was reduced considerably and, thereafter, membrane research was conducted predominantly by private industry in the USA and in other countries, notably Japan. The fields of RO and RO membranes were initially very well-documented with much information placed in the open literature in the form of reports, papers and symposia proceedings. More recently, however, this situation appears to have changed - probably because of the privatization of membrane research; patent literature is now a predominant source of new information.

An account of the evolution of RO membranes during the period 1953-1979 is given by Pusch and Walch(29).

During recent RO membrane research and development, emphasis has been placed on the development of membranes which can be used for lower-pressure desalination of brackish water(55). The advantages of low-pressure operation include: savings in energy, utilization of cheaper materials for membrane plant construction with consequent reduction in capital expenditure, reduction in membrane compaction and the expectation of minimal fouling. The development of chlorine-tolerant/resistant membranes using UTF membrane technology has also been stressed(55) (see also Section 2.3.4). Chlorination of RO feedwater is essential to control the growth of micro-organisms. Due to the chlorine sensitivity of polyamide UTF membranes, water has to be dechlorinated prior to use as a feed to RO equipment. It is most desirable to eliminate this added cost.

2.2.3 APPLICATIONS

The technique of reverse osmosis is applicable to the separation, concentration, and fractionation of inorganic or organic substances in aqueous or non-aqueous solutions(9). It may be regarded as a technique for separating the components of a waste-stream to attain any or all of the following goals:

(i) reclamation of water for re-use;
(ii) concentration of constituents for re-use or convenient disposal;
(iii) prevention of pollution of natural waters.

The general applicability of RO is governed by two sets of criteria(34):

(i) feed solution conditions, i.e. composition, temperature, pH, osmotic pressure, viscosity, and physical and chemical pretreatment;
(ii) chemical engineering variables, i.e. production capacity of unit, flux rate of solvent (expressed in lmd or litres per square metre per day), degree of separation attained (percentage rejection), applied pressure, flow velocity and cost.

Although the original main purpose behind the development of RO was the desalination of seawater, desalination of brackish water and purification of industrial water have emerged as the main applications of RO(56,57). RO, as a separation technique, can be used for a wide variety of purposes(58,59), some of which are mentioned here in Sections 2.2.3.1 - 2.2.3.11.

RO has been successfully introduced in a number of industrial applications and has gained commercial acceptance (the six major categories will be mentioned in Sections 2.2.3.5 - 2.2.3.10). Cohen(60) has described results of laboratory scale investigations into the recovery, by RO, of dichromate and water from chrome-plating rinse baths and the treatment of orange-peel wash water streams and of textile dyehouse waste streams and tannery waste streams. The application of RO to the treatment of complex industrial wastewaters has been discussed by Slater *et al.*(61). The renovation of waste waters, including industrial and municipal effluents, and treatment of polluted rivers has been reviewed by several authors(30,62,63). There has also been much interest in the application of RO in the food and beverage processing industry(33,61,62,64).

2.2.3.1 Desalination of seawater and brackish waters

Many field tests have been carried out by various research groups on the desalination of seawater, brackish water and other effluents by RO. A summary of these has been compiled by Dresner and Johnson(56). Brackish water (containing less than 10 000 ppm total dissolved solids) has been desalinated by RO on a commercial scale since the early 1970s(56). The technical and economic advantages of employing RO to produce potable water have been demonstrated(8) and a number of RO systems are currently producing potable water from brackish well-water. Desalination of seawater (35 000 ppm) by RO is more difficult than that of brackish water(65) as rejections must be about 98,5% in order to obtain a product containing a maximum of 500 ppm in a single pass. The world's largest RO system for seawater desalination was commissioned in 1979 to supply desalted water to supplement the drinking water supplies of Jeddah, Saudi Arabia(66,67). (Spiral-wound polyamide UTF membranes are used.) A list of the numerous RO plants which were in operation around the world by the year 1980 has been compiled by Pusch and Walch(29). The comparative economics of seawater and brackish water desalination have been discussed by Glueckstern and Kantor(68) and others(14,21). Desalination of seawater by RO is estimated to be two to three times more costly than desalination of brackish water.

2.2.3.2 Sewage effluent treatment

This has received considerable attention and developments for this purpose in the USA have been summarized by Belfort(33) and Delyannis(30). Membrane fluxes tend to be low due to membrane fouling(8,33). A small plant for the reclamation of secondary sewage effluent by RO, using locally made tubular RO membranes, is currently in use in Port Elizabeth, South Africa(69). Results indicate that relatively simple tubular cellulose acetate RO systems(70) have the potential to produce potable water from chlorinated, filtered secondary sewage. Satisfactory flux levels could be maintained.

2.2.3.3 Treatment of polluted river waters

In the 1970s several studies were made to ascertain whether RO could be used to treat polluted river waters(33,71). Asymmetric CA membranes in tubular configurations were used. Results of investigations into the treatment of water from the Rhine river in The Netherlands, the Thames in Great Britain and the Tennesee in USA, have been reported.

2.2.3.4 Treatment of domestic and municipal waters

RO has also been successfully used in the treatment of domestic and municipal water(30,63). Water Factory 21 in Orange Country, California, USA is one of the largest and most advanced municipal wastewater treatment facilities in the world(66,67,72). Here, secondary effluent is processed by RO to within drinking water standards. This effluent is injected into ground water wells to replenish the aquifier and to retard intrusion of seawater(66,73,74).

2.2.3.5 Treatment of paper and pulp effluents

The application of RO to the paper and pulp industry has been described by Wiley and Bansal(75), Olsen(76), Glimerius(77) and Belfort(33). It has been found that RO is well-suited to the treatment of a variety of dilute pulp-mill effluents. Yields of re-usable water have been high, and success has been achieved in the concentration of dissolved substances to the point at which they can be disposed of by conventional means e.g. evaporation or incineration, and valuable sugars and resins can be recovered.

2.2.3.6 Treatment of electro-plating and metal-finishing operation wastewaters

Interest has been shown in examining the feasibility and cost-effectiveness of the recovery, for re-use, of chemicals, valuable metals and water by RO in effluents from these processes(63,78,79).

Many electroplating waste streams contain substances which, apart from being directly toxic to humans and wildlife, are poisonous to the bacteria which are used in the processing of organic material in municipal wastewater. Moreover, the large volumes of plating rinse-water that are discharged contain substantial quantities of potentially recoverable materials. Recovery of the following materials is currently being done by RO, on commercial scale: nickel, brass cyanide, chromic acid and chromium(78). Petersen and Cobian have reported on novel RO membranes which may be used successfully for treating metal-finishing effluents and on the feasibility of the commercial application in electroplating installations(80). NS-100 UTF membranes (see Section 2.2.3) were successfully used for treatment of electroplating wastes of extreme pH (pH 1 acid copper rinses and pH 13 zinc cyanide rinse water effluents).

2.2.3.7 Treatment of acid mine waters which contain sulphuric acid and valuable minerals

Acid mine waters may contain ferrous sulphate, sulphur, ferric sulphate and sulphuric acid (produced by bacterial action upon the ferrous sulphide in coal). Such waters are harmful to fish and wildlife. Field tests have indicated that mine waters can be economically upgraded by RO for industrial and municipal use(81,82). The application of RO to reduce or prevent mine-drainage pollution has been reviewed by Belfort(33) and Slater *et al.*(61). Squires and Hart(57) have reported on the application of RO to the South African coal mining industry.

2.2.3.8 Treatment of textile industry effluents

RO has been cited as an attractive method for treating textile industry wastewater to produce quality effluent for re-use(33,61). Over the past decade, treatment of textile effluent and water recovery has been carried out in South Africa using RO and the low-pressure process of ultrafiltration(83,84).

2.2.3.9 Treatment of effluents from food and beverage processing plants

RO has been used for the following applications:

(a) Concentration and fractionation of components of cheese whey. Whey is a by-product of cheese-making and its disposal has become a world-wide problem(34). Whey contains valuable nutrients including lactose, protein, vitamins and minerals, potentially recoverable in solid form by evaporation and drying. It has been found that 75 - 80% of whey in water can be economically removed at room temperature by RO, which solves the disposal and pollution problems. RO shows promise for fractionating whey into individual components(34,85).

(b) Concentration of sugar solutions
e.g. cane sugar, beet juice, maple syrup and corn syrup(34).

(c) Concentration of fruit juices(34,86,87)
e.g. orange, apple(88), tomato.

(d) Concentration of coffee and tea(34)
This is done prior to freeze-drying.

2.2.3.10 **Miscellaneous applications**

Some additional areas of application to industrial waste treatment have been mentioned by Slater *et al.*(61) and Delyannis(30). These include: treatment of photographic processing effluents, treatment of wastewater from an electronic plant for re-use, treatment of wastewater from an electro-painting process, treatment of petrochemical complex wastewaters and treatment of wastewater from the pharmaceutical industry.

The application of membrane technology to the rapidly growing field of biotechnology has been discussed by Michaels(89).

2.2.3.11 **Applications on the South African front**

Application of membrane separation processes to the treatment of industrial effluents for water reuse has been reviewed by Groves(90). The role of membrane technology and wastewater management in South Africa has been discussed by Squires and Hart(57). They indicated where RO could be successfully used to concentrate and separate inorganic and organic contaminants in industrial effluents. These included the areas of: mining, abbatoir effluents and the pulping industry.

Membrane desalination of service water from gold mines has been reviewed by Juby(91). Desalination and recovery of cooling water blowdown is an important aspect in achieving a closed water circuit at a modern wet-cooled power station(92). The results of the treatment of such water at the Lethabo power station, using tubular RO membranes(93), has been discussed by Smith *et al.*(94).

2.3 ULTRATHIN-FILM COMPOSITE MEMBRANES

2.3.1 HISTORY AND BACKGROUND
(see also Section 2.2.2)

Ever since the conception of RO membranes there have been efforts to improve the permeability of RO membranes. Francis(43) and Riley(95) introduced the concept of the thin-film CA membrane which has a very thin active desalting layer. Such a membrane was prepared by the casting of a thin film of CA on the surface of a water-bath by a solution-spreading technique, lifting it off and laminating it onto the surface of an asymmetric support membrane - hence the name composite membrane. This concept was developed further by Cadotte(45), and even thinner desalting barriers were created. Thin permselective films (200-300 nm) were created by performing an interfacial polycondensation reaction between, e.g. an amine and acid-chloride crosslinking agent, directly on the surface of an asymmetric ultrafiltration (UF) support membrane. This technique of membrane fabrication broadened the scope of the selection of materials from which membranes could be fabricated. By varying the choice of reactive species, a large number of membranes with various performance characteristics could be obtained.

Thin-film composite membranes, henceforth referred to here as ultrathin-film (UTF) membranes, comprise an ultrathin (20 - 200 nm) permselective layer of polymer deposited and insolubilized on the surface of a microporous substrate membrane. This is in contrast to the much thicker desalting barrier (0,1 - 1,0 μm) of the earlier asymmetric CA RO membranes. The substrate membrane acts merely as a support for the thin film and does not contribute to the salt rejection performance of the thin permselective layer. UTF membranes are fabricated by a two-step procedure, namely, formation of the substrate membrane, followed by creation of the thin-film desalting barrier on the surface of the substrate membrane (as described in Section 2.3.2). The ultrathin barrier layer results due to the inability of the crosslinking agent to penetrate into the membrane as the barrier layer is formed. The cross-section of a commercial composite membrane, PA-300(67), is shown in Figure 2.2.

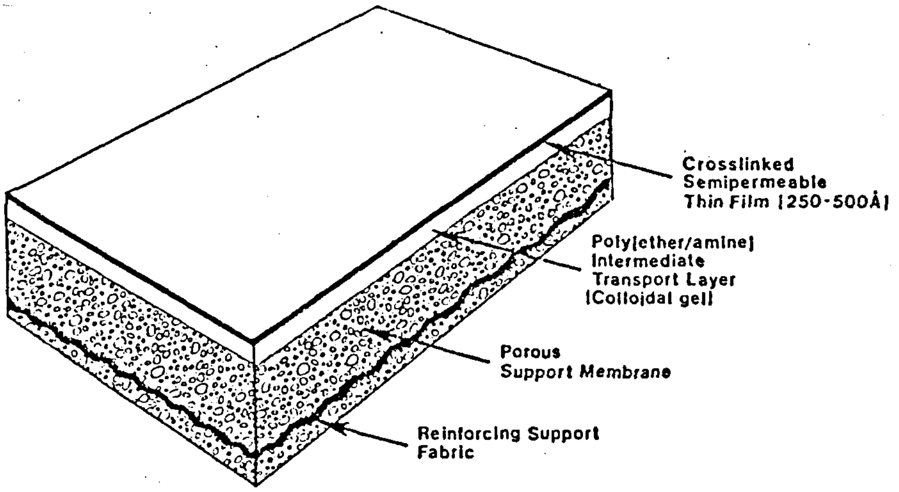


FIGURE 2.2: SKETCH OF A TYPICAL INTERFACIALLY POLYMERIZED, ULTRATHIN-FILM COMPOSITE MEMBRANE (PA-300) IN CROSS-SECTION(67)

The water flux through a UTF composite membrane depends on the chemical composition of the ultra-thin skin and its water permeability and thickness, the characteristics of the pores on the surface of the support membrane and the amount of pressure applied(95). As the rate of permeation through a membrane is inversely proportional in the thickness of the barrier layer, this layer is made as thin as possible.

Composite membranes provide a flexibility not available with asymmetric membranes in that the thin semipermeable barrier is formed independently of the support structure. The advantage of this is that the properties of each layer of material used can be improved separately.

The general methods of thin-film composite membrane preparation (described in the following Section 2.3.2) provide for flexibility beyond that previously possible with conventional methods of preparation of asymmetric membranes, making UTF composite membranes attractive.

These include(28,67):

(a) Independent selection of materials from which to prepare the thin semipermeable barrier and the finely porous supporting membrane.
(b) Independent development and preparation of the thin film and the porous supporting membrane which make it possible to optimize each component for its specific function.
(c) Reproducible variation and control over the thickness of the thin film as needed for different applications.
(d) Preparation of thin semipermeable barriers from any solvent-soluble polymer by the solution-deposition technique.
(e) Formation of thin semipermeable barriers with normally insoluble polymers by the in situ interfacial polycondensation technique (see Section 2.3.2.1).

UTF RO membranes have been increasingly designed with special fields of application in mind. During research carried out to date on UTF RO membranes, performance goals have been focused on attaining high permeate volumes coupled with high selectivity(55). Initially, most UTF RO membrane development was done on single-pass seawater-desalting membranes. For seawater, the minimum goal was a membrane of 600-800 lmd flux (15-20 gfd) and 99,5% salt rejection while operating at 5500 kPa (800 psi) at 30% recovery. The corresponding goal for a low-pressure brack-water membrane was a membrane with a similar flux of 600-800 lmd (15-20 gfd) but a minimum salt rejection of 95% at operating pressures of 1700 kPa (250 psi) on a 3200 ppm TDS feedwater. Over the last few years, emphasis in membrane development has been directed at lower-pressure, water-softening membranes which operate at pressures of below 1000 kPa. The greatest emphasis in research and development of UTF composite membranes has been on a class of polyamides, namely, the nitrogen-containing aromatic-backbone polymers (see Section 2.4.1)(66). Hence, during the following discussion of UTF membranes, the chemistry and properties of these types will be emphasized.

2.3.2 MEMBRANE PREPARATION

Preparation of RO membranes, both asymmetric and UTF, has been reviewed by Pusch and Walch(29). The different methods which have been used to form UTF composite membranes fall into four categories(96,97):

(a) Casting of the barrier layer separately, followed by lamination of the layer to the support film (early, discontinued, technology used to make the first CA UTFs)(43,95).

(b) Dip-coating of the support film into a precursor solution (polymeric, reactive monomeric or oligomeric prepolymer), followed by curing of the membrane with heat or radiation (an example of this type is the NS-200 membrane)(98).

(c) Gas-phase deposition of the barrier layer from a glow-discharge plasma(99,100).

(d) Interfacial polymerization of reactive polymers, oligomers or monomers on the surface of the support film, to create a thin skin(50,53,96) (examples of this include the NS-101 and FT-30 membranes, described in Section 2.3.3).

Method (d) has emerged as the most effective and is widely used. Membranes can be made exceedingly thin, with a thickness of 50 - 150 nm. The ultrathin barrier layer of the PEC-1000 membrane is reported to have a thickness as low as 30 nm(101).

2.3.2.1 Interfacial polycondensation

Interfacial polycondensation comprises the reaction of two multifunctional reactive components at the interface of two mutually immiscible solvents. If the reactants are mutually reactive, the film forms very rapidly. In most of the interfacially polymerized membranes the film must be annealed after it has been formed in order to complete the reaction(102). A brief discussion of the theoretical background of the preparation of polyamides by the interfacial polycondensation reaction is presented in Section 2.4.4. A typical experimental procedure for the fabrication of polyamide UTF membranes by this method has been described in experimental Section 3.4.2.1.

The science of interfacially forming membranes involves many fabrication variables(103). These are shown in Table 2.1. In order to arrive at a set or sets of fabrication conditions under which membranes with adequate RO performance can be made from chosen reagents, consideration must be given to the following practical fabrication variables.

TABLE 2.1: VARIABLES IN UTF RO MEMBRANE FABRICATION BY THE INTERFACIAL POLYCONDENSATION REACTION

Action	Variable
1. Choice of the porous substrate, e.g. polysulphone.	Pore-size and pore-distribution of substrate.
2. Dipping of substrate in aqueous solution of precursor.	Chemical and physical nature of precursor. Solution concentration; dipping time; addition of acid acceptor and/or surfactant if needed; concentration of acid acceptor and/or surfactant.
3. Drainage	Time
4. Dipping of coated substrate in organic solution of crosslinking agent.	Chemistry of crosslinking agent; organic solvent used; solution concentration; dipping time.
5. Drainage	Time
6. Heat curing (to effect complete crosslinking).	Oven temperature; oven residence time; position.

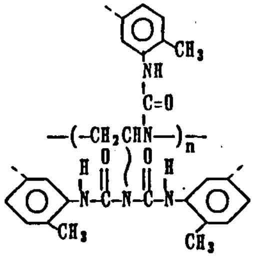
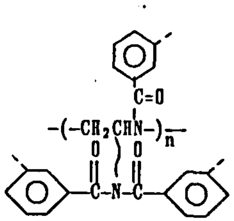
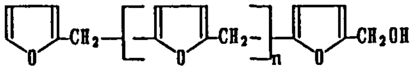
The effects of structural changes on membrane performance caused by changing membrane chemistry or the method of preparation are well known and have been discussed by Bartels(104).

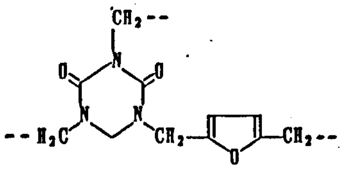
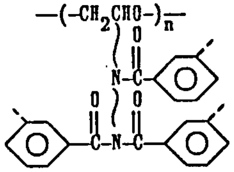
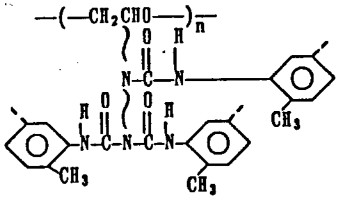
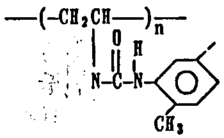
2.3.3 CHEMICAL COMPOSITIONS AND RO PERFORMANCES OF UTF MEMBRANES

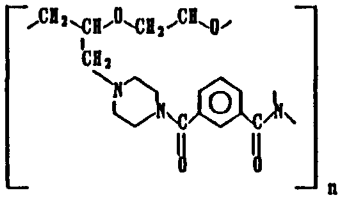
Numerous chemical combinations have been used to make experimental UTF RO membranes. An overview of hyperfiltration membranes made from non-cellulosic materials up until 1982 has been presented by Pusch and Walch(29). This includes reference to both asymmetric and composite types of membranes, and to their RO performances. A brief overview of commercial composite membranes which includes mention of the type of active desalting layer, manufacturer and commercial membrane form has been presented by Rautenbach *et al.*(13).

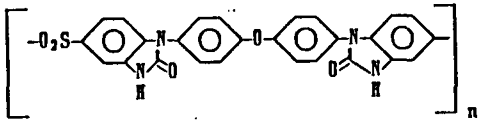
Rather than presenting a discussion of the many types of chemical combinations which have been used in the making of composite UTF polyamide membranes and the RO performances recorded, a selection of membranes which have been investigated by other researchers in the field has been summarized in Table 2.2. This selection includes only those membranes which have been well-documented and which showed promise as RO membranes for various applications. The table depicts various types of chemicals: precursors and crosslinking agents, which have been used in the making of polyamide UTF membranes; the membranes' repeat unit structures (where known) and the reported RO performances. Included in this table are the two commercial polyamide membranes PA-300 and FT-30, and the commercial polyether PEC-1000 membrane, PBIL and various examples of experimental membranes investigated by the following research groups: Fluid Systems (UOP) and Film Tec (formerly North Star) of the U.S.A., Toray, Teijin and Nitto of Japan. Reference will be also made to sulphonated polysulphone membranes and polyvinylalcohol-based membranes both of which are non-nitrogen-containing membranes.

TABLE 2.2: UTF COMPOSITE RO MEMBRANES

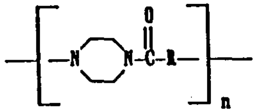
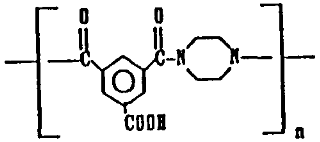
Membrane Designation	Reactants: Active layer	Chemical structure of active layer repeat unit	Test Conditions (see footnote)	RO performance - salt rejection [%] permeate flux [lmd]	Membrane features	Ref.
NS-100 (MS-100)	PEI + TDI: aryl-alkyl polyurea		a	99,4% 720 lmd	Relatively low fluxes Surface brittleness Acid-alkaline pH-resistant Very sensitive to chlorine High rejection of organics	4 28 48 80
NS-101 (PA-100)	PEI + IPC: polyamide		a	99,3% 1200 lmd	Improved fluxes over NS-100 Sensitive to chlorine	4 28 105
NS-200	Furfurylalcohol + sulphuric acid: sulphonated *polyfuran resin*		b	>99% 800 lmd	High ionic charge Long-term membrane instability	28 53 98
Toray exp.	THEIC (1pt) + furfurylalcohol (2pt)		c	99,9% 500 lmd	High rejection of organic solutes - higher than that of NS-200	53 106

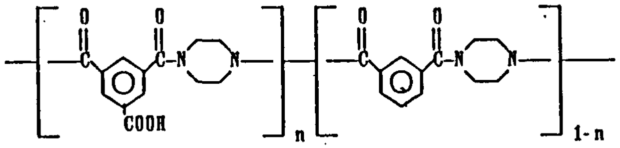
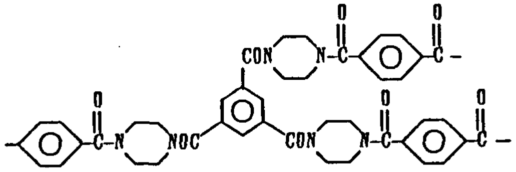
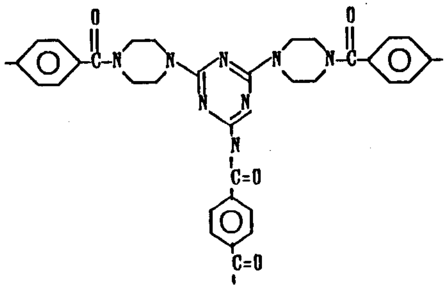
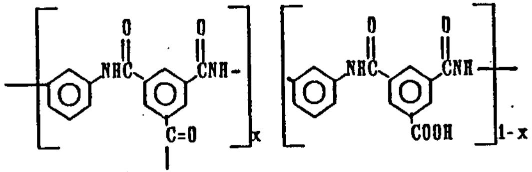
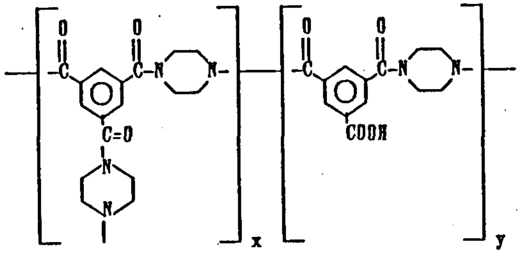
PEC-1000	Copolymer of THEIC and furfurylalcohol		d	99,85% 200-300 lmd	Commercialized Film thickness 300Å Very sensitive to oxidation O_2 must be removed from feed Durability for high pressure operation Stable at high temperatures	101 107
PA-300 (TFC-800)	(polyepichlorohydrin + ethylenediamine) condensate + IPC: polyether/amide		b (pH 5,9)	>99% 800 lmd	More chlorine-resistant than NS-101 Dry-storable Flux greater than that of NS-101 Commercialized	66 67 108 109 110
RC-100 (TFC-801)	(polyepichlorohydrin + ethylene diamine) condensate + TDI: polyether/urea		b (pH 5,9) e	>99% 1000 lmd 99,4% 560 lmd	Improved flux and chlorine resistance over PA-300 Remains chlorine-sensitive Commercialized	55 108 109
TFC-806	polyvinylamine + TDI: polyurea		d (pH 5,5)	99% 830 lmd	Difficulty in processing these membranes More chlorine resistant than RC-100 but deteriorated rapidly after few hundred hours of exposure.	111
TFC exp.	vinyl(alcohol/amine) copolymer (9:1) + TDI		d	about 20% < 3000 lmd		111
	vinyl(ethylene/amine) (3:1) + TDI		d	95-99,5% 300-700 lmd		111
TFC-851	Epiamine (1%) piperazine (0,5%) + TDI		d (pH 5,5-6)	99,5% 600 lmd	Shows promise as RO membrane but no chlorine-resistance	111

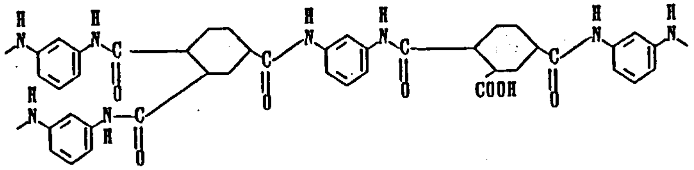
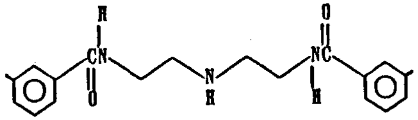
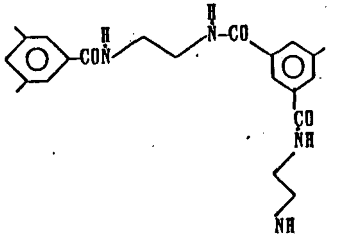
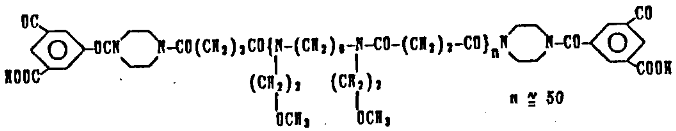
TFC-861	Epiamine (0,5%) m-phenylenediamine (0,5%) + TDI		d	99,4% 550 lmd		111
	Epiamine (1,0%) o-phenylenediamine (0,1%) + TDI		d	98,8% 520 lmd		111
TFC-871	Epiamine (1,4%) ethylenediamine (0,14%) + IPC		d	99,4% 470 lmd		111
	Epiamine (1,4%) ethylenediamine (0,14%) + TDI		d	99,8% 220 lmd		111
Toray exp.	AMP modified polyepiiodohydrin(3) + AMP(1) + IPC		d	99,5% 350 lmd		96
Toray exp.	Piperazine substituted polyepiiodohydrin + IPC		c	99,7% 700 lmd	Stable at pH 4-12, 40°C	112
Teijin exp.	Polyamine of TETA and MAM copolymer + IPC/TMC (5:1)		f	96,8% 1450 lmd		96 113
	(PEI + HCl) + TMC or 3-chlorosulphonyl isophthaloylchloride		-	12,4% 1800 lmd 95,3% sucrose rejection	Amphoteric membrane Very hydrophilic	96 114
Teijin exp.	Amine-modified AEVE + IPC		f	95,6% 1440 lmd		115
	Amine-modified AEVE + TMC		f	90,4% 2350 lmd		115

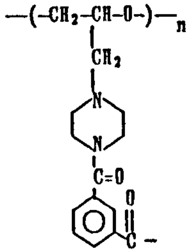
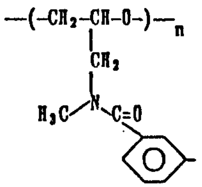
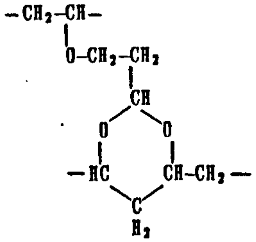
Teijin exp. (continued)	Amine-modified AEVE + TDI		f	94,5% 1800 lmd		115
	Amine-modified copolymer of EVE and MVE + IPC		f	92,7% 1700 lmd		115
	Copolymer of MA and glycidyl MA reacted with N-methyl-ethylene-diamine + IPC/TMC (5:1)		f	90,5% 2400 lmd		115
PBIL			g	97-99,3% 1000-3000 lmd	Commercialized Stable between pH 1-12 Stable at 60°C Susceptible to chlorine and to non-ionic surfactants	112 116
TFCL-LP			1378 kPa net.* Brack water 25°C	>97% 800 lmd	Chlorine resistance (>1000 ppm h and up to 9000 ppm h at low pH and temp.) Stable up to 85°C	117 118
TFCL-HP			2756 kPa net.* SSW 25°C	>99% 800 lmd	Operates over pH range 5-11 (max. rejection at pH 7-8)	117 118
NTR-7400 series 7410	Sulphonated polyether sulphone (skin layer)		2000 ppm NaCl 496 kPa	10% 6700 lmd	Charged desalting layer Resistant over pH range 0,5-13,0 and up to 80°C in static test, 1 month Chlorine-resistant: no decrease in performance after exposure to 10 000 ppm for 30 days, in static test *(higher chlorine resistance than* that of CA membranes)	119
7450			2000 ppm NaCl 992 kPa	50% 2200 lmd		

* net pressure = applied pressure minus osmotic pressure

NTR-7100 series			d (pH 8,1-8,3)	99% 800 lmd	Good seawater and brackwater *desalination* No chlorine resistance	120
NTR 7250 series			2067 kPa 2000 ppm NaCl 2000 ppm $MgSO_4$	50% NaCl 3000 lmd 98% $MgSO_4$ 2000 lmd	Fixed carboxyl groups in rejection layer High flux at low pressure Tolerates chlorine: 1 ppm cont , 100 ppm/70 h Resistance to practical levels of chlorine greater than that of CA membranes Useful lifetime at 60°C is > 10 000 h Operates at pH 2-8	120
NTR-739 HF			992 kPa NaCl	>95% 1000 lmd (pH 1-12)	Good pH-resistance up to 60°C Higher rejection of organics than by CA membranes	121
NTR-729 HF				>92% < 2000 lmd (pH 1-10)	More chlorine-resistant than CA membranes	
PIP	Piperazine + IPC: piperazine-isophthalamide		a	98% 840 lmd	Sensitive to disturbances in preparation Low flux and rejection, compared with NS-100. Initial chlorine sensitivity, followed by stabilization No degradation after 200 h with > 1 ppm Cl (pH 5,5)	122 123
NS-300 family	Piperazine monomer + TMC: homopolyamide (NS-300)		a	98% 800 lmd	Potentially useful brackwater or waste water reclamation membranes	53 122

NS-300 family (continued)	Piperazine monomer + (TMC + IPC): copolyamide (NS 301)			Varies, depending on isophthalamide content, from 68%, 3200 lmd (99% $MgSO_4$) to *performance of* NS-300	High rej. of divalent salts: 99%, 3000 lmd (5000 ppm $MgSO_4$, 1360 kPa) Salt passage is anion controlled due carboxylate groups on surface Variability in RO performance observed *when inferior quality support used*	53 124
	Oligomer of piperazine and TMC + IPC		h	99,0% 530 lmd	Higher rejection membrane than NS-300 (prepared from monomeric piperazine) Variability in performance not resolved with use of oligomers	96 122 124
	Oligmer of piperazine and cyanuric chloride + IPC		h	99,2% 550 lmd	Membranes show high rejection of organics Stable in pH range 1-13 Temp. stable at 25-55°C	96 122 124
FT-30	1,3-diaminobenzene + TMC: Aromatic polyamide		3,5% SSW 25°C 6891 kPa 5513 kPa 4134 kPa	 99,4%, 1200 lmd 99,2%, 960 lmd 99%, 480 lmd	Commercialized High-performance seawater membrane Long life: 5 years Stable at pH 2-11 during cont. operation Stable at pH 1-12 in periodic cleaning Steralizable in boiling water *Chlorine resistance higher than that of other* commercial membranes, eg. PA-300	53 96 125 126 127 128
NF-40	Piperazine + TMC: Aromatic polyamide		689 kPa net 25°C 0,2% NaCl 0,2% sucrose	 1000 lmd 10-40% 98%	Properties between those of RO and UF at very low pressure Stable at pH 5-8 during continuous operation and pH 4-9 during periodic cleaning	129

UTC-60	Crosslinked piperazine polyamide with carboxylate groups		350 kPa 500 ppm 25°C	> 60% 900 lmd	Ultra-low-pressure membrane Tolerates continuous dosage of chlorine (at level required for sterilizing)	130
UTC-70	Crosslinked fully aromatic polyamide with carboxylate groups		1500 kPa 1500 ppm 25°C	> 99,5% 1300 lmd	Low-pressure membrane Chlorine resistant in periodical cleaning and sterilizing	130
Exp.	1,3 phenylene-diamine + 1,3,5 cyclohexane tricarbonyl chloride: polyamide		1553 kPa 5000 ppm NaCl	> 96% 12000 l/day (for 4" cartridge)	High flux membrane No deterioration in RO performance after 300h at pH 5,5-9,9 (rejection increases with pH, flux constant at increased pH)	131
3N8(OL)	Oligomer of DETA + IPC, crosslinked with IPC		i d	97,3% 1000 lmd 94,8% 560 lmd	More chlorine resistant than NS-101 or RC-100 Comparatively low salt rejection	132
2N31	Ethylenediamine + TMC		i	96,9% 320 lmd	Moderate salt rejection and low flux No decrease in performance after exposure to 10 ppm chlorine for 22 days. More chlorine resistant than FT-30	132
DIPIP-50	Oligomeric piperazine-capped polyamide (mm 15000) + TMC		e	32-74% 800-2000 lmd	No change in performance after 3 days' exposure to 5 and 100 ppm chlorine (static conditions). Dramatic and rapid loss of RO properties upon exposure to chlorine (15-20 ppm) under dynamic conditions.	133

MSI-500	Pepiamine (piperazine substituted polyepichlorohydrin) + IPC: tertiary polyamide		1725 kPa 5000 ppm NaCl	97% 700 lmd	Chlorine sensitivity similar to that of PA-300	123
Exp.	Mepiamine (methylamine substituted polyepichlorohydrin) + IPC: tertiary polyamide		1378 kPa 5000 ppm NaCl	< 50% about 2000 lmd	After initial increase in performance, after 400h with > 1 ppm chlorine (pH 5) appeared chlorine resistant. Flux decline due to compaction	123
PVOH-based membranes	Polyvinylalcohol + aldehyde (CH_2O) + acid		h	87% < 100 lmd	Very low flux membrane	134
	Polyvinylalcohol reacted with 1,5 propanesultone + CH_2O			82% 700 lmd		
	Polyvinylalcohol + acrolein + Na_2SO_3 + acid			97% 1200 lmd	Membrane slowly attacked by by chlorine, (chlorine sensitivity possibly due side reactions during membrane curing)	
SPS membranes	Sulphonated polysulphone (water soluble), heat cured: polymer with sulphone linkages	$Ar-SO_2-Ar$	a	< 90% 680 lmd		135

SPS membranes (continued)	Sulphonated polysulphone + polyalcohols, heat cured: polymer with sulphonated ester crosslinks	$Ar-SO_2-OR$	b	98% 60 lmd	Chlorine stable at 100 ppm, 500 h (pH 8)	135

Footnote to Table 2.2:

Test conditions a - i:

a 35000 ppm NaCl feed solution
10337 kPa* applied pressure
25°C

b 35000 ppm NaCl
6891 kPa applied pressure
25°C

c 2500 ppm NaCl
3928 kPa applied pressure
25°C

d 35000 ppm NaCl
5513 kPa applied pressure
25°C

e 5000 ppm NaCl
2756 kPa applied pressure
25°C

f 5000 ppm NaCl
4134 kPa applied pressure
25°C

g 7000 ppm NaCl
4824 kPa applied pressure
60°C
pH 1-12

h 35000 ppm synthetic seawater (SSW)
10337 kPa applied pressure
25°C

i 1000 ppm NaCl
5513 kPa applied pressure
25°C

* 100 psi = 690 kPa

Abbreviations

SSW = synthetic seawater
THEIC = 1,3,5 - tris (hydroxyethyl) isocyanuric acid
AMP = amino-(methyl piperazine)
TETA = tri-ethylenetetramine
MAM = maleic-anhydride-methacrylate copolymer
AEVE = poly-(2-chloro-ethyl vinyl ether)
IPC = isophthaloyl chloride
TMC = trimesoyl chloride
EVE = ethyl-vinyl ether
MVE = methyl-vinyl ether
MA = methacrylate
DETA = diethylenetriamine
TFC = trademark of Fluid Systems Thin-Film Composite Membranes
TDI = toluene diisocyanate
ppm h = amount of membrane exposure to chlorine, calculated in terms of the product of chlorine concentration (ppm) and exposure time (h)

From Table 2.2 and the literature studied, it appears that the most promising polyamide membranes have been prepared from the monomeric diamine precursors: 1,3 diaminobenzene and piperazine and the acid halide crosslinking agents IPC and TMC. Such membranes include the NS-300 family, prepared from piperazine and TMC or IPC/TMC (the RO properties being determined by the isophthalic/trimesic acid ratio) and the FT-30 membrane, prepared from 1,3 diaminobenzene and TMC. Of all the polyamide RO membranes developed to date the FT-30 membrane is claimed as coming closest to being the ideal membrane for seawater desalination in terms of product, chemical stability and non-biodegradability(53,96). All nitrogen-containing UTF composite membranes tested in the field to date have eventually shown irreversible performance decline when exposed to chlorine. In some cases, however, UTF membranes were successfully tested for several hundred hours before unacceptable levels of performance were reached. (See Section 2.3.4 for the effect of chlorine on polyamide RO membranes.)

The comparative performances of several commercially available RO membranes, as compiled by Kamiyama *et al.*(120), are shown in Figure 2.3.

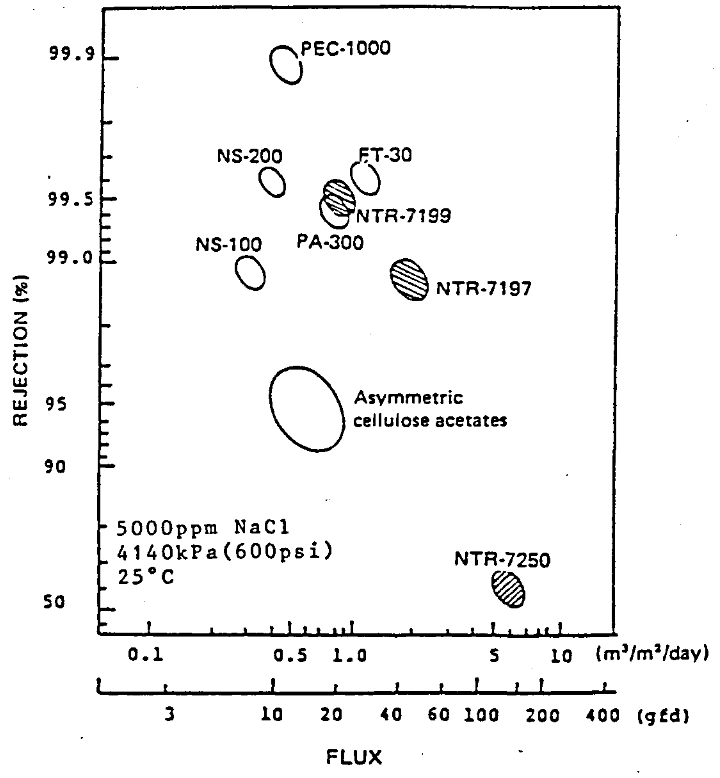


FIGURE 2.3: GRAPHIC COMPARISON OF THE RO PERFORMANCES OF VARIOUS RO MEMBRANES(120)

2.3.3.1 Membranes prepared with polymeric precursors

In the fabrication of one of the first successful interfacially polymerized UTF composite membranes, NS-101, the polyamine precursor polyethyleneimine (PEI) was reacted with isophthaloyl chloride (IPC) to effect crosslinking and to insolubilize the resultant polyamide desalting barrier(105). As a final step in the preparation process the membrane was heat cured at 110°C for 10 minutes. It is suggested that this promotes more complete crosslinking of the desalting barrier and effects a condensation reaction between adjacent primary amine groups of the PEI precursor, with the elimination of ammonia, so giving rise to an intermediate layer or gel layer of crosslinked PEI(96,105). This layer serves as a transition zone between the polysulphone substrate and the polyamide barrier layer, and provides additional support to the thin interfacial membrane over any defects in the polysulphone support (e.g. pinholes). This layer is believed to be necessary to ensure high salt-rejection performance by the NS-101 membrane(104,105). Polyamines (and oligomeric amines) have been reported to yield more uniform membranes because they form a gel layer between the thin interfacial membrane and the polysulphone support during heat curing(105,135).

In attempts to replace PEI in the NS-101 membrane type, many other polyamines have been used . Patents(113-115) were granted to Kawaguchi of the Teijin group (Japan) in 1981 and 1982 covering the use of numerous novel polyamine precursors. (This group is very active in the fabrication of new experimental RO membranes, but their findings are disclosed mainly in Japanese patents.)

2.3.3.2 Membranes prepared with monomeric precursors

For several years it was thought that a polymeric amine was needed to span the pores of the support membrane surface in order to obtain a polyamide UTF membrane with high salt-rejection performance(136). Subsequently, however, some monomeric precursors were used successfully in the preparation of adequate UTF membranes. The poly(piperazine isophthalamide) (PIP) membrane was prepared from the monomeric amine precursor piperazine and IPC crosslinking agent; after optimization of the interfacial reaction, the membrane showed 90 to 96% rejection of salt from seawater(53,96,122).

It has been suggested that piperazine is an attractive building block for RO membrane polymers for two reasons:

(a) it adds both cyclic structure and hydrophilic sites to the desalting barrier, both of which are favourable for good water flux, and

(b) upon complete reaction of both the secondary amine groups with crosslinking agents such as carboxylic acid chlorides, there should be little or no remaining activity with chlorine present in chlorinated feedwaters (see Section 2.3.4).

The use of piperazine polyamides as RO membrane polymers was first studied by Credali *et al.*(137) and these asymmetric membranes were found to exhibit some chlorine resistance(138). The PIP membranes were found to be more chlorine-resistant than the NS-101 membranes (see Table 2.3), but showed insufficient salt-rejection and flux for application as single-pass seawater membranes. Furthermore, membrane reproducibility was not good. These shortcomings were ascribed to the fact that in this membrane no intermediate zone is formed between the desalting barrier layer and the polysulphone support(105,135). Any significant discontinuation or defects in the surface structure of a support membrane would therefore disrupt the thin interfacially formed membrane desalting barrier layer, and this would have a major effect on the success or failure in achieving high salt-rejection barriers. During attempts to upscale the NS-300 membrane from laboratory scale to continuous production, a high degree of variability in membrane properties was evident(139). The difference was attributed in part to the variability of the machine-made polysulphone supports. Such support films which may have been adequate for NS-101 membranes, prepared from polyamine reactants, apparently presented a limitation for the monomeric amine reaction in NS-300 membrane preparation.

Recently, however, a commercially successful UTF membrane, FT-30 developed by the Film-Tec corporation, has been prepared by the interfacial polycondensation reaction between the monomeric diamine 1,3 diaminobenzene (DAB) and 1,3,5-benzenetricarboxylic acid chloride (TMC)(126,128). The resulting aromatic polyamide membrane is capable of single-pass seawater desalination with a salt-rejection capability of greater than 99%. Good-quality polysulphone supports are required to ensure adequate RO performance. The unusual surface appearance of the FT-30 membrane has led to some interesting speculations on the mechanism of membrane formation(136).

Preparation of UTF membranes from monomeric percursors would be advantageous since the quality of reagents used in membrane preparation could be easily controlled.

2.3.3.3 Membranes prepared with oligomeric precursors

As with polyamine precursors (Section 2.3.3.1), oligomeric amine precursors are claimed to yield more uniform UTF membranes because of their ability, when heat cured, to form some gel structure between the thin desalting barrier and the polysulphone substrate(135). Oligomers could possibly generate a lightly crosslinked intermediate zone between the surface barrier layer and the microporous polysulphone substrate(53).

Oligomeric precursors of piperazine have been successfully prepared by reacting an excess of piperazine with TMC or a mixture of IPC and TMC in an inert solvent e.g. dichloroethane and used in the fabrication of the NS-300 membrane, crosslinked with IPC or TMC(122). Some improvements e.g. higher salt rejection were obtained when membranes were prepared with piperazine oligomers, as opposed to the monomer. The problem of membrane variability was, however, not adequately solved.

A further example of an experimental UTF membrane fabricated from an aliphatic trifunctional amine oligomer is described by Lee(132). An oligomer of di-ethylenetriamine (DETA) and IPC is crosslinked with IPC to form a UTF composite membrane with good RO performance (see Table 2.2, example 3N8(OL)).

2.3.4 UTF MEMBRANE STABILITY IN A CHLORINE ENVIRONMENT

2.3.4.1 Background

Chlorine is the oldest and most widely-used material used for disinfection. It is frequently added in concentrations of 0,5 ppm to the feedwater at many RO desalination facilities as part of the pretreatment process to prevent fouling of membrane modules and microbial degradation of membrane polymers. Municipal water and wastewater are often treated with chlorine for reasons of public health. A dechlorination step is then required before chlorinated water can be purified by chlorine-sensitive membranes(140). Degradation and subsequent failure of polyamide RO membranes are well known(140-143) and have been widely reported in the literature (see references pertaining to Table 2.3). Most of the polyamide and polyurea rejection layers that provide the best RO performances e.g. NS-100/-101, PA-100/-300 are highly susceptible to even trace amounts of chlorine, as shown in Table 2.3. The membranes are degraded with a typical loss in salt rejection below acceptable RO performance levels and an increase in water flux. Glater *et al.*(142,144) reported on the sensitivity of the Du Pont B-9, RC-100 and FT-30 polyamide RO membranes to halogen disinfectants after their study of the deterioration in performance of membranes exposed to such conditions. Sensitivity to chlorine represents a substantial practical deterrent to the application of RO in domestic water treatment or in small plants where pretreatment to remove chlorine is difficult or costly. Dechlorination of feedwater has been described by Chanabasappa and Strobel(145). Chu *et al.*(140) have discussed the limits of dechlorination.

According to Light *et al.*(117) a membrane can be considered to be chlorine-resistant if exposure to a biocidal concentration of chlorine (1 mg/l) for several years does not cause membrane damage, whereas a membrane can be considered to be chlorine-tolerant if it can withstand intermittent exposure to chlorine. The chlorine sensitivity of a membrane and the extent of chlorine membrane-polymer interactions resulting in membrane degradation vary, depending on several factors, chiefly the polymer and the functional groups present and the pH of the aqueous chlorine medium. The latter determines the reactive chlorine species present(142). Chlorine in a saline feed solution exists in two predominant forms. In the pH range 2 - 7,5 hypochlorous acid (HOCl) predominates while at pHs above 8 the hypochlorite ion (OCl^-) predominates. HOCl is the species which exhibits better disinfection properties; OCl^- is not as effective in controlling micro-organisms(146).

In the last decade much work has been directed at determining how membranes are degraded by chlorine and to searching for high-performance materials which will not be degraded by exposure to residual chlorine in the feedwater. Initially, the general reactivity of halogens was considered to be due to reaction of the chlorine with the active hydrogen on residual secondary amide groups in the polymer chain(147). When chlorine attack occurs at such sites in the backbone of a polymer which forms the salt-rejection barrier of a membrane, the barrier will gradually disintegrate and lose its permselective properties. Efforts were therefore initially directed at reducing the rate of chlorine attack by preparing polyamide UTF membranes from polyamine precursors with nitrogens in the polymer side-chain instead of in the main polymer backbone(55) e.g. PA-300 and RC-100 membranes(108). Later, efforts were directed at excluding secondary amide functional groups altogether from the structure of the effective polyamide UTF membrane, e.g. PIP membrane. The phenomenon of N-chlorination (see Section 2.3.4.3) is applicable to any polymer containing -NH groups(147), and has been assumed to be responsible for the decline of RO membrane performance(132,147). Hence, the idea of using amine percursors containing only secondary amines in the making of polyamide UTF membranes to eliminate chlorine sensitivity became attractive. During the interfacial polycondensation reaction all active amino hyrogens should be displaced upon reaction with an acid halide crosslinking agent, and the amine groups converted to tertiary amide groups. (Some residual secondary amino groups are, however, left unreacted due to steric hindrance factors).

The reported effect which chlorine has on the RO performance of selected UTF membranes, compared with that on CA membranes, is shown in Table 2.3, Section 2.3.4.2. Numerous further investigations have been made by others to determine the chlorine sensitivity of polyamide membranes. Some of these are referred to and discussed in Sections 2.3.4.2 - 2.3.4.6. The findings of some of these investigations permit the effect which chlorine has on some polyamide membranes to be explained, and predictions regarding the performance of novel membranes to be made (see Section 2.3.4.4).

2.3.4.2 The effect of chlorine on RO membrane performance

The effect which a chlorinated feed solution has on the RO performance of selected polyamide UTF membranes is summarized in Table 2.3. Included in the table are data on the baseline performance of the membranes (i.e. RO performance prior to chlorine exposure), the conditions under which the membranes are exposed to the chlorinated feed, and data of the resultant performance of the RO membranes. Chemical structures of the membranes (where known) have been shown in Table 2.2, Section 2.3.3. The chlorine stabilities of CA and Du Pont B-9 asymmetric membranes have been included in this table for comparison.

TABLE 2.3 : THE EFFECT OF CHLORINE ON THE RO PERFORMANCE OF SELECTED POLYAMIDE UTF MEMBRANES

Membrane Designation	Initial RO performance: salt rejection [%] permeate flux [lmd]	Conditions under which membrane exposed to chlorine	Membrane performance results after exposure to chlorine	References
Cellulose Acetate (CA)	97,5% 800 lmd	Static test: exposure to 30 ppm chlorine for 208 hours at various pH levels (3,5; 8; 8,6)	No deterioration due to chlorine. (Membrane failure can occur at high pH due to hydrolysis of CA.)	148
Du Pont B-9 polyamide	99% 720 lmd	Static test: exposure to 30 ppm chlorine at various pH levels (3,0; 5,8; 8,6) for up to 400 h.	At pH 5,8 : rejection remained constant; small decrease in water flux. At pH 8,6 : no change in performance for 328 h. At pH 3 : after 64 h - 99%; 200 lmd At pH 3 : after 112 h - 3%; 3600 lmd Membranes showed unusual increase in rejection and decrease in flux until point when there was sudden and dramatic decrease in rejection and increase in flux.	149
NS-100	> 99% 720 lmd	1-3 ppm chlorine in feed solution[a]	< 90% rejection within 10 min. of exposure. Membrane very sensitive to chlorinated feed.	150
NS-101 (PA-100)	99% 960 lmd	Dynamic test:[b] 3 ppm chlorine added to feed solution of 3500 ppm NaCl; 6900 kPa; 25°C	After 60 h: 98,8%; 1280 lmd After 150 h: 96%; 1720 lmd Membrane sensitive to chlorinated feed. (See Fig. 2.4)	4 28
PA-300 (TFC-803)	99,4% 960 lmd	b	After 180 h: 99,1%; 1000 lmd. Chlorine stability slightly better than that of PA-100 (See Fig. 2.4)	4 151
		a	Initial flux decline; < 90% rejection after 250 h.	150
RC-100 (TFC-801)	99,6% 560 lmd	Static test: exposure to 3 ppm chlorine for 40 hours at various pHs	pH 3: 54%; 2940 lmd pH 5,8: 56%; 2800 lmd pH 8,6: 60%; 2720 lmd	152

RC-100 (TFC-801) (continued)		Dynamic test:[c] Initial dose of 2ppm chlorine for first 250h, followed by dosage of 5-10 ppm after 325h to feed solution of 5000 ppm NaCl; 2760 kPa; 25°C; pH 5,7-6,1	After 500 h: 99%; 500 lmd After 550 h: 97%; 550 lmd After 575h: 96%; 570 lmd Membrane was chlorine-sensitive, showing typical performance decline. Chlorine stability better than that of PA-300.	153
		Dynamic test: Several hundred ppm chlorine in a 3500 ppm NaCl solution; 3 days; 6900 kPa	99,5%; 120 lmd (134 ppm chlorine remained after 3 days)	154
TFC-806	99,0% 830 lmd	c	After 500 h : 98,5%; 570 lmd After 575 h : 98,2%; 600 lmd Chlorine stability greater than that of TFC-801, but deteriorated after a few hundred hours of exposure to chlorine.	154
TFC-851	99,5% 600 lmd	Dynamic test:[d] Initial dose of 2ppm chlorine for first 50 h, followed by dosage of 3ppm after 100h; 5000ppm NaCl; 2760 kPa; 25°C; pH 5,7 - 6,1.	After 160 h : no drop in performance After 400 h : 98%; 560 lmd In long-term tests, no resistance to chlorine.	153
TFC-861	99,5% 480 lmd	d	After 160 h : no drop in performance After 400 h : 94%; 640 lmd	153
TFCL^{LP}	>97% 800 lmd, when tested at 1380 kPa	9000 ppm Cl.h at pH 6 10000 ppm Cl.h at pH 6	96% 95%	117
TFCL^{HP}	Similar properties to TFCL^{LP} when tested at 2760 kPa	4000 ppm Cl.h at pH 8 5000 ppm Cl.h at pH 8	< 96% 91% TFCL membrane tolerance to chlorinated feeds generally > 1000 ppm.h.	117
NTR-2500	98% 2000 lmd	Dynamic test: Tap water containing about 1 ppm chlorine	Membrane withstood 1 ppm continuous exposure to chlorine (up to 4000 h).	120

NTR-2500 (continued)		Static test: 100 ppm chlorine	After 70 h : no deterioration After 200 h : 70% rejection Decline in performance followed trend similar, albeit slower, to that observed for CA membranes under similar conditions of exposure. Chlorine resistance better than that of CA membrane.	
NTR-7100	99,7% 300 lmd		No chlorine resistance.	120
NTR-729^{NF}	92%	Dynamic test: ^{e} 100 ppm chlorine in feed of 1500 ppm NaCl; 1000 kPa 25^{o}C; pH 6	Chlorine resistance better than that of CA membranes tested under similar conditions. After 170 h : 92% (CA 92%) After 300 h : 90% (CA 65%)	121
NTR-739^{NF}	95%	^{e}	Chlorine resistance much greater than that of CA membranes After 170 h : 95% (CA 92%) After 300 h : 95% (CA 65%)	121
PIP	>85% 200-400 lmd	1-3 ppm chlorine in feed solution.	No loss in performance after 50 h.	150
NS-300				155
(Piperazine /TMC prepoly.+ IPC)	89% 40 lmd	Static test: 100 ppm; pH 8; 24 h	89% 1000 lmd	
(Piperazine/ cyanuric chlorine prepoly. + IPC)	96% 1200 lmd		67% 1600 lmd	
FT-30	99,5% 1000 lmd	Static test: exposure to 3 ppm chlorine for 40 h at various pHs	pH 3: 99%; 360 lmd pH 5,8: 99%; 1200 lmd pH 8,6: 99%; 1800 lmd Performance is strongly pH-dependent. Effect of chlorine on RO performance is reverse of that observed with other membranes eg. RC-100.	142

FT-30 (continued)		Dynamic test: 30 ppm chlorine; 40 h;		143
	99 %; 240 lmd	ph 3	95%; 1040 lmd	
	99%; 1100 lmd	pH 5,8	95%; 1600 lmd	
		Dynamic test: 100 ppm chlorine in feed of 2000 ppm NaCl; 1380 kPa; 25°C; pH 7 (chlorine level dropped to 60 ppm over 24 h - redosed)	Initial flux decline, followed soon by decline in salt rejection with increase in flux. Total membrane failure after 3 days continuous exposure to HOCl. (See text for further results.)	156
NF-40		Dynamic test: 100 ppm hypochlorite (+ ferric ions present)	Endurance of NF-40 about twice as good as that of FT-30. Chlorine damage caused flux increase and rejection decrease (no initial drop in flux, as shown by FT-30).	129 157
UTC-70		Static and dynamic test done at various pHs and for various chlorine concentrations	Membranes tolerated chlorine for periods of sterilization and cleaning. Membranes tolerated continuous chlorine dosage at level required for sterilization.	130
3N8 (OL)	97,1% 1060 lmd	Dynamic test: i) 0,5 ppm chlorine in feed of 10 000 ppm NaCl; 5520 kPa; 25°C; pH 6,5; 100 days	Salt rejection remained constant for 55 days exposure, whereafter rejection and flux decreased slowly to 93%; 880 lmd. (Degree of chlorine stability appeared comparable to that of FT-30.)	132
		Dynamic test:[f] (ii) 10 ppm chlorine in feed (i) at various pHs, 22 days	pH 8 : 70%; >1000 lmd pH 10 : 94%; 320 lmd pH 6,5 : 78%; 640 lmd pH 5 : 10%; >>1000 lmd pH 3 : 45%; 640 lmd Initial significant loss in salt rejection. Rate of loss higher under acid conditions. Flux first decreased, then increased.	132
2N31	96,9% 320 lmd	f	No degradation observed. Initial slight increase in rejection. Initial decline in flux which stabilised after 7 days exposure. Compared with FT-30 under similar test conditions: FT-30 showed 2% decrease in rejection after 20 days and significant drop in flux within first day followed by continuation in decrease at lower rate. Hence, 2N31 appeared more chlorine-resistant than FT-30 under test conditions used.	132

MSI-500	95-97% 640 lmd	Dynamic test: [g] > 1 ppm chlorine in 500 ppm tap water; pH 8	Chlorine sensitivity similar to that of PA-300. Initial flux decline; < 90% rejection after 250 h testing.	150
Mepiamine	< 50%	[g]	Appeared to be chlorine-resistant in tests done to date. RO performances with chlorinated and dechlorinated feed solution were similar.	158
PMT poly (m-phenylene-trimesamide)	99,3% 1440 lmd	Static test: [h] 500 ppm aq. NaOCl; pH 6; 23°C; 15 h	Decrease in water flux ($^1/_3$ - $^1/_4$ of initial). Flux not recovered after treatment with reducing agents. Decrease in salt rejection to 90,2%, indicated membrane deterioration.	159
		Dynamic test: [j] Membranes exposed to following test cycle at 4300 kPa; 23°C *until performance deteriorated.* (i) treated with HOCl (100 ppm, 25°C), 30 min (ii) washed with dechlorinated water, 30 min (iii) treated with hyposulphite soln. (300 ppm, 25°C), 30 min (iv) washed membrane with dechlorinated water, 30 min	Rejection decreased and flux changed. After 1 cycle : 960 lmd After 25 cycles : 90%; 1680 lmd After 50 cycles : 85%; 1800 lmd After 100 cycles : 80%; 2500 lmd	
PET poly(ethylene-trimesamide)	95% 1220 lmd	Static test: [h]	Decrease in water flux ($^1/_3$ - $^1/_4$ of initial). Flux recovered to 80-90% of initial value after treatment with 300 ppm aq. $Na_2S_2O_4$. *No decrease in rejection.*	159
		Dynamic test: [j]	After 1 cycle : 98%; 960 lmd After 25 cycles: 98%; 1000 lmd After 50 cycles: 95%; 1056 lmd After 500 cycles: 95%; 1128 lmd After 1000 cycles: 95%; 1800 lmd Retains salt rejection of >90% after 2300 h elapsed time (real membrane contact time 575 h). Improvement over CA membrane chlorine stability. (see comparative example below).	
PTP poly(trimesoyl-piperazine)	78%	Static test: [h]	Little change in rejection and flux.	159

CA (comparative example for PMT, PET and PTP membranes)	93% 840 lmd	Dynamic test:[j]	Rejection decreases and flux increases. After 25 cycles : 85%; 840 lmd After 50 cycles : 80%; 912 lmd After 75 cycles : 70%; 984 lmd	159
2N 30 (p-xylenediamide-diimide)	97,2% 580 lmd	Dynamic test: 10 ppm chlorine; pH 4,5; 40 days (6 h on chlorine, rinse, 18 h off chlorine)	After 5 days : 98,2%; 145 lmd After 10 days : 98,8%; 150 lmd After 40 days : 97,0%; 130 lmd	160

A graphic comparison of the RO performances of PA-100 and PA-300 UTF membranes with a chlorinated feed solution has been made(161) and is shown in Figure 2.4. From this figure the typical decrease in salt rejection and increase in water flux, due to chlorine degradation of the membrane, is clear. PA-100 is degraded much more rapidly than PA-300.

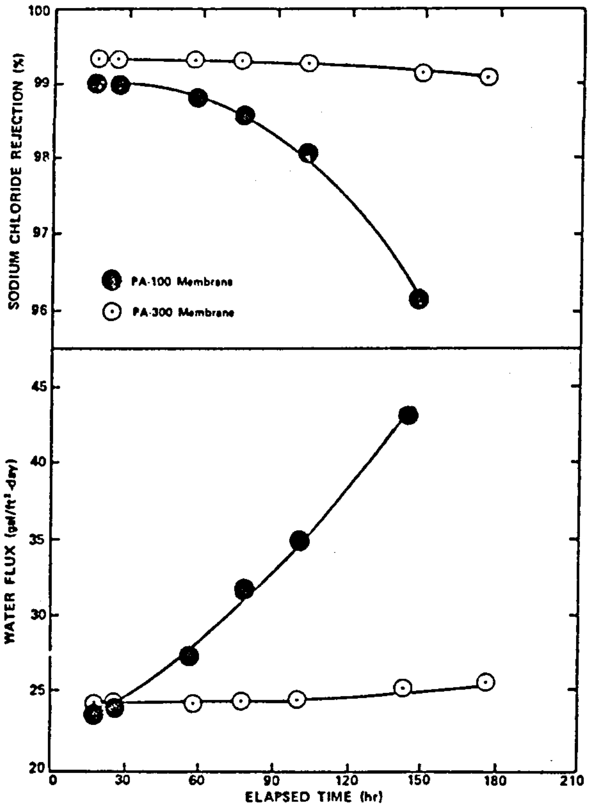


FIGURE 2.4: REVERSE OSMOSIS PERFORMANCE, AS A FUNCTION OF TIME, OF PA-100 AND PA-300 UTF MEMBRANES(161)
(Conditions: 1000 psi (6 900 kPa) applied pressure; 2 500 ppm sodium chloride feed; 25°C; 3 ppm chlorine added).

The FT-30 membrane has been regarded, to date, as the most suitable membrane for desalination of seawater. It has a much lower rate of oxidation (as determined in chlorine-resistance tests) compared with some other polyamide membranes e.g. NS-100 and PA-300. It is interesting to note that the rate of oxidation was lowest in an acid pH range 5 to 6 and higher in the alkaline pH range. The pH effect on chlorine oxidation of FT-30 membranes was opposite to that normally observed with other membranes. Because of the low rate of oxidation of FT-30 it can tolerate accidental exposure to chlorine; exposure to shock doses of chlorine is possible but not generally recommended(96). Long-term tests have indicated that FT-30 can withstand continuous exposure to 0,2 ppm chlorine at pH 7 for more than a year(53). Short-term exposure results in FT-30 degradation after about 200-1000 hours at a concentration of 1 ppm chlorine(129).

The endurance of the recently developed NF-40 membrane to 100 ppm hypochlorite in a continuous RO test has been reported to be twice as good as that of the FT-30 membrane(157) (see Table 2.4). This is to be expected, because the tertiary amide structure of the NF-40 membrane is less vulnerable to chlorine attack than the secondary amide structure of the FT-30 membrane, as proposed by Kawaguchi *et al.*(162). Salt rejection by this membrane is, however, very low (10-40% NaCl).

No UTF polyamide membrane now available is completely chlorine-resistant; all are degraded at various rates upon exposure to a chlorinated feed. Recently, several membrane manufacturers have begun marketing membranes which they claim have various degrees of chlorine resistance, but usually with some economic or performance disadvantages attached, e.g. NF-40, UTC-60 and -70, 2N-31, NTR-7250 series, NTR-739 HF (see Table 2.3).

Very recently, however, a new chlorine-resistant polyamide RO membrane has been disclosed by Gaeta *et al.*(163). It was prepared using proprietary polymers of the poly(piperazineamide) family and cast in asymmetric membrane form. (It is believed that the chemical composition is similar to a piperazine-amide membrane described by Credali *et al.*(138), namely t-2,5-DMPip-TFZ, prepared by an interfacial polymerization reaction between thiofurazan-3,4-dicarboxylic acid and 2,5-dimethyl piperazine.) Its chlorine resistance was studied over a period of six months, under both static and dynamic conditions. The resulting membranes were stable both at low pH values (3-4) or high pH values (8-10) at all chlorine concentrations and at any value of pH at chlorine concentrations in the range 15-25 ppm.

The powerful degradative effect of chlorine upon many polymers, some of which do not even contain nitrogen atoms in their structure (e.g. polypropylene), underlines the extreme difficulty in developing chlorine-resistant membranes. The relevance of chlorine-resistant RO membranes has been discussed by Birkett(141).

2.3.4.3 Response of the PA-300 membrane to chlorine

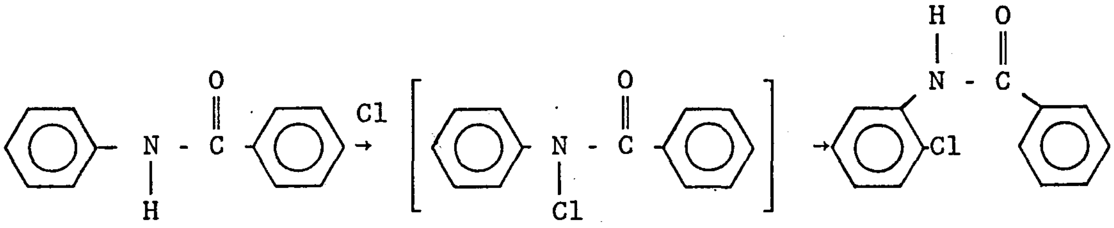
This membrane was selected to illustrate the effect of chlorine on membrane performance, as found by Riley(147). After chlorine-stability studies were conducted on PA-300, it was proposed that degradation of the membrane's performance may occur largely because of attack by chlorine on the polyamide gel structure. (The gel structure of UTF membranes is mentioned in Section 2.3.3.1 and shown in Figure 2.2.) The reason for this proposal was that the pH of the product water became progressively more basic as the selectivity of the membrane decreased as a result of attack by chlorine, reflecting amine breakdown and washout. The increase in pH is attributed to the formation of amine degradation products from the epiamine intermediate layer. A thicker substructure resulted in the effects of substructure degeneration taking longer to become noticeable. Riley then proposed that elimination of gel substructure degradation was very important and attempted to stabilize the epiamine gel-substructure by post-treatment and variations in fabrication techniques. It was found that good integrity and susceptibility of UTF membranes to chlorine attack may be altered but not eliminated by variation in fabrication conditions which affected the substructure gel(147). It was then suggested that, in order to eliminate sensitivity to chlorine, a barrier layer impermeable to active chlorine species should be formed so as to prevent such species from reaching and attacking the epiamine substructure. The RC-100 UTF membrane was prepared by the interfacial polycondensation reaction between an epiamine and TDI(154). *During this reaction no by-product of hydrochloric acid is formed, as would occur in the preparation of* the PA-300 membrane from an epiamine and IPC, which could retard the reaction and render it incomplete.The RC-100 membrane was reported to be slightly more chlorine resistant than the PA-300 membrane(154), although it was concluded that chlorine would penetrate the poly(ether/urea) barrier layer as it does the poly(ether/amide) layer.

(Glater *et al.*(144) used spectroscopic techniques in attempts to analyse the eventual degradation of the RC-100 membrane, but encountered difficulties associated with trying to study the crosslinked insoluble system which precluded the use of nmr spectroscopy. Attempts which were made to obtain solid samples of the crosslinked layer for infrared spectroscopic analysis were also unsuccessful.)

Universal Oil Products (UOP) has reported that the stability or oxidation resistance of their "TFC" membranes in the presence of chlorine generally decreases in the following order: poly(ether/urea), poly(ether/amide), polyurea, polyamide(55).

2.3.4.4 Mechanistic study of membrane-chlorine interaction

Glater(143) conducted an early study on the asymmetric Du Pont aromatic polyamide B-9 membrane to determine the membrane's sensitivity to halogen-based disinfectants. On exposure of the B-9 membrane to chlorine, analysis revealed that at pH 8,6 there was no chlorine uptake whereas at pH < 5,8, with HOCl predominating as the effective halogenating agent, initial rapid addition of halogen was detected which slowed down with continued exposure to chlorine. Changes in viscosity of the polymer extracted from chlorinated B-9 membrane samples were also observed. An initial increase in viscosity during the first 10 hours of chlorine exposure was then succeeded by a continuous decrease in viscosity as the membrane chlorine content increased. The membrane itself showed a unique response towards chlorinated feedwater. A phenomenon of "tightening up" followed by a "breakpoint" (the point at which there was a sudden and dramatic decline in salt rejection and increase in product flux) was observed(149). The original explanation offered for the performance behavior of the B-9 membrane was based on the initial increase in membrane-polymer viscosity, caused by addition of chlorine to the polyamide and a corresponding increase in molecular mass. It was suggested that continued exposure of the membrane to chlorine would result in bond cleavage accompanied by chlorine uptake; the chlorinated polymer fragments would be of significantly lower molecular mass, and the active desalting layer would disintegrate due to mechanical stress. This sequence of events would correlate with the initially observed membrane tightening and improvement in salt rejection which are followed subsequently by a decline in RO performance. The observed decline in membrane polymer viscosity may, however, also be the result of changes in hydrogen bonding within the polymer. This subsequently became the more accepted explanation for the decrease in viscosity and resulting deterioration in membrane performance, after a study of the mechanism of halogen interaction with the B-9 membrane and the model compound form of this membrane material, benzanilide, had been carried out(164). Experimental evidence (nmr and infrared spectroscopic data) from the reaction between benzanilide and chlorine showed aromatic ring-halogenation to be a dominant process; evidence for halogen ring-substitution of aromatic amides is discussed in the literature by Orton and Zabicky(165). The reaction scheme for the chlorination of benzanilide, is reported to be as follows(162):



Increasing ring-halogenation has the effect of increasing the hydrogen bonding of an amide proton and altering the hydrogen-bonding patterns within the polymer. Membrane failure was strongly suspected to result from alteration in hydrogen-bonding modes within the B-9 polymer. Shifting of the mode of hydrogen bonding from inter- to intra-molecular within a polypeptide chain may cause chemical deformation, resulting in puckering or coiling of chain segments, followed by alteration in gross polymer properties. Loss of salt-rejection function and enhanced water transport could result from such structural changes in a membrane. It was pointed out that the suggested reaction mechanism for the Du Pont polyamide B-9 membrane was not necessarily applicable to other polyamide membranes. It is, however, reasonable to assume that the dominant process in failure of aromatic polyamide membranes involves ring halogenation. It has been disclosed that the B-9 membrane contains sulphonic acid groups ($-SO_3H$) in approximately 10% of the aromatic rings. According to Glater, halogenation of the N-H-substituted rings containing sulphonic acid groups is unlikely, due to ring deactivation by this m-directing group. It was proposed that sulphonic acid groups have little or no bearing on the proposed model for failure of the B-9 membrane(164).

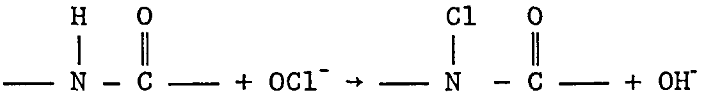
Arising from recent results of experiments done on the chlorine-damaged FT-30 membrane, which is similar in many respects to the B-9 membrane but is composed of 1,3 benzenediamine - isophthaloyl linkages, Koo(156) disputed the above suggested reaction mechanism proposed by Glater *et al.*(164). In the FT-30 membrane the high level of crosslinking would greatly limit conformational changes as a mechanism of salt-rejection loss. Yet, chlorine damage results in such losses. Koo *et al.*(156) claim that a depolymerization reaction (see Section 2.3.4.5) must be the principal explanation for loss of salt rejection, both in the FT-30 membrane and the Du Pont B-9 membrane.

In 1983 Lee(132) reported on the current understanding of factors affecting chlorine sensitivity of polyamide membranes and probable reaction mechanisms for chlorine attack; the discussion was based on the reactivity of the different chlorine species (HOCl and OCl^-) with the different functional groups present in an effective polyamide desalting membrane. Chlorine attack of a polyamide can occur at amide linkages and residual amine groups. Amide linkages are susceptible to attack by OCl^-, whereas residual amine groups, when they are present, are attacked by HOCl.

The amide or unreacted amine groups, present in polyamide membranes, could undergo reactions with the various chlorine species as described in (a) to (e).

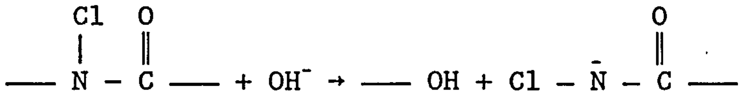
(a) **Secondary amide (-NH-CO-) linkages:**

These react primarily with OCl^- and undergo N-chlorination as follows:



$$—\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}— + OCl^- \rightarrow —\overset{\overset{\displaystyle Cl}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}— + OH^-$$

The N-chloroamide is quite stable under neutral conditions but hydrolyses slowly in alkaline medium, resulting in chain scission, as follows:



$$-\overset{\overset{Cl}{|}}{N}-\overset{\overset{O}{\|}}{C}- + OH^- \rightarrow -OH + Cl-\bar{N}-\overset{\overset{O}{\|}}{C}-$$

(b) **Tertiary amide (-NR-CO-) linkages:**

This group is regarded as the most stable to attack by OCl^- and HOCl, hence the NR-CO linkage can be considered to be the most chlorine-resistant functional group possible in polyamide membranes.

(c) **Primary amine ($-NH_2$) group:**

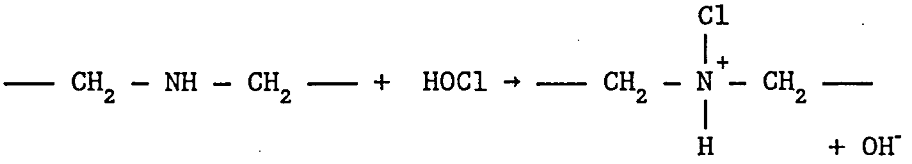
Primary amines can react with HOCl to yield N-chloroamines or N,N-dichloroamines, as follows:

$RNH_2 + HOCl \rightarrow RNHCl + H_2O$
$RNH_2 + 2HOCl \rightarrow RNCl_2 + 2H_2O$

The reactions are irrelevant to polyamides as any primary amine group present is a pendent group or an end group of a polymer chain, and reaction with HOCl does not cause chain scission.

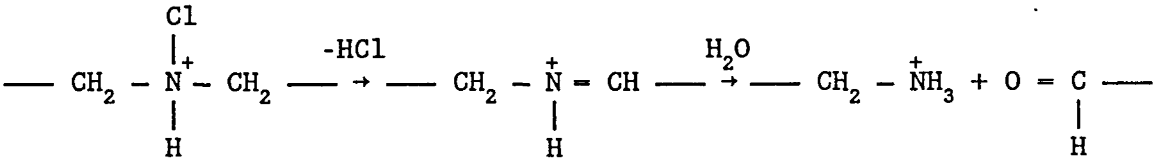
(d) **Secondary amine (-NH-) group:**

Secondary amines react with HOCl but not with OCl^-. N-chlorination takes place as follows:



$$-CH_2-NH-CH_2- + HOCl \rightarrow -CH_2-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{N^+}}-CH_2- + OH^-$$

This is followed by dehydrochlorination and hydrolysis which results in chain scission, as follows:



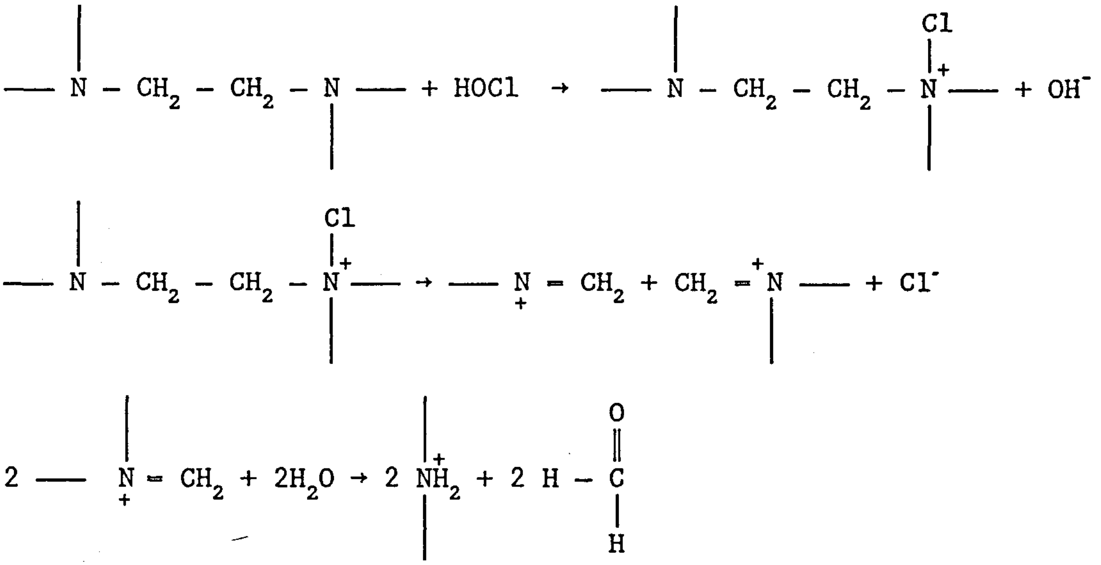
$$-CH_2-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{N^+}}-CH_2 \xrightarrow{-HCl} -CH_2-\underset{\underset{H}{|}}{\overset{+}{N}}=CH \xrightarrow{H_2O} -CH_2-\overset{+}{N}H_3 + O=\underset{\underset{H}{|}}{C}-$$

This reaction mechanism is termed oxidative dealkylation.

Residual secondary amine groups, located along the chain of a membrane polymer, are therefore sites of attack when HOCl is present in the feed solution.

(e) Tertiary amine (-$\underset{|}{\text{N}}$-) group:

Oxidative dealkylation occurs in tertiary amines by a reaction similar to that which occurs in secondary amines (equation d), except that the hydrogen atom is replaced by an alkyl group. A second mechanism, leading to chain scission, termed oxidative fragmentation, may occur(166).



$$-\overset{|}{N}-CH_2-CH_2-\underset{|}{N}- + HOCl \rightarrow -\overset{|}{N}-CH_2-CH_2-\underset{|}{\overset{\overset{Cl}{|}}{N^+}}- + OH^-$$

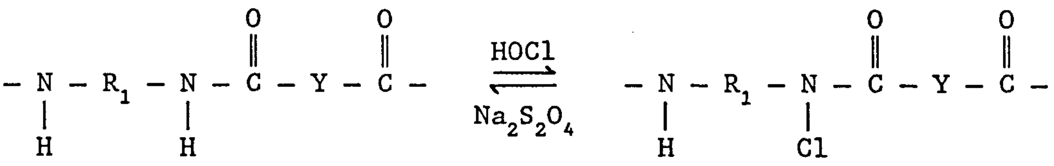
$$-\overset{|}{N}-CH_2-CH_2-\underset{|}{\overset{\overset{Cl}{|}}{N^+}}- \rightarrow -\underset{+}{N}=CH_2 + CH_2=\underset{|}{\overset{+}{N}}- + Cl^-$$

$$2 -\underset{+}{\overset{|}{N}}=CH_2 + 2H_2O \rightarrow 2\ \underset{|}{\overset{|}{NH_2^+}} + 2\ H-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}$$

Hence, it would appear that the tertiary amide is the preferred species for conferring chlorine stability on polyamide membranes. Residual secondary amine groups, which may remain after incomplete interfacial polycondensation between a secondary amine precursor and a crosslinking agent, are the least desirable. In acid solution, chlorine degradation of a membrane containing both -NH- and -NHCO groups is caused largely by attack at the site of any amine groups. In alkaline medium, in which the concentration of OCl$^-$ is high, the degradation results mainly from slower attack on the amide linkages. This is supported by kinetic studies which have shown that the rate of reaction between amines and HOCl is much greater than that of the reaction between amides and OCl$^-$. On the basis of the reactions proposed by Lee(132), explanations are offered below for the performances of the NS-101 and FT-30 membranes upon exposure to chlorine. PEI-based membranes, e.g. NS-101 represent an extreme case of high sensitivity to chlorine(4,28). This is now explained by the presence of residual secondary amine groups and many tertiary amine branching points in the finished membrane. Both species are subject to HOCl attack. The FT-30 membrane is less resistant to chlorine in an alkaline medium due to the presence of the aromatic secondary amide groups. It is concluded that since normal RO operation is carried out at slightly acidic pH it is most desirable that secondary and tertiary amine groups should be eliminated from the polyamide barrier in order to reduce its vulnerability to chlorine attack. If the membrane is to be used at all pHs then the structure of the polyamide should be such as to contain only the -NR-CO- tertiary amide linkages.

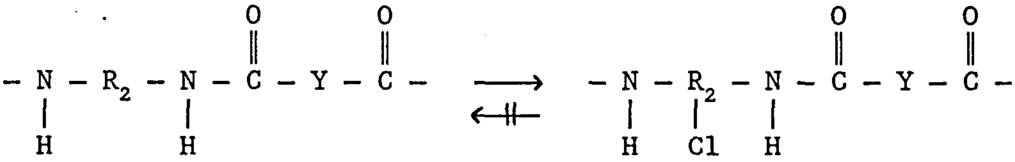
Kawaguchi and Tamura(162) attempted to correlate the chemical structure of polyamides and their reactivity to HOCl to evaluate their resistance to chlorine and suitability as membrane materials for RO. They prepared various polyamides and allowed them to react with HOCl whereafter they classified their modes of interaction according to whether there was no reaction, reversible chlorination at the amide nitrogen, or irreversible chlorination at the aromatic nucleus. The diamine components (precursors) were found to play an important role in the determination of the reactivity of polyamides to oxidative chlorination. The following results emerged:

(a) no reaction with chlorine in the case of tertiary polyamides;
(b) reversible chlorination at the amide nitrogen where the amine component is an aliphatic (reaction a);
(c) irreversible chlorination when the amine component is aromatic (reaction b).



$$-\mathrm{N(H)}-\mathrm{R}_1-\mathrm{N(H)}-\mathrm{C(=O)}-\mathrm{Y}-\mathrm{C(=O)}- \underset{\mathrm{Na_2S_2O_4}}{\overset{\mathrm{HOCl}}{\rightleftharpoons}} -\mathrm{N(H)}-\mathrm{R}_1-\mathrm{N(Cl)}-\mathrm{C(=O)}-\mathrm{Y}-\mathrm{C(=O)}-$$

(a)



$$-\mathrm{N(H)}-\mathrm{R}_2-\mathrm{N(H)}-\mathrm{C(=O)}-\mathrm{Y}-\mathrm{C(=O)}- \underset{\not\leftarrow}{\longrightarrow} -\mathrm{N(H)}-\mathrm{R}_2\mathrm{(Cl)}-\mathrm{N(H)}-\mathrm{C(=O)}-\mathrm{Y}-\mathrm{C(=O)}-$$

(b)

On the basis of these results, Kawaguchi and Tamura claimed that:

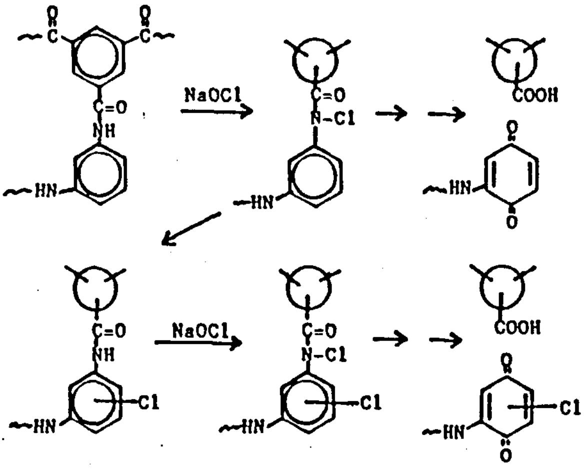
(a) tertiary polyamides are the preferred compounds for chlorine resistant polyamide membranes;
(b) aliphatic secondary polyamides are the next most suitable;
(c) polyamides from aromatic primary diamines are the least favourable materials for chlorine-resistant membranes because they are susceptible to attack by active chlorine, which may enhance membrane hydrophobicity and lead to deterioration in performance.

On the basis of these findings, a poly(ethylenetrimesamide)(PET) UTF membrane was prepared from an aliphatic diamine, and this showed potential as a material for a chlorine-resistant RO membrane(159) (see Table 2.3).

2.3.4.5 ESCA characterization of chlorine-damage to polyamide RO membranes

Only very recently was the technique of electron spectroscopy as used for chemical analysis, ESCA(167), employed to investigate surface compositions (in terms of the percentages of elements present) of some polyamide membranes and the changes which the membranes undergo because of attack by the hypochlorite ion or hypochlorous acid. Koo *et al.*(156,157) used ESCA to investigate the surface compositions of the FT-30 and NF-40 membranes and the changes which take place after attack by chlorine species. Uemura and Kurihara(130) used ESCA to study the changes in structures of the UTC-60 and UTC-70 membranes after exposure to chlorine. The results of ESCA analyses of chlorine-damaged FT-30 and NF-40 membranes led to suggestions regarding mechanisms for their degradation.

Koo *et al.*(157) proposed that the chlorine damage in the NF-40 membrane was due to oxidation of the piperazine groups, followed by accelerated hydrolysis of amide bonds of the piperazine moieties. Degradation of the FT-30 membrane was due to initial N-chlorination and/or ring chlorination followed by polymer chain cleavage, leading to an increase in water flux and accompanying decrease in salt rejection. It was postulated that oxidative chain cleavage occurred to generate quinone groups, specifically by chemical alteration of the benzenediamine rings. The overall mechanism for the degradation of the aromatic polyamide of the FT-30 membrane as suggested by Koo *et al.*(156) is shown below:



2.3.4.6 Model compounds as predictors of chlorine sensitivity of polyamide RO membranes

The use of a limited number of model compounds, the non-polymeric analogues of a polymeric unit, was investigated during studies of the behaviour of certain membrane polymers towards chlorinated solutions(123,162,164). (The concept of model compound studies will be described in Sections 2.5.2.1.)

Glater *et al.*(164) used the model compound of the Du Pont B-9 membrane polymer, benzanilide, in investigations into the chemical reactions which take place during chlorination (see Sections 2.3.4.4).

After exposing various amine and amide model compounds to hypochlorite solutions and analysing the products, Sudak(123) reported on the apparent stability of tertiary amides, instability of secondary amides and suspected instability of tertiary amines towards sodium hypochlorite. N-Methyl-benzamide, a secondary amide, showed an immediate reaction with HOCl. N,N -dimethyl-benzamide, a tertiary amide, showed no reaction with HOCl.

Recently, a rapid screening method using model compounds to predict the sensitivity of UTF RO membranes to chlorine solutions has been reported(168). The model compounds used were chosen on the basis of functional group arrangements found in polymers of potential interest as interfacially formed UTF membranes, which included polyamides and polyureas. The screening method involved addition of the model compound to an aqueous solution of hypochlorite and monitoring the disappearance of starting material and the appearance of reaction products by high-pressure liquid chromatography (HPLC). A chlorine-susceptibility index (CSI) was then developed which ranked the chlorine susceptibility of the functional group arrangements studied at pH 4,5 and pH 10. Results obtained with this procedure indicated that polyamides can form chlorine-resistant membranes if the amide nitrogen atoms are not directly bonded to an aromatic ring. Results of long-term RO tests on three representative polyamide membranes, including FT-30, were consistent with predictions based on the CSI values.

2.3.5 THE EFFECT OF ACIDIC AND BASIC ENVIRONMENTS ON RO MEMBRANE PERFORMANCE

Stability over a wide range of pH is a desirable physicochemical property of RO membranes. Acid is frequently used in the pretreatment of seawater prior to desalination by RO. It is employed to depress the pH, to prevent the formation of alkaline-earth scales and to inhibit organic fouling, all of which improve overall RO performance(55). Low pH conditions also often exist during cleaning of the membranes. (A 2% citric acid solution, adjusted to pH 3 with ammonium hydroxide and used at 50°C for 45 minutes at a system pressure not exceeding 410 kPA (60 psi), has been widely used for a number of years to clean commercial RO plants(169)). Alkaline detergent cleaning solutions may be used to remove certain types of deposit from the surfaces of fouled RO membranes.

Unlike CA membranes, which are unstable at pHs below 4 and above 8 at temperatures above 25°C, UTF polyamides are much more resistant to low- and high-pH conditions. Generally the limits of these UTF RO membranes in continuous operation are considered to be in the ranges of 3 - 11 pH units and 0 - 35°C(170). The salt-rejection efficiency of a number of the latter membranes, otherwise suited for single-pass seawater desalination, may, however, be affected by the pH of the feed solution. The dependence of the performance of numerous RO membranes on the pH of a feed solution has been measured and the pH limits of some selected polyamide UTF membranes are shown in Table 2.2.

The PA-300 membrane displays best salt-rejection efficiency at a pH of around 5,5(171). This dependence was suspected to be a result of an inherent charge on the desalting barrier layer and on the nucleophilic nature of the reactants used. It is known that there is a charge on the surface of several TFC UTF membranes. It is also well known that the transport of monovalent ions through charged membranes is dependent on the feed solution pH, due in part to the Donnan effect(67,172). (The nature and extent of charge on the surface of TFC membranes is quite significant from an application point of view, as discussed by Riley(172)). Evaluation of the effect of feedwater pH on NS-300 membrane performance indicated that there was little change in membrane properties at high pH(124). At low pH the membrane salt rejection did not change but there was a drop in flux at pH below 7. A likely explanation for this is the presence of carboxylic acid groups in the membrane. In the acid pH range the ionization of the -COOH groups would be restricted, reducing their water-binding capacity and membrane flux. The salt rejection of the FT-30 membrane is not a strong function of pH in the range 3,9 to 8,7(129).

After tests of the relative stabilities of TFC-800, -801, -802 and -803 membranes towards citric acid solutions over a pH range 2 to 3, two interesting facts emerged(169):

(i) the overall stability of TFC membranes-801 and -803 (epiamine-based) is significantly greater than that of TFC membranes-800 and -802 (PEI-based)

(ii) none of the TFC membrane systems withstood citric acid cleaning in the flat-sheet RO test-cell system.

The following explanation for this behaviour, based on membrane swelling at low pH, is offered. At low pH the polyamine of the intemediate layer of the membrane is converted from the amine form to the acid salt, which expands and swells. Membrane swelling cannot be tolerated within a test cell because of physical damage which is incurred by the membrane at the O-ring/membrane interface. The TFC membrane within a spiral element, however, has no constraints or points of contact on the surface of the

UTF, with the result that the intermediate layer of the membrane can expand and contract with changes in feed pH without causing damage to the thin desalting barrier. In general, PEI appears to swell to a greater extent, at a given pH, than does the epiamine. Unlike acids, bases would not be expected to cause swelling of the strongly alkaline intermediate layer of either PEI- or epiamine-based membranes. Transport properties should therefore not be affected by strongly basic feed solutions in either flat-sheet or spiral-wound test elements.

2.3.6 THE EFFECT OF TEMPERATURE ON RO MEMBRANE PERFORMANCE

The use of asymmetric CA membranes was limited to a maximum operating temperature of 35°C. At temperatures above this, the membranes undergo irreversible compaction and densification, especially under applied operating pressure. As a result, there is a marked decline in water flux(173). The UTF membranes have, in general, been found to be able to withstand temperatures exceeding 35°C(53,170). Examples of such membranes include the North Star Research Institute's experimental membrane series: NS-100/NS-200/NS-300; UOP Fluid Systems Division commercial PA-300 (TFC-800) and RC-100 (TFC-801) membranes, Toray's commercial PEC-1000 membrane and the Film Tec corporation's FT-30 membrane (see Table 2.2). The NS-100, NS-300 and FT-30 membrane have all been exposed to boiling water in laboratory tests and remained intact and fully functional.

The polysulphone support layer of UTF membranes shows good resistance to elevated temperatures, and does not compact or densify to the same extent as would the spongy sublayer of an asymmetric membrane. The thin desalting barrier of the TFC membrane is normally highly crosslinked, which renders it more resistant to the effects of elevated temperature than asymmetric membranes are(173).

It has, however, been found for the FT-30 membrane that the combination of high operating pressure and high temperature of the feed solution (200-800 psi / 1380 - 5520 kPa., 50°C) can result in irreversible lowering of membrane fluxes. As UTF membranes and other membrane module components are plastic materials, they may be expected to show creep behaviour under conditions of combined elevated temperature and pressure. This was initially suggested as a possible mechanism for loss of flux by the FT-30 membrane. It was, however, later established that the problems of flux decline originated in the polyamide barrier layer and not in the underlying microporous polysulphone support(173).

The water flux and salt rejection of a membrane are functions of feedwater temperature. An increase in operating temperature usually leads to a substantial increase in water flux through a membrane(66). Elevated operating temperatures have been reported to accelerate degradation of membranes exposed to chlorinated feedwater e.g. FT-30 and TFCL membranes(177). The operational temperature ranges and limits of some selected polyamide UTF membranes have been shown in Table 2.2.

2.4 POLYAMIDES

2.4.1 USE AS BARRIER MATERIALS

As mentioned in Section 2.3.1, the greatest emphasis in research and development on UTF composite membranes has been on a class of polyamides, namely, the nitrogen-containing aromatic backbone polymers(66). These exhibit water and salt permeability characteristics, as well as thermal, biological and chemical properties, superior to those of cellulose acetate. This class of polymers can be conveniently prepared by an interfacial polycondensation reaction (see Sections 2.3.2 and 2.4.4). Although the polyamides are a large family of polymers, only some classes have properties which make them suitable compounds for use as RO membranes.

Blais(27) has reported on the development of polyamides as membrane materials, fabrication of polyamide membranes and the relationship of the chemical structure to membrane performance and properties. This relationship was discussed in terms of the hydrogen-bonding ability, hydrophilicity, polymer rigidity and resistance to creep of the polymer. Barrier materials of various polyamides used for RO membranes have been reviewed by Sumitomo(174) and their permeability characteristics discussed from the point of view of their chemical structures. It has emerged that to be functional in water desalination the polyamide desalting barrier must, amongst other requirements, have a balanced content of hydrophilic and hydrophobic groups and also have a fairly rigid chemical structure overall so that it will resist compaction under high operating pressure(50). Generally speaking, a higher ratio of hydrophilicity to hydrophobility in the polymer chain will ensure greater water flux of membranes from this material(25). It is claimed, however, that an increase in the ratio of polar groups in a membrane polymer structure results in a decrease in chemical stability of the material. This is due to degradation reactions which occur on the polar "weak link" in the main polymer chain e.g. the amide group is sensitive to some polar solvents because of its polarity, and may be easily hydrolysed under the action of acid or alkali(175). (An aromatic polyamide containing sulphone linkages has recently been used in the preparation of asymmetric RO membranes which were found to exhibit high permselectivity and water flux and excellent resistance to acid, alkali, chlorine and heat(175). The reason given for these favourable properties is the existence of the strong electronegative sulphone groups in the main polymer chain, which increase the stability of the amide groups conjugated with the benzene ring.)

The polyamide membranes which currently exhibit good desalination performance do, however, suffer from a serious limitation in that they are particularly subject to degradation by chlorine, as described in Section 2.3.4 and shown in Table 2.3.

2.4.2 CHEMICAL PROPERTIES

Chemical properties, which are relevant to the long-term stability of polyamide membranes and their performance under hostile conditions, have been reviewed by Blais(27). The chemical reactivity of these polymers is associated mainly with the amidic nitrogen. Acid or base hydrolysis can occur through the amide linkage of the less stable members of the polyamide family and reduce the molecular mass to a point at which the polyamide membrane integrity is threatened or at which the polymer's mechanical properties are no longer adequate. Aromatic polyamides, in general, show better hydrolytic stability than the aliphatics do(176). The latter are, in turn, much better than CA. Outright chemical attack is not the only manner by which the properties of membrane barrier polymers can be reduced or lost. Plasticization or swelling of a membrane in the presence of certain feed-solutions may be sufficient to cause certain irreversible changes in the barrier layer.

2.4.3 POLYSULPHONAMIDES

Since the early days of the RO separation industry, fouling of membranes has been recognised as one of the most severe problems(12,177). Research on the reduction of fouling tendencies of membranes continues. The most common approach has been to coat membranes with polymers rich in sulphonate groups(12,177-179). According to Gregor and Gregor(12) the extremely hydrophilic nature of the sulphonate group and stability in its ionized salt form, could inhibit absorption of hydrophobic constituents of the feed stream onto a highly sulphonated membrane surface. In addition, since almost all naturally occurring colloidal fouling materials are negatively charged, it is believed that ionic repulsion effects would occur between the electronegatively charged sulphonate groups of the membrane and natural colloids. Incorporation of sulphonate groups into a desalting-membrane structure may, furthermore, offer the following advantages:

(a) the fixed charged of a sulphonate group could enhance salt rejection of a membrane because of the creation of an electrical field in the area of the desalting barrier; and

(b) the high affinity which a sulphonate group has for water, could lead to greater water flux through a membrane.

The formation of sulphonamides by the condensation reaction between amines and sulphonyl chlorides is well known and forms the basis of the well-known Hinsberg reaction(180). Residual sulphonyl chloride groups can hydrolyse to form sulphonic acid groups(181). The preparation of polysulphonamides by interfacial polycondensation methods from diamines and aromatic disulphonyl chlorides has been well described by Morgan(182).

Various aliphatic polysulphonamides have been prepared by the reaction of 1,3-benzenedisulphonyl chloride with aliphatic diamines under conditions of interfacial and solution polycondensation. These exhibited excellent stability to hydrolysis in both acid and alkaline conditions(183,184). Aromatic polysulphonamides have been prepared by solution polycondensation of aromatic disulphonyl chlorides and aromatic diamines, using extended reaction times(185). (Aromatic amines show a low reactivity towards aromatic disulphonyl chlorides.)

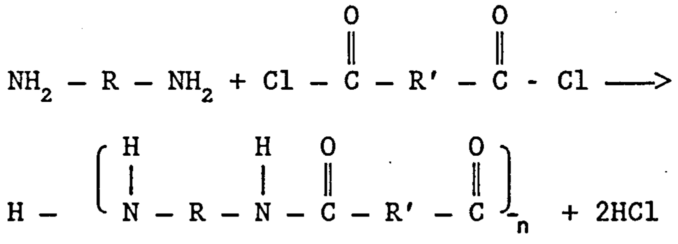
The interfacial polycondensation reaction between piperazine and 1,3-benzenedisulphonyl chloride to yield a low molecular mass polymer has been reported by Kwolek(184). Evers and Ehlers(186) found the piperazine polysulphonamides to be of considerably lower molecular mass and appreciably less stable than most aromatic polyamides. A series of polyamide-polysulphonamides was synthesized by the interfacial polycondensation of 1,3- and 1,4-chlorosulphonylbenzoyl chloride with aliphatic and aromatic diamines at room temperature(187). Most of these polymers were of high molecular mass and had film-forming properties. No membranes have yet been fabricated from these compounds. Kawahara *et al.*(188) fabricated an asymmetric aromatic poly(amide imidesulphonamide) RO membrane and a similar copolymeric membrane having additional pendent sulphonate groups. The latter was found to exhibit greater water permeability and salt rejection than the former did.

The incorporation of sulphonate groups into a UTF membrane by preparing such membranes with sulphonyl chloride crosslinking agents has attracted very little attention. It is undocumented, apart from Cadotte's(96) mention of a patent issued to Kawaguchi of Teijin, Japan, in 1982. This patent mentions the possible use of 3-chlorosulphonylisophthaloyl chloride as an example of a crosslinking agent in the preparation of UTF membranes with polyethyleneimine precursor. As far as can be ascertained, the incorporation of sulphonyl groups in crosslinking agents for the fabrication of UTF RO membranes by the interfacial polycondensation process as described in this thesis, was a new approach towards fabricating novel and better membranes - the preliminary findings of which were disclosed in a South African patent(189) granted to the author in 1977.

2.4.4 PREPARATION OF POLYAMIDES BY THE INTERFACIAL POLYCONDENSATION REACTION

Interfacial polycondensation is a well-known method for the preparation of polyamides under mild conditions(190-192), starting from an aqueous solution of a diamine and a diacid chloride dissolved in an organic solvent which is immiscible with water e.g. hexane or benzene. Immediately after the two components are brought together a polymeric film (membrane) is formed at the solvent interface. The solution interface then becomes the site of reaction. The chemical and physical properties of the resultant film depend on factors such as reacting species, concentrations, contact time, ionic strengths, interfacial tensions and reaction temperature(190,193). The film which forms controls the introduction of the aqueous soluble reactant into the excess of acid halide in the organic phase, across the interface, and thus controls the growth and thickness of the film. As the thickness of the polymer film increases, the reaction slows down and then stops. The scope of this method of preparation of polyamides and numerous relevant preparative aspects have been well described by Morgan(190). A limiting factor of this preparation method is the selection of a diamine which is water soluble.

Interfacial polyamidation is an example of a Schotten-Baumann reaction(194):



$$NH_2 - R - NH_2 + Cl - \overset{\overset{\displaystyle O}{\|}}{C} - R' - \overset{\overset{\displaystyle O}{\|}}{C} - Cl \longrightarrow$$

$$H - \left[\underset{\underset{\displaystyle H}{|}}{N} - R - \underset{\underset{\displaystyle H}{|}}{N} - \overset{\overset{\displaystyle O}{\|}}{C} - R' - \overset{\overset{\displaystyle O}{\|}}{C} \right]_n + 2HCl$$

During this reaction, hydrochloric acid is liberated (and transferred to the water phase). This is neutralized by addition of an acid-acceptor or by excess amine reagent. Similarly, diamines and diisocyanates will react and undergo an addition reaction to form a polyuarea. No acid byproducts are released. There is strong support for the claim that the interfacial polycondensation reaction takes place primarily in the organic solvent side of the interface, and that the membrane grows in this organic phase(190,193), the diamine being the only migrating component. According to Morgan(190) no polymer has been observed to form on the aqueous side of the interface. (Some polymers which are water-sensitive, however, yield a film in the organic phase, and then this may be slowly penetrated by water which shows as small drops of newly forming polymer film.) More recently this was disputed by Bartels *et al.*(104) who claimed that growth of the thin film in a UTF membrane is in the aqueous phase.

There are several types of side-reactions commonly associated with polyamide formation by interfacial polycondensation, including hydrolysis of the acid chloride and formation of cyclic or branched-chain polyamides. These are discussed by Morgan(190) and Bradbury *et al.*(193). It is claimed that hydrolysis of acid halides is the principal interfering side reaction in an interfacial polycondensation process. An acid chloride is susceptible to hydrolysis and the free acid may be formed. In the event of one end-group of the initial difunctional acid chloride reactant molecule being hydrolysed, incorporation of the molecule in the forming oligomer chain would block the diamine which had already crossed the interface and lead to termination of the polymer growth and to a reduction in polymer molecular mass and an increase in disorientation or non-homogeneity of the membrane structure. In the less likely event of both end-groups of the difunctional acid chloride being hydrolysed, the concentration of this reagent would be effectively reduced.

Branched-chain polyamides and polysulphonamides have been obtained from reactions in which aliphatic primary amines were used(193,195). Branching results from acid chloride attack at the nitrogen atom of the amide or sulphonamide group initially formed in the polymerization process. The degree of branching was found to increase with increasing concentration of the acid chloride in the organic phase. This type of side-reaction was reported to lead to polymers of reduced molecular mass and lower polymer yield but, unlike hydrolysis, would not necessarily lead to termination of the chain(195). Branching by imide formation did not occur with secondary diamines.

Interfacial polyamidation may be terminated by:

(a) hydrolysis of the acid chloride functional group;
(b) protonation of the amine group which would then no longer be accessible for further reaction (acylation of the amine-HCl species will not take place);
(c) precipitation of the polymer which will affect the rates of further reaction.

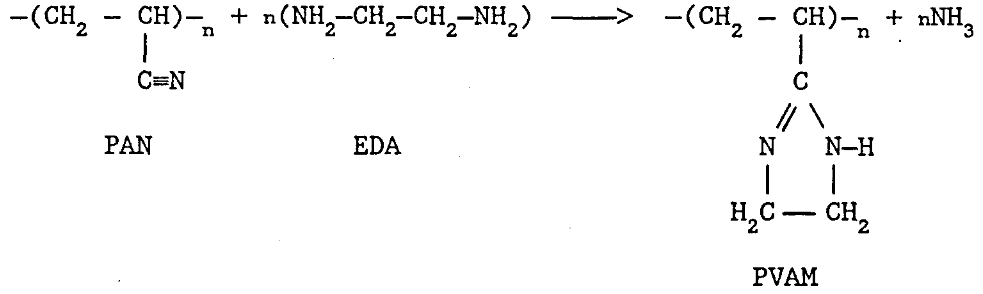
The reaction mechanism of interfacial polycondensation gives rise to the bi- or multilayer structure of the polyamide UTF membrane, with a non-homogeneous distribution of functional groups. The surface exposed to the water phase during the reaction contains predominantly amino end-groups while the opposite surface is rich in carboxylic acid end-groups. In between, both the nature and concentration of structures vary. The effects of membrane non-homogeneity (asymmetry) have been discussed by Enkelman(196). It has been proposed that the membranes have two different surfaces, namely, a smooth surface near the water phase and a rough surface near the organic phase. This has been confirmed (in certain examples) by scanning electron microscope photographs.

UTF membrane formation by interfacial polymerization is not limited only to fabrication of polyamide and polyurea membranes. Polyester membranes may be prepared in the same manner from reagents having two or more alcohol groups, although the reaction rates with these reagents are slower in membrane preparation than those of polyamines in polyamide preparation. Polysulphonamide films can be prepared by an interfacial reaction by choosing the right reaction conditions, including concentration level of reagents, ratio of reagent concentrations, solvents and reaction times(182).

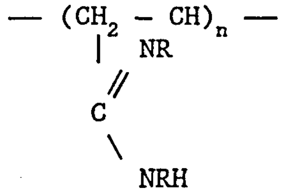
2.5 POLY-2-VINYLIMIDAZOLINE

2.5.1 AS POLYMERIC PRECURSOR

Polymers of 2-vinylimidazoline have been disclosed in patents by Panzer(197), Hurwitz and Aschkenasy(198), and Pollio(199). These materials are suitable as coagulating agents for the clarification of aqueous media and more particularly for the removal of anionic water-soluble materials from various aqueous media such as polluted river water. The polymers are water-soluble and can be prepared by reacting an acrylonitrile polymer (or copolymer) with a water-soluble alkylene polyamine having two nitrile reactive basic amino groups. As an example, polyacrylonitrile (PAN) and ethylenediamine (EDA) yield poly-2-vinylimidazoline (PVAM), as shown:



Substantially no side reactions were reported to occur(197). Because these polymers contain the linkage as shown, they are also termed vinylamidine polymers:



The following features of homopolymeric poly-2-vinylimidazoline (PVAM) make this compound an attractive material, worthy of investigation for use as a polymeric precursor in the fabrication of thin-film composite RO membranes by interfacial polycondensation (see Section 2.3.2.1):

(a) water solubility;
(b) apparent ease of preparation from known reagents;
(c) amidine functionality, in which one of the nitrogen atom has one reactive hydrogen (after reaction with an acid chloride crosslinking agent can be expected to form a tertiary amide), the second nitrogen has no reactive hydrogen;
(d) functionality in the polymer side-chain.

A polymeric precursor material with a nitrogen atom with one reactive site which was positioned in the polymer side chain should be preferable for the fabrication of polyamide membranes which would have some stability towards chlorinated feedwaters (see Section 2.3.4.1).

Apart from the patents(197-199) which describe the preparation and applications of 2-vinylimidazoline polymers, there is no literature on the chemical reactions which these compounds undergo, except mention of their hydrolysis in basic medium. Hurwitz(198) found that poly-2-vinylimidazoline (PVAM) hydrolyses when it is heated to 50°C for 5 days and that it formed poly(N-aminoethylacrylamide). Acidifying PVAM with sulphuric acid leads to the formation of the water-soluble sulphate salt.

Oligomeric vinylimidazolines, with molecular masses greater than 200, have been reported as useful corrosion inhibitors in oil- and gas-field pipes(200). Recently, spectroscopic methods e.g. ^{13}C nmr were used to investigate the actual chemical composition of the imidazoline used for corrosion inhibition(201). It was found that the imidazoline functional groups were fairly rapidly hydrolysed to the amide form upon ageing. Amide peaks appeared in the ^{13}C nmr spectrum.

2.5.2 MODEL COMPOUNDS OF 2-IMIDAZOLINES

2.5.2.1 Background

Because of the paucity of literature on the reactions of PVAM, and in efforts to gain some insight into the chemical properties of these polymeric materials, the chemistry of model compounds simulating the polymeric PVAM precursor is important. Of prime concern is the information regarding the proposed reaction between the PVAM precursor and aromatic acid chloride crosslinking agents containing carboxylic acid- or sulphonic acid-chloride functional groups by which membranes were to be made (see Section 4.3.1).

This investigation was to be undertaken to elucidate, by means of model compound reactions, the chemical structure of a PVAM/SCl UTF membrane desalting barrier at molecular level, so as to facilitate determination of the chemical structure/s which give rise to the RO performance.

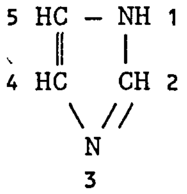
The investigation could also be directed at correlating any changes in RO performance which may have resulted from exposure of the membrane to adverse (harsh) operating conditions with possible changes in the chemical structures of the chosen model compounds under similar conditions. Harsh operating conditions for RO membranes would include high- and low-pH feedwaters and chlorinated feedwaters (see Sections 2.3.5 and 2.3.4); such conditions often prevail in the industrial applications of membranes.

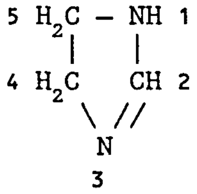
These model compounds were so chosen as to represent the functional group arrangements found in the thin, crosslinked PVAM/SCl membrane desalting barrier.

A model compound can be visualized as a single molecule representing a functional repeat unit of a polymer chain. Model compounds contain essential structural features of the polymer without the complexities associated with macromolecules such as e.g. insolubility. Because of their having lower molecular masses and a wide range of solubilities it was simpler to analyze them by standard techniques, e.g. nuclear magnetic resonance, mass spectroscopy and high-pressure liquid chromatography. Model compounds have been used to investigate particular aspects of polymeric structures including sterochemistry of polymers and of reaction products which are difficult or impossible to evaluate at the polymeric level$^{(202)}$. The use of the model compounds as predictors of chlorine sensitivity of polyamide RO membranes has been mentioned in Section 2.3.4.6.

The monomeric, model compound form of homopolymeric poly-2-vinylimidazoline is 2-ethylimidazoline.

The numbering system commonly used for imidazoles is extended to the imidazolines, which are dihydroimidazoles, as shown below:

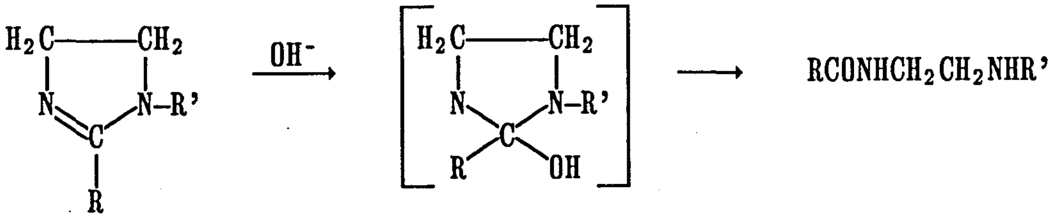




Although the imidazolines have been known since the late 1890s, few investigations on the reactions which they may undergo have been reported. Because of the envisaged relevance which the hydrolysis and benzoylation reactions of 2-imidazolines could have on the eventual chemical composition of a thin-film membrane desalting barrier prepared with a PVAM precursor, the literature pertaining to these reactions was investigated and some findings are reported in Sections 2.5.2.2 and 2.5.2.3.

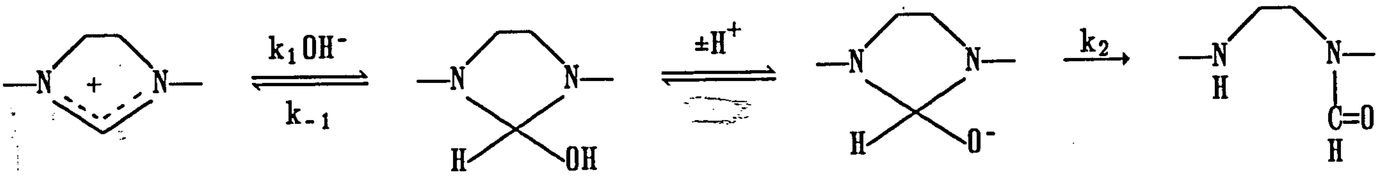
2.5.2.2 **Hydrolysis reactions**

2-Imidazolines are cyclic amidines and hence are susceptible to hydrolysis(203). The ease of hydrolysis depends on their molecular mass as well as on the degree of substitution of the nitrogen atoms(204). 2-Methylimidazoline is hygroscopic and hydrolyses easily in warm water to the monoacyl derivative of ethylenediamine(205), N-acetylethylenediamine. Aspinall(206) reports complete hydrolysis of a 10% solution of 2-methylimidazoline within 10 minutes. 2-Phenyl-imidazoline hydrolyses more slowly with the reaction being complete only after the reactants have been boiled for one hour in 50% ethanol. According to Harnsberger and Riebsomer(207) the course of the hydrolysis reaction may be formulated as follows:



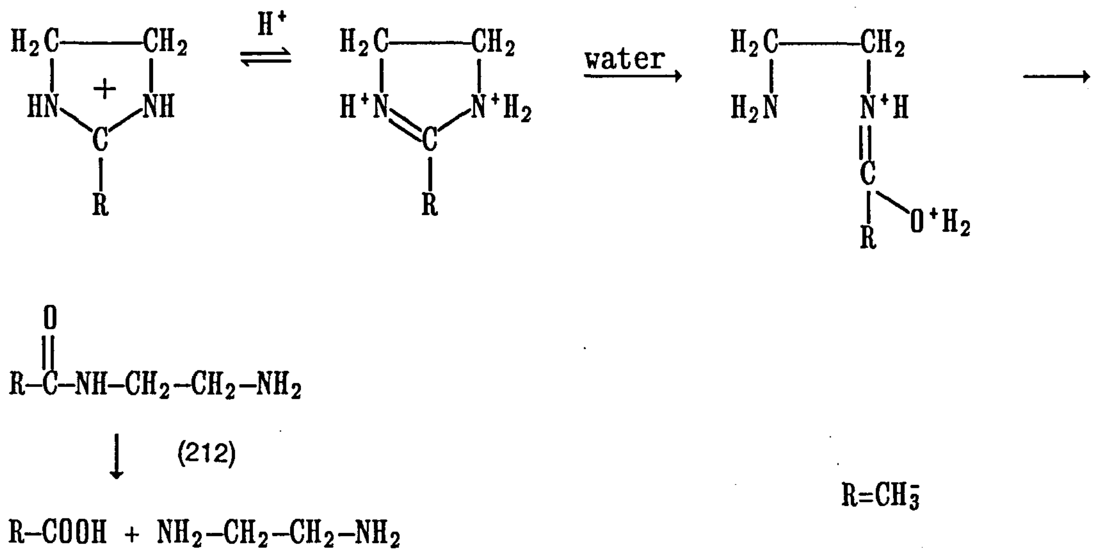
Kinetics of the hydrolysis of lysidine in alkaline solution have been interpreted in terms of the rate determining decomposition of the intermediate resulting from the addition of a hydroxide ion to lysidine.

Direct evidence of the intermediacy of a 2-hydroxy-imidazoline in the hydrolysis reaction was found by Robinson(208). The following mechanism was proposed for the base-catalyzed hydrolysis reaction of 1,3-diphenyl-imidazoline (DPIC):



A tetrahedral addition intermediate is formed by the attack of a hydroxide ion on DPIC, which accumulates during the initial rapid phase of the reaction. The intermediate then decomposes to form the amide product during the subsequent slower reaction.

Miescher *et al.*(209) reported that imidazoline salts were generally resistant to acid-catalyzed hydrolysis. Acid-catalyzed hydrolysis under severe conditions could, however, bring about complete cleavage of the imidazoline ring to the free acid and ethylenediamine. The mechanism of this reaction has been proposed by Limatibul and Watson(210) an Haake and Watson(211).



A lysidinium ion is protonated to form a strongly acidic dication which undergoes a rate-determining nucleofilic attack by water, at position 2, to form a tetrahedral addition intermediate which decomposes to the hydrolysis products.

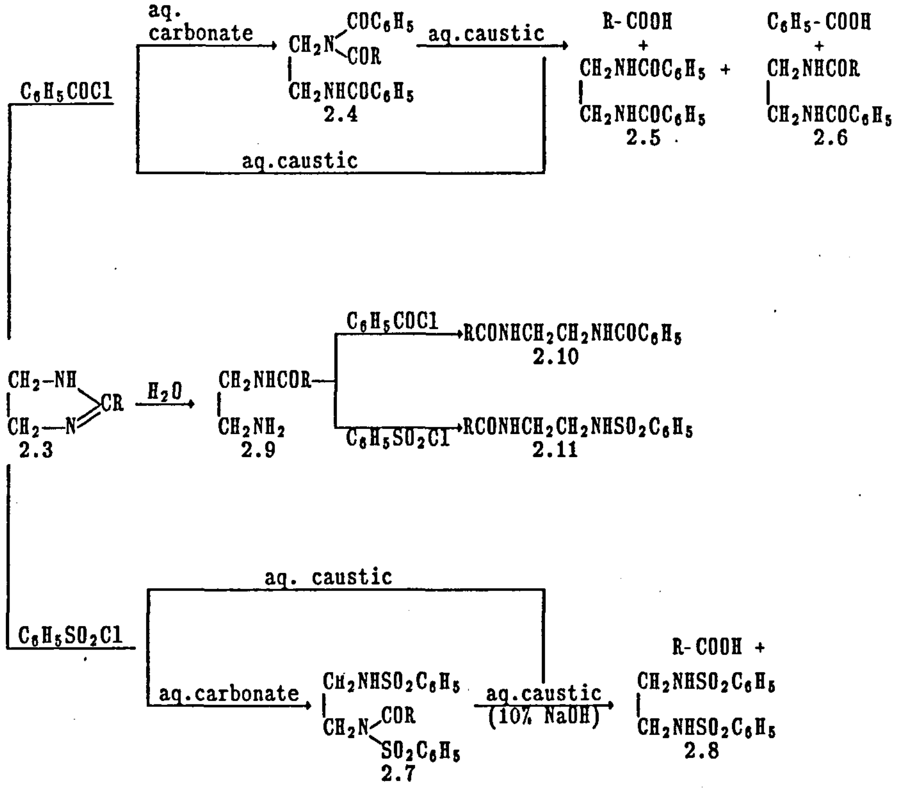
Aspinall(206) reports that the monoacyl derivatives, resulting from the hydrolysis of 2-imidazolines, can undergo benzoylation to form diacyl compounds. This reaction will be described later in Section 2.5.2.3.

2.5.2.3 Benzoylation

A number of workers has reported the opening of the 2-imidazoline ring under various hydrolytic conditions including those which may prevail during benzoylation with carboxylic acid chlorides and benzenesulphonation with benzene sulphonyl chlorides. This is described below.

In the late 1890s Ladenberg(213) described the benzoylation of imidazolines which is accompanied by ring-cleavage. 2-Methylimidazoline reacted with benzoyl chloride in a carbonate solution to yield 1-benzoyl-2-acetyl-2-benzoylethylenediamine which, when treated with sodium hydroxide, then decomposed into dibenzoylethylenediamine and acetic acid.

After a most extensive study into the reactions of 2-methylimidazoline and 2-phenyl-imidazoline with benzoyl chloride and benzenesulphonyl chloride, Aspinall(206) reported that the reactions presented in Figure 2.5. take place.



$R = -CH_3$

FIGURE 2.5: REACTIONS OF 2-METHYLIMIDAZOLINE WITH BENZOYL CHLORIDE AND BENZENESULPHONYL CHLORIDE

Analysis of the products of the reaction of benzoyl chloride and 2-substituted-2-imidazolines revealed the presence of additional hydrolysis products to those reported by Ladenberg(213). Aspinall(206) reported that ring-opening, in the presence of a sodium carbonate solution, resulted in the formation of the triacyl diamine 2.4 which decomposed in the presence of aqueous potassium hyroxide to form a mixture of the diacetyl derivatives of ethylenediamine 2.5 and 2.6 in the ratio of 55:45. Some of each of the two groups attached to the diacylated nitrogen atom were expelled, rather than only the one originating from the 2-position of the 2-imidazoline ring being eliminated.

Ring-opening reactions with benzenesulphonyl chloride were found to be similar except that, as expected, hydrolysis of the monoacyldisulphonyl diamine (2.7) with caustic (10% NaOH) eliminated exclusively the substituent originating from the 2-position of the 2-imidazoline ring. This was due to the much greater stability towards alkali of the N-SO_2-R group over the N-CO-R group(206,214).

Imidazolines react with acid chlorides in caustic media to form the same products in the same yields as result from the stepwise treatment of the imidazolines in carbonate followed by caustic(206).

Zienty(215) was the first to isolate an acyl derivative of an imidazoline in which the ring structure was preserved, as shown in Figure 2.6.

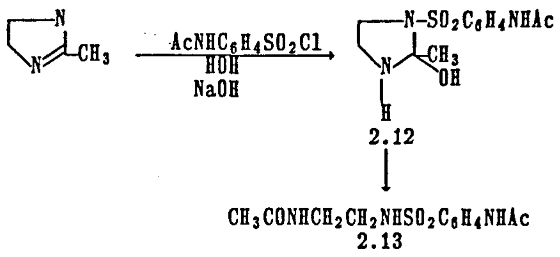


FIGURE 2.6: REACTION OF 2-METHYLIMIDAZOLINE WITH N-ACETYLSULPHANILYL CHLORIDE

The reaction of 2-methylimidazoline with N-acetylsulphanilyl chloride yielded a quantity of the imidazolidinol (2.12) which was isolated although it hydrolyses easily to the diacetyl derivative of ethylenediamine (2.13). The formation of the hydroxy acylated species is not unknown, since Gerngross(216) had observed that the treatment of 1-benzoyl-benzimidazole with benzoyl chloride in anhydrous medium, followed by addition of water, resulted in the formation of 1,3-dibenzoyl-benzimidazolol. See Figure 2.7.

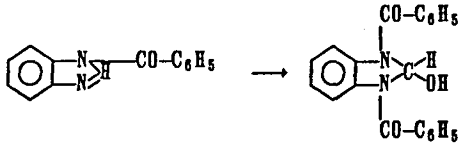


FIGURE 2.7: FORMATION OF 1,3-DIBENZOYL-BENZIMIDAZOLOL

The reaction of 2-methylimidazoline with p-nitrobenzenesulphonyl chloride in benzene, followed by quenching in water, is shown in Figure 2.8.

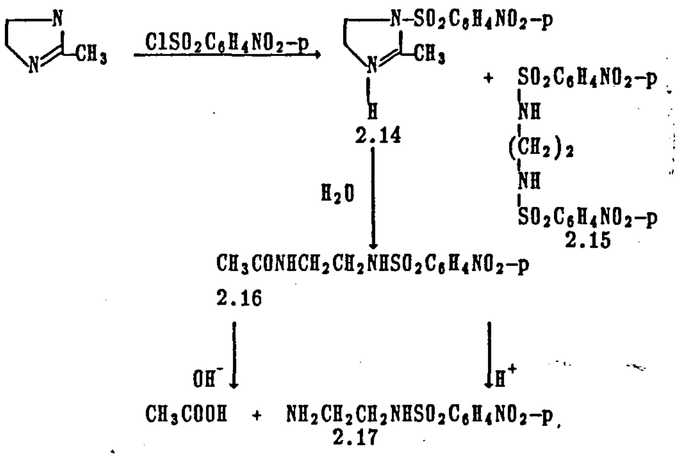


FIGURE 2.8: REACTION OF 2-METHYLIMIDAZOLINE WITH p-NITROBENZENESULPHONYL CHLORIDE

This reaction produced the ring-closed monoacyl derivative of 1-(p-nitrobenzenesulphonyl)-2-methylimidazoline (2.14) as major product. Some N,N'-di(p-nitrobenzenesulphonyl)-ethylenediamine (2.15) was also isolated. In the presence of aqueous acid, the ring-closed product (2.14) hydrolysed readily to N-acetyl-N'-(p-nitrobenzenesulphonyl)-ethylenediamine (2.16). Hydrolysis of this compound (2.16) in both acidic and basic media yielded the monoacyl aromatic sulphonyl derivative of ethylenediamine (2.17). A reaction similar to this was reported by Amundsen and Longley(217). N-Benzenesulphonylethylenediamine was prepared by heating N-benzenesulphonyl-N'-acetylethylenediamine with aqueous HCl(217,218).

Miescher *et al.*(209) also investigated the reactivity of the imidazolines, including the acetylation, diacetylation, benzoylation and hydrolysis reactions. The reaction of 2-(diphenyl-aminomethyl)-imidazoline with benzoyl chloride in the Schotten-Baumann reaction as described by Miescher *et al.*(208) is summarized here in Figure 2.9.

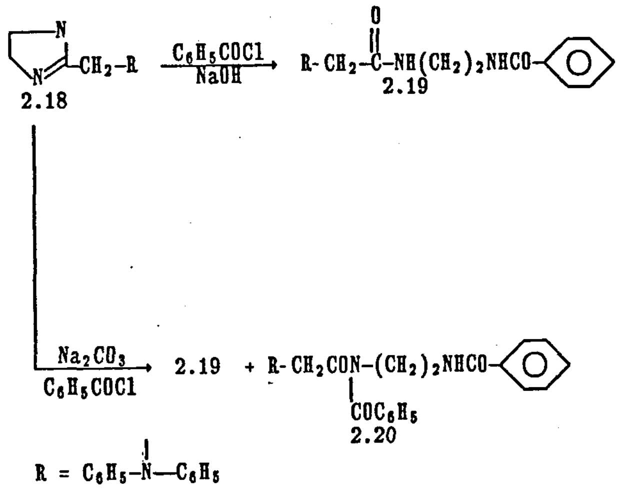
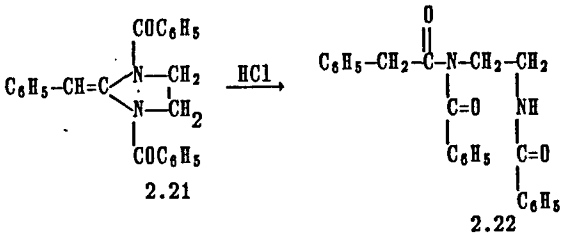


FIGURE 2.9: REACTION OF 2-(DIPHENYL-AMINOMETHYL)-IMIDAZOLINE WITH BENZOYL CHLORIDE

Upon reaction of 2-benzoyl-imidazoline and benzoyl chloride in benzene, under similar conditions, similar products of the mono- and di-benzoyl species were formed(209).

The reaction between 2-benzoyl-imidazoline and benzoyl chloride (mol ratio 1:1) in dry benzene yielded the hydrochloride of 2-benzoyl-imidazoline as an insoluble product. After exposure of the benzene-soluble fraction to the air, the mono- and dibenzoyl derivatives were identified. A ring-closed derivative was isolated upon reaction of 2-benzoyl-imidazoline and benzoyl chloride (mol ratio 2:1) in benzene medium, followed by stirring with water. This was formulated, analogous to the corresponding diacetyl compound, as 1,3 dibenzoyl-2-benzylidene-imidazolidine (2.21). This compound proved to be stable to boiling water and cold acid. Upon reaction of the compound with warm dilute acid, the ring cleaved with formation of the dibenzoyl compound (2.22), as shown:



2.21 2.22

According to Aspinall(206), although it cannot be stated with certainty whether the reactions of imidazolines with benzoyl chloride and benzenesulphonyl chloride in alkaline solution proceed as do those of imidazoles, the similarities observed in the reactions and products heavily favour that belief. It is claimed that the diacylated diamines (e.g. 2.5, 2.6 and 2.8) cannot arise from hydrolysis of the imidazoline during acylation, because the cyclic compound, although readily hydrolysed by hot water, is quite stable under the conditions of benzoylation. Furthermore, the triacyl diamines (e.g. 2.4 and 2.7) which are shown to be intermediates in the formation of diacyl diamines, cannot be formed by simple Schotten-Baumann reaction with monoacetylethylenediamine (2.9) but must arise from some more complex reaction of benzoyl chloride with the original cyclic compound.

Aspinall(206) reported that it is generally agreed that the stability towards acylating agents increases in the order imidazoles, benzimidazoles and naphthimidazoles (i.e. acylation of the secondary nitrogen rather than ring-fission is more likely to occur in that order); and that the tendency of the medium to favour cleavage of the ring rather than the acylation reaction increases in the order benzene, pyridine, aqueous carbonate and aqueous caustic. Hence he claims that imidazoles are successfully benzoylated in benzene on the secondary nitrogen, when one mole of imidazole is used to absorb the HCl formed and any other technique of acylation results in ring-fission(206,216).

As can be seen from Figure 2.5, the hydrolysis product of 2-methylimidazoline, N-acetylethylenediamine (2.9), could be converted into N-acetyl-N′-benzoylethylenediamine (2.10) and N-acetyl-N′-benzenesulphonylethylenediamine (2.11) upon reaction with one equivalent of benzoyl chloride and benzenesulphonyl chloride respectively. These reactions proceed quantitatively.

2.5.3 MODEL COMPOUNDS OF A POLY-2-VINYLIMIDAZOLINE / 3-CHLOROSULPHONYLBENZOYL CHLORIDE MEMBRANE

The structure of a PVAM/SCl membrane was at first thought to be predominantly in the 2-imidazoline ring form. Because of dual functionality imported to the membrane structure by both carboxyl- and sulphonyl-groups of the crosslinking agents, SCl, two model compounds would represent this membrane structure, namely:

1-Benzoyl-2-ethylimidazoline, abbreviated to MC 1 and
1-Benzenesulphonyl-2-ethylimidazoline, abbreviated to MC 2.

These are shown in Figure 2.10.

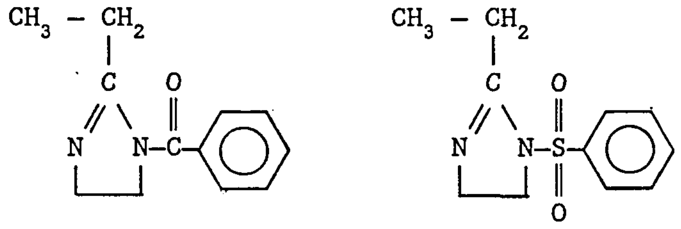
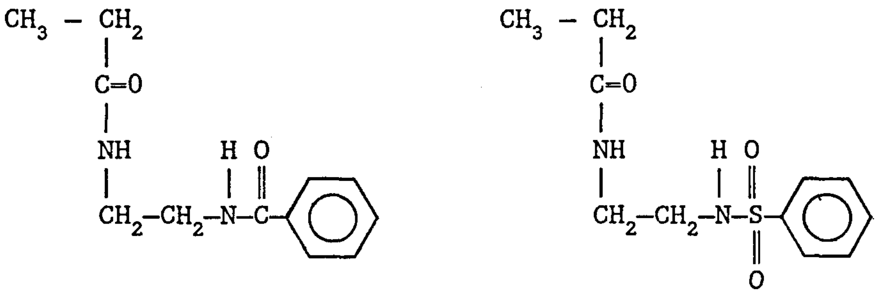


FIGURE 2.10: CYCLIC 2-IMIDAZOLINE MODEL COMPOUNDS OF THE PVAM/SCL UTF MEMBRANE

The literature relating to 2-imidazoline type structures reveals that the imidazoline ring hydrolyses and cleaves with ease (see Section 2.5.2.2) to form a linear amide structure with primary amine functionality which is also expected to react with the SCl crosslinking agent, through its terminal primary amine group, in a condensation reaction. This was supported by findings of Aspinall(206). Hence, the following two structures were additional model compounds, representing the condensation products of the hydrolysed repeat units in the PVAM membrane precursor (PVAM-Hy) and the SCl crosslinking agent.

1-Benzoyl-2-propionylethylenediamine, abbreviated to HMC 1.
1-Benzenesulphonyl-2-propionylethylenediamine, abbreviated to HMC 2.

These are shown in Figure 2.11:



HMC 1 HMC 2

FIGURE 2.11: LINEAR AMIDE MODEL COMPOUNDS OF THE PVAM/SCL UTF MEMBRANE

These structures may also be formed upon hydrolysis of the benzoylated imidazolines as described in the theoretical Section 2.5.2.

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CHAPTER 3

EQUIPMENT AND EXPERIMENTAL METHODS

3.1 EQUIPMENT

3.1.1 ANALYTICAL

Routine ^{1}H nmr spectra of medium resolution were recorded with a Hitachi Perkin-Elmer R24 (60 MHz) spectrometer.

High resolution ^{13}C nmr spectra were recorded with a Varian FT 80 (80 MHz) spectrometer and ^{1}H nmr spectra were recorded with either a Varian FT 80 (80 HMz) spectrometer or a Varian HA-60IL spectrometer.

All mass spectra were recorded and accurate mass determinations made with a Varian MAT 311 A spectrometer.

Combustion analyses were carried out by the Microanalytical Section, Chemistry Department, University of Cape Town.

Infrared spectra were recorded on a Pye Unicam SP 3/200 spectrometer as either KBr discs or as thin films between standard NaCl windows.

Melting-points were determined on a Differential Scanning Calorimeter: 910 DSC module of a du Pont 9900 Thermal Analyser Section.

High Pressure Liquid Chromatography (HPLC) analyses were done with the following equipment and under the conditions listed:

Equipment : Waters Associates Type 6000 pump
: Waters Associates Type M45 injector
: Waters Associates Type 450 UV/vis detector
: Waters Associates Type 730 Data Module
Column : Waters Associates Type I Porasil Column 300 mm long
Solvent : Methanol/water (55/45), filtered daily prior to use through a Millipore Type HA filter of 0,45 μm porosity under pressure.
Flow rate : 60 cm^3 h^{-1}
Detector Wavelength : 254 nm
Chart speed : 0,3 mh^{-1}
Injection volume : 0,025 cm^3

Thin-layer chromatography (TLC) analyses were carried out on 0,2 mm silica gel plates (Merck Silica 60 F 254) using 1-butanol as mobile phase.

3.1.2 UTF RO MEMBRANE FABRICATION

3.1.2.1 Flat-sheet membranes

No elaborate equipment was required for the manual fabrication of batches of UTF RO membranes (approximately 15 x 30 cm in size) as described in Section 3.4.2.1. The polysulphone substrate used, however, had been supplied after semi-automated fabrication on a continuous casting machine. This machine had been developed at the Institute for Polymer Science, and is described elsewhere(1).

3.1.2.2 Tubular Membranes

The tubular polysulphone substrate was fabricated on tubular-membrane production equipment developed at the Institute for Polymer Science(2). The process involved the simultaneous fabrication of a support fabric tube and extrusion of a thin layer of the substrate-membrane solution onto the inside of the support tube. Fabrication of tubular UTF RO membranes was the subject of a parallel study at the Institute for Polymer Science, involving the use of speciality equipment, and is described in detail by Jacobs(3).

3.1.3 UTF RO MEMBRANE EVALUATION

The equipment used for membrane evaluation was specially designed and consisted essentially of a pressurized closed-loop system connected to the test section, and cells within which the membranes were individually housed. The equipment is shown schematically in Figure 3.1. The test section was designed to house either flat-sheet membranes (see 3.1.3.1 and Figure 3.2) or tubular membranes (see 3.1.3.2). Test facilities for the two types of membrane were similar, except that no allowance was made for filtration of the feed water in the tubular system.

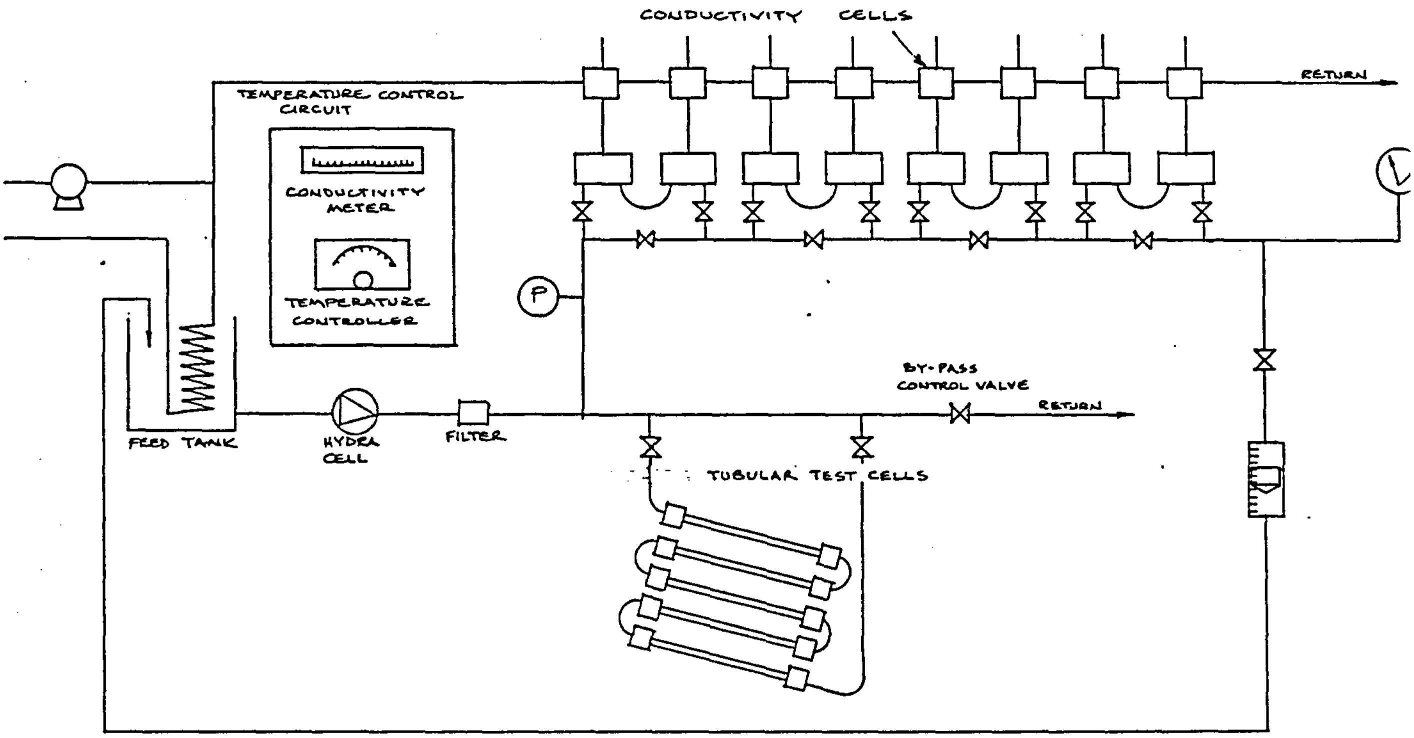

FIGURE 3.1: HIGH-PRESSURE TEST LOOP FOR UTF MEMBRANE EVALUATION(3)

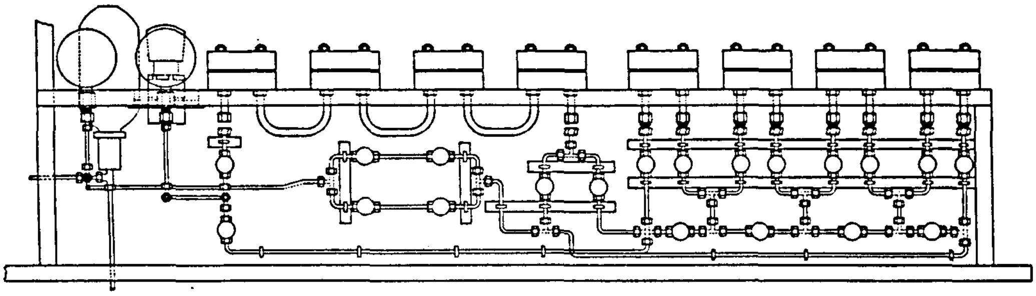

FIGURE 3.2: SCHEMATIC DIAGRAM OF TYPICAL FLAT-SHEET MEMBRANE TEST CELLS[4]

3.1.3.1 Flat-sheet test cells

These were constructed from 316 stainless steel. A schematic diagram of flat-sheet test cells, similar to those used in this study, has been presented by Pienaar[4] and is shown in Figure 3.2. The test rack could house eight oval-shaped flat-sheet membranes each 2 206,8 mm^2 in area.

3.1.3.2 Tubular test cells

These were designed and described by Jacobs [1,3]. The test rack could house twelve tubular membranes each 0,4 or 1 metre long.

3.2 PREPARATION OF MONOMERIC CROSSLINKING AGENTS

3.2.1 ISOPHTHALOYL CHLORIDE (IPC)

IPC is commercially available and was recrystallized from petroleum ether (b.p. 60-80°C) then thoroughly dried, prior to use.

3.2.2 3-CHLOROSULPHONYLBENZOYL CHLORIDE (SCL)

Step 1: Sodium salt preparation

Benzoic acid was sulphonated by the method of Smiles and Harrison[5], to yield the monosodium salt of 3-sulphonylbenzoic acid. Fuming sulphuric acid containing 30% SO_3 (1008 g = 520 cm^3; 10,2 mole) and benzoic acid (400 g; 3,3 mole) were carefully heated, under reflux cooling, to 210-240°C for 6 hours. After cooling, the crude reaction product was poured into ice water (1000 cm^3). When cool, it was filtered and the white paste-like product was recrystallized from a saturated sodium chloride solution (400 g NaCl in 1000 cm^3 water). A mass of cream-coloured crystals (717 g) soon appeared and these were filtered off and dried in a vacuum oven at 70°C to constant weight to yield the sodium salt of 3-sulphobenzoic acid (97%).

Step 2: Conversion to acid chloride

The dry sodium salt of 3-sulphobenzoic acid (300 g: 1,34 mole) was heated together with thionyl chloride (1696 g = 1060 cm^3; 14,64 mole) and N,N-dimethylformamide (36 cm^3), as catalyst, to 80°C for 6 hours in a well-ventilated hood(6). After cooling, the by-product of NaCl was filtered off and then extracted with ether. This extract was combined with the crude reaction product. The ether and excess thionyl chloride reagent were then removed by distillation before the 3-chlorosulphonylbenzoyl chloride product was distilled under high vacuum. The fraction boiling at approximately 146-150°C/5 mm Hg was collected as a dense, viscous yellowish liquid. Typical yields ranged from about 493 to 559 g (73-83%, based on the quantity of benzoic acid starting material). This product was stored in a tighly sealed container, under nitrogen, at 4°C and was redistilled just prior to use to ensure the absence of any hydrolysed product which may have formed during storage. Structure was confirmed by mass spectroscopy. (m/z, relative intensity) 238 ($M^{+\cdot}$, 0,26), 242 (0,08), 240 (0,22), 205 (47), 203 (100), 177 (3), 175 (8), 141 (7), 139 (20), 105 (23), 76 (58).

3.2.3 1,3-BENZENEDISULPHONYL CHLORIDE (2S)

This product, which was commercially available, was recrystallized from benzene/petroleum ether(7) then thoroughly dried prior to use.

3.2.4 3,5-DICHLOROSULPHONYLBENZOYL CHLORIDE (CL2S)

Step 1: Sodium salt preparation(8)

Benzoic acid (360 g; 3 mole) was heated under reflux cooling with fuming sulphuric acid (1820 g = 938 cm^3; 18,6 mole) for 9 hours at 250°C. The cooled reaction product was then poured into stirred ice water (5400 cm^3) containing sodium chloride (1100 g). The thick yellow precipitate of the sodium salt was filtered off and dried under reduced pressure at 50°C to constant weight, to yield the desired product. A typical yield was 575 g (59%).

Step 2: Conversion to acid chloride

Method 1: with thionyl chloride

The dry sodium salt of 3,5-disulphobenzoic acid (575 g; 1,74 mol) was mixed with thionyl chloride (2053 g; 17,4 mole) and a catalytic quantity of N,N-dimethylformamide (115 cm^3). This mixture was boiled under reflux for 6 hours and then allowed to cool. The by-product sodium chloride was carefully filtered off and the excess thionyl chloride removed by distillation. The remaining crude reaction product was then recrystallized from benzene to yield large white crystals (254 g; 43,5%). Structure was confirmed by elemental analysis. Found C, 25,0; H, 0,95. Calculated for $C_7H_3Cl_3O_5S_2$: C, 25,0; H, 0,89. The mass spectrum was recorded. (m/z, relative intensity) 336 ($M^{+\cdot}$; 0,18), 340 (0,07), 338 (0,18), 305 (21), 303 (89), 301 (100), 241 (2), 239 (9), 237 (12), 204 (7), 202 (18), 135 (4), 133 (10), 103 (6), 76 (7), 75 (96), 74 (32).

Method 2: with phosphorus pentachloride

The dried sodium salt of 3,5-disulphobenzoic acid (200 g; 0,6 mol) and phosphorus pentachloride (385 g; 1,87 mol) were heated together to 120°C and then allowed to reflux for 22 hours. After cooling, the by-product of phosphorus oxychloride was removed by rotary evaporation under reduced pressure. Recrystallization of the crude product from benzene afforded the desired product (78 g; 35%) as thick prisms. Structure was confirmed by elemental analysis. Found C, 25,3; H, 1,0. Calculated for $C_7H_3Cl_3O_5S_2$: C, 25,0; H,0,89.

3.3 PREPARATION OF POLYMERS, THEIR REACTIONS AND CHARACTERIZATION

3.3.1 PREPARATION OF POLYACRYLONITRILE (PAN)

Polyacrylonitrile (PAN) was prepared for use as the starting material from which poly-2-vinylimidazoline (PVAM) was to be synthesized by amine modification of the nitrile repeat unit.

3.3.1.1 Purification of acrylonitrile monomer

Acrylonitrile (500 cm^3; Merck product No. 800834) was washed twice with 500 cm^3 of sodium hydroxide solution (4% mass) to remove the hydroquinone-monomethylether stabilizer, filtered, separated, then dried over calcium chloride (50 g). The aqueous acrylonitrile wash-solution was kept as cool as possible with ice water, to minimize the amount of acrylonitrile that dissolved in the water layer.

3.3.1.2 Polymerization by solution method(9)

A solution of benzoyl peroxide (29,2 g; 0,17 mole) in DMF (430 cm^3) was dripped into a stirred solution (33% v/v) of acrylonitrile (344 g; 430 cm^3; 6,5 mole) in DMF solvent (1290 cm^3) under a nitrogen atmosphere. This mixture was allowed to react for 24 hours at 70°C under reflux cooling. The cooled PAN product was precipitated by pouring the crude reaction mixture in a thin stream into a four-fold volume of water which was adequately stirred. The fine suspension of yellowish brown flakes which formed, was filtered off, washed once with water and then spread out in open trays to dry, first in a well-ventilated hood-area at room temperature, and then in a vacuum oven at 40°C to constant weight. The structure of the dark brown PAN product was confirmed by ^{13}C nmr spectroscopy (see Table 4.2, Section 4.3.2.2).

This reaction was carried out a number of times and yields of between 310-330 g (90,1 - 95,9%) were obtained. Molecular masses ranged from 7 000 - 20 000, as determined by dilute-solution viscometry (see Section 3.3.5.1).

3.3.1.3 Polymerization by redox method

Acrylonitrile (4,0 g; 0,76 mole) was mixed with a volume (1,0 cm^3) of a cerium ammonium sulphate solution (0,1 molar) in sulphuric acid (20,0 cm^3; 0,5 molar). The reaction mixture was stirred for 10 minutes at room temperature (22°C) and the temperature was then gradually increased to 60° C. Methanol (12,0 cm^3) was slowly added, and stirring at 60°C continued for 3 hours. The white crystalline product was filtered off, washed with methanol and dried in a vacuum oven. The yield of white fluffy crystals was 1,26 g (31,5%). These had a molecular mass of 263 000 as determined by dilute-solution viscometry (see Section 3.3.5.1).

3.3.2 PREPARATION OF POLY-2-VINYLIMIDAZOLINE Polyvinylamidine (PVAM)

After preparation of PVAM on laboratory scale (50 g quantities) by the method of Hurwitz *et al.*(10), quantities were increased to batch preparation of about 500 g quantities per reaction sequence. The experimental procedure followed was as described here:

3.3.2.1 Apparatus

The apparatus used for synthesis of PVAM comprised: a 5-litre wide-neck reaction flask, with a strong magnetic stirrer bar. This was fitted into a 5-litre electric heating mantle on a magnetic stirrer box. The flange lid of the reaction flask had inlets for a thermometer, nitrogen gas inlet tube and coiled cooling condensor.

3.3.2.2 *Preparation of PVAM-OD by the oven-drying method*

Ethylenediamine (418,5 g = 465 cm^3; 6,98 mole) was added dropwise to a solution of PAN (170 g; 3,2 mole) in DMF (1700 cm^3) containing 0,5% thioacetamide (8,5 g) as catalyst. The mixture was heated under reflux for 6 hours at 110°C under a nitrogen atmosphere until evolution of ammonia had ceased. The product was isolated by precipitating the cooled mixture in a large excess of acetone (2 x 2500 cm^3) with effective stirring. After the mixture had been filtered, great care was taken not to expose the crude product for too long to water vapour which could make it become very tacky and extremely difficult to handle. The brown precipitate was transferred rapidly to a vacuum oven and dried for at least 12 hours, powdered, then dried further under vacuum at 40°C to constant mass. This product, termed PVAM-OD required storage in a tighly sealed container under nitrogen atmosphere. Numerous preparations were carried out and yields were about 250 g PVAM-OD (80%). Routine elemental analyses were carried out on each batch of PVAM-OD product. (Results are given in Table 4.3, Section 4.3.3.2.)

3.3.2.3 Preparation of PVAM-FD by the freeze-drying method

The reaction vessel, described in Section 3.3.2.1 was charged with PAN (300 g; 5,7 mole), 0,5% sulphur (15 g) as catalyst and ethylenediamine (1710 g = 1900 cm^3; 28,5 mole). This mixture was heated to 110°C for about 6 hours with stirring and reflux cooling and under a nitrogen atmosphere. After this time, and once the colour of the reaction mixture had turned from green to brown, the product was allowed to cool and then stored in a well-stoppered container until it could be dried. (Drying was done as soon as possible after the preparation.) PVAM was recovered by drying numerous small batches of crude product (about 70 cm^3 per 250 cm^3 flask) on a freeze-dryer until the crude viscous solution product became a light and an almost cream-coloured powder which came away from the walls of the drying flasks and could be pulverized. This product, termed PVAM-FD, appeared to be of finer texture and of lighter brown colour than PVAM-OD. It was also stored under nitrogen in tightly sealed containers. This preparation was carried out frequently and yields were about 540 g (99,4%).

Routine elemental analyses were carried out on early batches of the PVAM-FD product (as had been done of PVAM-OD). Results are given in Table 4.5, Section 4.3.4.2. Later, ^{13}C nmr spectroscopic analyses were carried out for each new batch of PVAM-FD synthesized. This data is presented and discussed in Section 4.3.4.3.

3.3.2.4 Preparation of PVAM-CFD by the purification of PVAM-FD

The typical procedure followed to extract excess ethylenediamine from PVAM-FD products and yield a "cleaner" product, termed PVAM-CFD, is described below:

A quantity (50 g) of PVAM-FD was added to a volume of dry acetone (150 cm^3) in an Erlenmeyer flask and stirred for 5-10 min at room temperature. (The neck of the flask was stoppered with a drying tube.) The mixture was filtered through a Buchner filter under slightly reduced pressure and the PVAM-FD recovered. The washing and filtering process were repeated three times, after which the product was dried overnight under reduced pressure in a vacuum oven at 30°C to yield PVAM-CFD. The relative percentages of ethylenediamine present in the PVAM-FD and PVAM-CFD product were determined by ^{13}C nmr spectroscopy (as described in Section 4.3.4.3c). PVAM-CFD was stored dry in a well-stoppered brown bottle.

3.3.3 PREPARATION OF AN AROMATIC PVAM (PVAM-AR)

Polyacrylonitrile (3 g; 0,06 mole; mol mass 1100) was dissolved in DMF (30 cm^3) and an amount of sulphur (0,15 g) added as catalyst. 1,3-Diaminobenzene (13 g; 0,12 mole) was dissolved in DMF (30 cm^3) and the mixture was slowly dripped into the stirred solution of PAN. The reaction mixture was boiled under reflux for 6 hours at 110°C, under nitrogen. After the reaction product had been cooled it was dried under reduced pressure in a vacuum oven and then on a freeze-dryer for a few days. The product remained tacky and had a black colour. The crude product was not water-soluble and could not be analysed by nmr spectroscopy because no suitable solvent could be found.

3.3.4 PREPARATION OF POLY-N-AMINOETHYLACRYLAMIDE
Hydrolysed PVAM (PVAM-HY)

An aqueous 10% solution of PVAM-FD (pH 10,9) was boiled gently overnight under reflux cooling. The hydrolysis product PVAM-Hy was isolated by removing most of the water by evaporation on a rotary evaporator at 50°C, and then allowing it to dry completely on a freeze-dryer. This entailed drying of several small quantities (about 40 cm^3) of the viscous concentrated polymer solution over periods of a few days. The PVAM-Hy product was isolated in a quantitative yield as a coarse brown powder and was characterized by ^{13}C nmr spectroscopy (see Figure 4.11). ^{13}C nmr (80 MHz, D_2O) δ 178,17 - 177,48; 44,05 - 42,88; 41,67; 40,39; 37,21 - 35,21.

3.3.4.1 Determination of the rate of hydrolysis of PVAM and formation of PVAM-Hy in aqueous medium

The course of the conversion of PVAM to PVAM-Hy was followed by ^{13}C nmr spectroscopy as described below. A solution (28%) of PVAM (120 mg) was made up in deuterated water (0,430 cm^3) in a 5 mm nmr tube. This was allowed to hydrolyse at 22°C. At frequent intervals of days, a ^{13}C nmr spectrum of the reaction product was recorded. As the hydrolysis reaction proceeded, the peak height of the 2-imidazoline (amidine) group (δ 172) decreased, with a corresponding increase in the peak height of the ring-opened linear amide group (δ 177) of the newly formed hydrolysis product. The changes in intensities of peak heights were measured and from these the relative percentages of the two different groups present in the reaction product could be calculated. Results are tabulated in Section 4.3.4.4. The rate constant was calculated as $k = 1{,}87 \times 10^{-7}\ sec^{-1}$, $t_{1/2} = 42{,}8$ days.

3.3.5 DETERMINATION OF MOLECULAR MASSES

3.3.5.1 Polyacrylonitrile (PAN)

The molecular mass of each batch of PAN was calculated after determination of the intrinsic viscosity and substitution in the Mark-Houwinck equation (see Section 4.3.2.2). K and a values of $33{,}5 \times 10^{-5}$ and 0,72 respectively, were used(11). The intrinsic viscosity was determined by dilute-solution viscometry in DMF solvent using an Ubbelohde viscometer. For this, dry PAN samples of about 1,000 g mass were weighed out accurately, dissolved and made up volumetrically to 100 cm^3 with clean DMF. This solution was filtered, if necessary, to remove any dust particles which may have blocked the capillary of the viscometer. Exactly 20 cm^3 of the PAN polymer solution was transferred by pipette to a clean dry Ubbelohde dilution-viscometer, maintained at 30°C in a water bath. Temperature was controlled by means of a heater and circulator. After time had been allowed for temperature equilibrate, the efflux time of the solution was determined repeatedly until three reliable readings were obtained. The initial 1% polymer solution was then precisely diluted by addition of an equal volume of DMF solvent, mixed thoroughly and the temperature again allowed to equilibrate before the efflux time of this new dilution, was determined. The procedure for dilution, temperature equilibration and efflux time determination was carefully repeated for 3-4 dilutions. After thorough rinsing of the viscometer, the efflux time for the pure solvent DMF was then determined.

The intrinsic viscosity of the PAN was calculated, according to the procedure as described by McCaffery(12) (see also Section 4.3.2.2), and the molecular mass of PAN determined.

3.3.5.2 Poly-2-vinylimidazoline (PVAM)

The above method for determining molecular mass could not be used for the determination of the molecular mass of PVAM as no recorded K and a values exist for this uncommon polymer. The molecular mass of a PVAM homopolymer is, however, theoretically directly related to that of the PAN reagent from which it is prepared. A pure PVAM product, resulting from the reaction between PAN and ethylenediamine would have a molecular mass 1,8 times greater than that of the PAN reagent(10), assuming that no degradation took place during synthesis. In all batches of PVAM prepared and analysed, hydrolysis was found to have taken place and this relationship would therefore not give an accurate molecular mass for PVAM.

3.4 UTF RO MEMBRANE FABRICATION

3.4.1 SUBSTRATE UF MEMBRANES

Irrespective of their geometry, these membranes are typically made by:

(a) preparation of a casting solution of a polysulphone material in a suitable solvent (e.g. DMF);
(b) application of the casting solution to support fabric and drawing out;
(c) immersion of the coated support into an aqueous medium in a smooth motion to precipitate the substrate membrane by phase inversion; and then
(d) washing with fresh water to remove any traces of solvent.

Wet storage is necessary to prevent shrinkage and deterioration. The top surface (air-side) was used as the support surface for membrane formation.

3.4.1.1 **Flat-sheet membranes**

Early UTF membranes were fabricated on hand-cast polysulphone substrates. Poly-bisphenol A sulphone (PS) of grades Udel 1700 and 3500, supplied by Union Carbide, were used. A solution of polysulphone in DMF (typically about 13% m/m) was prepared by slow agitation of the mixture for a few days. If the solution became cloudy, it was gently heated to about 80°C, to drive off any moisture present and until clarity was restored.

A casting base-plate was prepared by affixing a length of non-woven fabric (eg. Villedon FO 2406) to a clean glass plate, approximately 15 cm x 30 cm in size. A quantity (about 20 cm^3) of polysulphone solution was poured over the one end of the fabric and then spread out over the length of the plate by means of a Gardiner applicator knife, using an 200 μm knife gap.

The plate plus deposited solution was then carefully immersed in a bath of distilled water, to effect precipitation of the polysulphone onto the fabric backing. This membrane was leached in running water for at least 2 hours prior to use, to remove any traces of solvent. The polysulphone-coated porous backing was then removed from the glass plate and stored wet. Prior to use, polysulphone substrates were checked for the presence of pinholes on a light table. Areas with many pinholes were not suitable for use and were discarded.

More consistent substrate membranes were later fabricated on the continuous casting machine, as mentioned in Section 3.1.2.1. It was these substrates which were used for the fabrication of the UTF membranes in this study. Briefly, the process of continuous casting involved the application of a polysulphone solution to a fabric support which was then taken up on drum rollers, with leaching effected in a large waterbath. A detailed description of the fabrication process has been given elsewhere(1).

3.4.1.2 **Tubular membranes**

During a parallel study carried out at the Institute for Polymer Science, tubular substrate membranes for use in UTF RO-membrane fabrication were developed(1,3). These were fabricated under continuous casting conditions on specially designed equipment(2), referred to in Section 3.1.2.2. Numerous "different" substrates were fabricated by changing the casting solution composition and casting conditions. These were coded and are on file at the Institute for Polymer Science, University of Stellenbosch. A polyethersulphone substrate (Victrex 4800 CT, ICI) and Villedon support fabric (FO 2406; Carl Freudenberg, BRD) were the most commonly used components.

3.4.2 UTF PERMSELECTIVE BARRIERS

Throughout this study, the method of interfacial polycondensation was used to form the ultrathin desalting layer on the surface of the substrate membrane. The process involved coating of the substrate membrane with a reactive polymer, and then applying a solution of a suitable crosslinking agent to effect insolubilization of the polymer by a crosslinking reaction; this was followed by thermal curing of the polymer. The steps used in the formation of UTF RO membranes and the variables involved in the process have been mentioned in Section 2.3.2. It is known that even slight changes in membrane fabrication conditions may affect the RO performance of UTF membranes. The basic procedure employed in fabrication of UTF RO membranes is described in Section 3.4.2.1.

3.4.2.1 Flat-sheet membranes

These were fabricated manually by the dip-coating method. One large polysulphone substrate membrane sheet (minimum size 15 cm x 22 cm) was used per fabrication; from this, four smaller membranes could be cut out to fit the flat-sheet test-rig cells for RO performance testing.

The following typical procedure was followed for the manual fabrication of the UTF membranes and include the following steps:

(1) A suitable polysulphone substrate (hereafter abbreviated to PS) was cut to suitable size to enable it to fit the dip baths and be large enough to permit four membranes to be cut from it for evaluation;

(2) The aqueous amine precursor solution (e.g. 3% m/m) was freshly prepared and filtered if necessary;

(3) The organic solution of crosslinking agent in dry hexane (e.g. 1% m/m) was freshly prepared and filtered if necessary;

(4) The PS substrate membrane was immersed in the dip-bath containing the aqueous precursor solution, for a predetermined time (e.g. 2 min), removed and then held in a vertical position for a predetermined time (2 min) to enable it to drain;

(5) The coated PS was then immersed in a dip-bath containing the organic crosslinking agent solution for a predetermined time (e.g. 5 min), removed, then held in a vertical position for a predetermined time (2 min) to allow it to drain;

(6) The UTF membrane was heat-cured in an air-oven pre-set at a certain temperature (e.g. 100°C) for a certain time period (e.g. 10 min), and then removed;

(7) After the membrane had cooled, individual membranes were cut to size from it and mounted on the test rigs for testing as soon as possible after fabrication of the membrane. Membranes could be stored in a water bath if necessary, until tested for RO performance.

Details of conditions of fabrication of the flat-sheet membranes described in this study are presented in Section 4.4.2, together with their RO performance results.

3.4.2.2 Tubular Membranes

Tubular UTF membranes could be made by either the dip-coating or fill-coating techniques with *equipment developed and described by* Jacobs(3). *The basic steps as described for flat-sheet* membrane fabrication (Steps 1 to 6, Section 3.4.2.1) apply to the fabrication of tubular membranes. The tubular UTF membranes described in this study were fabricated by the manual dip-coating of 1,2 m-long tubes. Membranes were coated in 65 mm-diameter glass tanks, into which seven tubes fitted snugly. The minimum volume of solution required was 800 cm^3. The membranes were cured in either a horizontal radiation oven or in a vertical updraft oven. The vertical-oven method was preferred. Details of membrane fabrication conditions of the tubular UTF membranes described in this study are presented in Section 4.4.4, together with their RO performance results. (Heat-curing of UTF tubular membranes was generally done at lower temperature and for shorter times then was done for UTF flat-sheet membranes.)

3.5 UTF RO MEMBRANE TESTING

3.5.1 CONDITIONS

RO membranes were routinely tested for their salt rejection and water-permeability capabilities. The membrane permeability coefficient, the A^2/B value(13) was used when reporting results for tubular membranes, to compare the RO performances of membranes with different salt rejections and water permeabilities(3). The standard conditions employed during testing of the two forms of membranes were:

UTF flat-sheet membranes

Operating pressure	4,1 or 2 MPa
Feed-water temperature	25°C
Feed-solution composition (NaCl in distilled water)	5000 or 2000 mg/l
Test time	>24 h
pH	6,4 - 6,8

UTF tubular membranes

Operating pressure	2 MPa
Linear flow velocity	1,0 m/s
Feed-water temperature	20°C
Feed-solution composition (NaCl in distilled water)	2000 mg/l
Test time	>18 h
pH	6,4 - 6,8

3.5.2 MEASUREMENT OF SALT REJECTION

The salt rejection of an RO membrane is determined by the difference between the conductivity of the feed solution (C_c) and that of the permeate (P_c), expressed as a percentage of the former. Salt rejection [R%] = $(1 - P_c/C_c)$ 100%.

3.5.2.1 Flat-sheet membranes

Radiometer conductivity cells (CDC 329) were connected directly to the permeate outlet of each test cell. Water of a controlled temperature of 25°C was passed through the outer jacket of the conductivity cell in order that all conductivity readings would be made at that temperature. The conductivity cells were in turn connected to a Radiometer CDM 83C conductivity meter so that the measurements of the conductivity of the permeate from each cell could be read automatically. The conductivity of the concentrated feed solution was measured manually in a Radiometer flow-through cell at 25°C.

3.5.2.2 Tubular Membranes

A radiometer flow-through conductivity cell connected to a Radiometer CDC 83 conductivity meter was used to test the permeate conductivity of each of these membranes. The test procedure differed from that followed for flat-sheet membranes in that it was not automated.

3.5.3 MEASUREMENT OF WATER PERMEABILITY (FLUX)

Water permeability of a membrane is expressed as the volume of the permeate through a unit area of membrane in a given time. Membrane flux may be expressed as: litres per square metre per day, abbreviated to lmd.

3.5.3.1 Flat-sheet membranes

In the determination of the flux capability of a membrane, a stopwatch is used to measure the time period (in seconds) within which a given volume (e.g. 10 cm^3) is filled with permeate. This flow rate is then divided into a precalculated membrane cell factor (33 272 for a 10 cm^3 volume here) to arrive at the membrane flux value (in lmd). (This membrane cell factor incorporates the membrane area and includes necessary corrections for dimensions of volume, area and time.)

3.5.3.2 Tubular membranes

These values were similarly determined, as described elsewhere(3), except that another, appropriate, cell factor was used.

3.6 UTF RO MEMBRANE EVALUATION FOR CHLORINE STABILITY

3.6.1 STATIC METHOD

Early evaluations of the chlorine stability of flat-sheet membranes were done under static conditions. The baseline RO performance of a set of membranes was determined, as described in Section 3.5. Membranes were then carefully removed from the test cells and immersed in an aqueous sodium hypochlorite solution, the pH and the level of chlorine having been determined (as described in Section 3.6.2), in a sealed container. After a certain period of exposure the membranes were removed from the chlorine solution, rinsed with distilled water and then re-tested for their RO performance. Assessment of any membrane damage, due to chlorine attack, was based on the RO performance determined before and after exposure to chlorine.

3.6.2 DYNAMIC METHOD

The following procedure was used in the evaluation of RO membranes for their stability towards chlorinated feedwaters under dynamic conditions.

Membranes were first tested routinely for their baseline RO performance under standard conditions, as described in Section 3.5. The feed solution was then manually chlorinated to a predetermined level, by addition of a small volume of sodium hypochlorite solution (Jik; 3,5% NaOCl). This volume depended on what concentration level of free chlorine (ppm) was required in the chlorinated feed solution; this in turn depended on the volume of the feed solution, temperature, pH and rate of chlorine dissipation. It was therefore not possible to calculate accurately the amount of hypochlorite solution required in order to chlorinate the feed solution accurately to a desired level. Through experience, however, it was found that addition of 20 cm^3 Jik to a 40 litre volume of feed solution at 25° C and pH 6-7 produced an initial free-chlorine content of approximately 5 ppm. After chlorination of the feed solution, the chlorine level was determined by the DPD titration method(14). (In practice, when the amount of chlorine required to produce the desired free-chlorine level was not known, it was found to be more satisfactory to underdose with chlorine, determine the chlorine level by titration, and then dose further if necessary, in order to reach the desired level, rather than to "over-shoot the mark".) Maintaining a constant level of free chlorine in the feed solution over extended periods of time for this dynamic evaluation method was laborious. Because of the high rate of dissipation the chlorine from the feed tank, frequent monitoring of the chlorine level by titration and re-dosing with hypochlorite solution when the level decreased, were necessary. The pH of the chlorinated feed solution also required monitoring. In practice, the chlorine level required adjusting almost hourly. After the membranes had been exposed to the chlorinated feed solution for some period of time, their RO performance was recorded. The instability of a membrane was judged on the basis of any decrease in RO performance between the post-chlorination RO performance value and the originally determined baseline value. The time period over which any deterioration in performance took place was carefully noted as was the pH of the chlorinated feed-solution.

3.6.3 QUANTITATIVE DETERMINATION OF CHLORINE IN FEED SOLUTIONS

The level of free, available chlorine present in the feed solution was determined by titration, using N,N-diethyl-p-phenylenediamine (DPD) as indicator with ferrous ammonium sulphate FAS as titrant. The background to this procedure has been described elsewhere(14).

3.6.3.1 Procedure

The following procedure is used to determine the concentration of free available chlorine up to 5 ppm. When higher chlorine concentrations were used, smaller samples of the chlorinated solution were taken and diluted to a total volume of 100 cm^3, prior to titration. This was taken into account when calculating the concentration (see Section 3.6.3.3).

Phosphate buffer reagent solution (5 cm^3) and DPD indicator solution (5 cm^3) were placed in a titration flask and mixed. A sample, or a diluted sample, of the chlorinated solution (100 cm^3) was added and well mixed in. This was titrated rapidly with standard FAS titrant until a red colour appeared. The volume of titrant used was recorded.

3.6.3.2 Reagents

Phosphate buffer solution:

Anhydrous - Na_2HPO_4 (24 g) and anhydrous KH_2PO_4 (46 g) were dissolved in distilled water. Disodium ethylenediamine tetraacetate dihydrate (EDTA; 800 mg) was dissolved in distilled water (100 cm^3) and added to the above. $HgCl_2$ (20 mg) was added to this solution, which was then diluted to 1000 cm^3.

DPD indicator solution:

Anhydrous DPD sulphate (1,1 g) was dissolved in chlorine-free distilled water containing sulphuric acid (8 cm^3; 2 cm^3 water + 6 cm^3 H_2SO_4) and EDTA (200 mg). This solution was then diluted to 1000 cm^3 and stored in a brown glass stoppered bottle. When it became discoloured, it was discarded.

FAS titrant:

$Fe(NH_4)_2(SO_4)_2.6H_2O$(1,106 g) was dissolved in distilled water containing sulphuric acid (1 cm^3; 1 cm^3 water + 3 cm^3 H_2SO_4) and diluted to 1000 cm^3 with freshly boiled and cooled distilled water. This primary standard could be used for one month before a fresh one was required.

3.6.3.3 Calculation

For a 100 cm^3 sample of chlorinated solution, 1,0 cm^3 standard FAS titrant was equivalent to 1 ppm available residual chlorine(14). Hence, the number of millilitres FAS solution titrated would be equivalent to the number of parts per million (ppm) of chlorine present in the solution. For a 50 cm^3 sample of chlorinated solution, diluted to 100 cm^3 with chlorine-free distilled water, double the number of millilitres of FAS titrant used would be equivalent to the amount of chlorine present in the solution (ppm).

3.7 UTF RO MEMBRANE EVALUATION FOR PH STABILITY

3.7.1 STATIC METHOD

Membranes were evaluated for their stability at low and high pH by the so-called "static method" using the following procedure:

Membranes were tested routinely for their baseline RO performance, as described in Section 3.5. They were then carefully removed from the test cells and immersed for a certain period of time in water which had been either acidified with HCl to a desired pH value of <7 or made alkaline with NaOH to a desired pH value of >7. Membranes were then left to age in the unbuffered acidic or alkaline media for a predetermined time whereafter they were removed, rinsed with distilled water, replaced on the test-rig and evaluated for their RO performance, under conditions similar to those used in the determination of the baseline RO performance (Section 3.5).

3.7.2 DYNAMIC METHOD

Membranes were routinely tested for their baseline RO performance, as described in Section 3.5. The pH of the feed solution was then reduced, by addition of HCl, or increased, by addition of NaOH, to the pH at which the membrane stability was to be evaluated. Care was taken not to allow the total concentration of NaCl in the feed solution to become too high; this was done by dilution of the feed solution with water, if required. The conductivity of a 2000 ppm NaCl feed solution is about 4,8 mS and efforts were made to maintain this throughout the experiment.

3.8 PREPARATION OF MODEL COMPOUND MATERIALS

3.8.1 2-ETHYLIMIDAZOLINE (MC)

3.8.1.1 Method 1(15):

(a) Ethylpropionate (51 g; 0,5 mole) and ethylenediamine (90 g; 1,5 mole) were heated together to 100°C for 42 hours under a nitrogen atmosphere. The low-boiling excess ethylenediamine and ethanol by-product were removed under reduced pressure. N-Propionylethylenediamine was then distilled at 130°C/3 mm Hg to yield a yellow liquid. The yield was 42 g (72%). Structure was confirmed by ^{13}C and ^{1}H nmr spectroscopy. ^{13}C nmr (DMSO, 80 MHz) δ 173,06; 42,31; 41,44; 28,58; 9,95. ^{1}H nmr (DMSO, 60 MHz) δ 8,0 - 7,42 (s broad, 1 H amide); δ 3,21 - 2,78 (m, 2H); δ 2,7 - 2,34 (m, 2H); δ 2,12 (s, 2H amine); δ 2,07 (q, J = 7,5 Hz; 2H); δ 0,98 (t, J = 7,5 Hz, 3H).

(b) N-Propionylethylenediamine was cyclized by lime dehydration. N-Propionylethylenediamine (15 g; 0,13 moles) and finely powdered calcium oxide (35 g; 0,65 moles) were mixed well and heated together under reflux at 225°C for 76 hours in a nitrogen atmosphere. After the mixture had cooled the organic product was extracted from the lime by adding absolute alcohol (50 cm^3) and the solid lime was then filtered off. After the alcohol had been evaporated off under reduced pressure, 2-ethylimidazoline was vacuum-sublimed at 70°C/2 mm Hg. Because of the relatively low melting point of 2-ethylimidazoline (43°C), care had to be taken to not allow the product to solidify along the walls of the apparatus. The yield was 9 g (71%). The purity of 2-ethylimidazoline was confirmed by ^{13}C and ^{1}H nmr spectroscopy. ^{13}C nmr (DMSO, 80 MHz) δ 168,56; 49,33; 22,10; 10,98. ^{1}H nmr (DMSO, 60 MHz) δ 5,49 (s, 1 H amine); δ 3,35 (s, equivalent 2 x 2H); δ 2,09 (q, J = 7,5 Hz, 2H); δ 1,03 (t, J = 7,5 Hz, 3H).

3.8.1.2 Method 2(16):

Ethylenediamine (60 g; 1 mole) and propionitrile (55 g; 1 mole) were heated together with sulphur powder (1,5 g) for 4 hours at 100°C under reflux conditions. After the reaction mixture had cooled, zinc powder (15 g) was added and the reaction allowed to run for a further 2 hours. The crude reaction mix was then sublimed under vacuum at 75°C/2 mm Hg to yield the very hygroscopic product of 2-ethylimidazoline (72 g; 73,5% yield). The product was characterized by mass spectroscopy and accurate ^{13}C and ^{1}H nmr spectroscopy. ^{13}C nmr (DMSO, 80 MHz) δ 168,76; 49,33; 49,26; 22,12; 11,01. ^{1}H nmr (DMSO, 80 MHz) δ 3,41 (s, 2 x 2H); δ 2,09 (q, J = 7,6, 2H); δ 1,06 (t, J = 7,5 Hz, 3H). MS (m/z, relative intensity) 98 ($M^{+\cdot}$, 47), 97 (56), 69 (100), 68 (28), 54 (47), 42 (28), 41 (29). This was the preferred method of synthesis as it entailed only one step. 2-Ethylimidazoline required storage under vacuum in a desiccator.

3.8.2 1-BENZOYL-2-ETHYLIMIDAZOLINE (MC1)

A procedure similar to that described by Zienty(17) was followed for the synthesis of MC 1.

3.8.2.1 Reaction of 2-ethylimidazoline with benzoyl chloride at room temperature

A solution of 2-ethylimidazoline (4,9 g; 0,05 mole) in benzene (50 cm^3) was boiled and any water which may have been present in the system was removed with a Dean-Stark apparatus. When the system had cooled, benzoyl chloride (3,5 g; 0,025 mole) was dripped into the anhydrous solution while it was stirred. After 3 hours a white precipitate appeared. This was filtered off, washed with benzene and dried under vacuum to yield the HCl salt of 2-ethylimidazoline (3,0 g; 89,6% of theoretical quantity possible).

The benzene filtrate was evaporated to dryness under reduced pressure on a rotary evaporator and then dried further in a vacuum oven. The yield of the crude reaction product was 3,1 g (61,4% of the theoretical quantity possible). Analysis by mass spectroscopy indicated the presence products with higher molecular mass than MC 1 (202).

The crude benzene-soluble reaction product was then analysed by high-pressure liquid chromatography (HPLC) under conditions described in the experimental Section 3.1, and was found to contain three major components with three different retention times of about 4, 7 and 10 min.

In order to correctly assign structures to each of these components, an attempt was made, first, to isolate and characterize the major 7-min peak by preparative separation on the HPLC column. This was unsuccessful because insufficient pure sample could be obtained for analysis, since as soon as it was preparatively collected it was lost by decomposition in the aqueous methanol solvent used. A sample of the crude product was then distilled on a semi-micro scale (molecular distillation). The desired product MC 1 was isolated after high-vacuum distillation at 100 - 120°C /1 mm Hg, into glass phials which could be sealed off under vacuum. HPLC analysis showed that this distilled fraction contained 100% of the HPLC 7-min peak component (retention time 7,4 min). This was positively identified as the desired cyclic model compound product MC 1 : 1-benzoyl-2-ethylimidazoine by ^1H and ^{13}C nmr spectroscopy and mass spectroscopy. ^1H nmr (DMSO, 80 MHz) δ 7,58 - 7,47 (m, 5H); δ 3,70 (m, 2 x 2H); 2,57 (q, J = 7,3 Hz; 2H); δ 1,09 (t, J = 7,3 Hz; 3H). ^{13}C nmr (DMSO, 80 MHz) δ 167,75; 161,92; 136,78; 130,64 (2H); 128,34; 127,06 (2H); 52,60; 49,03; 24,60; 10,79. MS (m/z, relative intensity) 202 ($M^{+\cdot}$, 48), 201 (22), 174 (5), 173 (12), 105 (100), 77 (14). A further sample of the crude reaction product was then used in an attempt to isolate the 10-min peak on the HPLC column. Isolation of the component with the 10-min retention time was done by introducing samples (250 $\mu\ell$) of the crude reaction product onto the same HPLC column as used for analysis of the product and then preparatively collecting the material under the 10-min absorbance peak. The collected dilute aqueous methanol solution was dried on a freeze-dryer prior to analysis. After an adequate amount of sample was obtained it was analysed by HPLC and found to be 100% pure. This compound was identified by mass spectroscopy, which included an accurate molecular mass measurement, as the dibenzoylated compound 1,3-dibenzoyl-2-ethylideneimidazolidine (DBEI). (A similar dibenzoylated species has been reported by Miescher *et al.*(18)). M^+ calculated for $C_{19}H_{19}N_2O_2$ 306, 136806; found 306, 135288. MS (m/z, relative intensity) 306 ($M^{+\cdot}$, 13), 305 (26), 105 (100), 77 (40).

The component comprising the 4-min peak in the HPLC was identified as the hydrolysed and linear benzoylated product: 1-benzoyl-2-propionylthylenediamine (HMC 1). A prepared sample of HMC 1 (Section 3.8.5) had the same HPLC retention time as did the component with the 4-min retention time in the crude MC 1 product, i.e. 4,4 min. The final synthesis reaction product therefore comprised:

2% 1-benzoyl-2-propionylthylenediamine (4-min peak)
74% 1-Benzoyl-2-ethylimidazoline (7-min peak)
24% 1,3-dibenzoyl-2-ethylideneimidazolidine (10-min peak)

3.8.2.2. **Reaction of 2-ethylimidazoline with benzoyl chloride at elevated temperature**

2-Ethylimidazoline (9,8 g; 0,1 mole) and benzene (100 cm^3) were boiled together and any water present was removed with Dean-Stark apparatus. Benzoyl chloride (7 g; 0,05 mole) was then added dropwise and the reaction mixture was refluxed for 3 hours. When the mixture was cooled, a white precipitate of the ethylimidazoline hydrochloride salt appeared. This was filtered off, washed with benzene and dried; the yield was 6 g (89,6%).

The benzene filtrate was evaporated to dryness under reduced pressure, then further dried in the vacuum oven to yield 9,7 g (96%) of crude reaction product containing MC 1. Mass spectroscopy and a DSC melting-point determination indicated some impurities present in the product.

HPLC analysis of this product showed it to comprise three major components, each with different retention times and similar to those described in 3.8.2.1. Identification of these components has been described in Section 3.8.2.1. The final reaction product was found to comprise:

0,9% 1-benzoyl-2-propionylethylenediamine (4-min peak)
89,9% 1-benzoyl-2-ethylimidazoline (7-min peak)
8,8% 1,3-dibenzoyl-2-ethylideneimidazolidine (10-min peak)

MC 1 is very hygroscopic so that is decomposed when it is exposed to the atmosphere.

3.8.3 1-BENZENESULPHONYL-2-ETHYLIMIDAZOLINE (MC 2)

2-Ethylimidazoline (9,8 g; 0,1 mole) and benzene (100 cm^3) were refluxed together, using a Dean-Stark apparatus to remove any traces of moisture. After cooling of the mixture, benzenesulphonyl chloride (8,8 g; 0,05 mole) was added dropwise and a white precipitate of the reagent base HCl salt appeared almost immediately. Refluxing was continued for 3 hours. After the reaction mixture had cooled, the precipitate was filtered off, washed with benzene and dried under vacuum to yield the HCl salt of 2-ethylimidazoline (3,5 g; 52,2%).

The filtrate was evaporated to dryness under reduced pressure on a rotary evaporator and further dried in a vacuum oven to produce 9,8 g crude sulphonamide product (82,4% yield). Analysis by HPLC showed that this crude product comprised only one component (one absorbance peak of 7,8 min retention time). The desired product MC 2 was positively identified by accurate ^{1}H and ^{13}C nmr spectroscopy and mass spectroscopy. ^{1}H nmr (DMSO, 80 MHz) δ 7,99 - 7,58 (m, 5H); δ 3,75 - 3,58 (m, 2 x 2H); δ 2,56 (q, J = 7,3; 2H); δ 1,09 (t, J = 7,3 Hz, 3H). ^{13}C nmr (DMSO, 80 MHz) δ 158,78; 137,95; 133,82 (2H); 129,82; 126,90 (2H); 51,82; 48,14; 22,69; 10,67. MS (m/z, relative intensity) 238 ($M^{+\cdot}$, 0,35), 141 (12), 97 (35), 77 (54), 69 (100), 68 (18), 42 (32), 41 (33). An accurate molecular mass determination was obtained by mass spectroscopy. M^+ calculated for $C_{11}H_{14}N_2O_2S$ 238,077582; found 238,0776663.

A DSC temperature scan showed a single sharp melting point at 100,64°C.

(The fact that only the benzene sulphonyl ring adduct MC 2 was isolated, whereas three adducts were isolated under equivalent reaction conditions during the preparation of MC 1, indicated that MC 2 is more stable than MC 1. This was evident again later, as described in Section 3.9.3.)

3.8.4 N-PROPIONYLETHYLENEDIAMINE (HMC)

3.8.4.1 Method 1

As described in 3.8.1.1.(a).

3.8.4.2 Method 2

HMC was obtained in a quantative yield from the unhydrolysed ring-product, 2-ethylimidazoline (MC), by boiling a 10% solution of 2-ethylimidazoline for 24 h, drying it first under reduced pressure on a rotary evaporator and then on the freeze dryer. Structure was confirmed by routine ^{1}H nmr analysis. ^{1}H nmr ($CDCl_3$, 60 MHz) δ 7,7 - 7,0 (broad peak, ^{1}H amide); δ 3,35 - 2,65 (m, 2x2H); δ 2,4 (s, 1 H amine); δ 2,2 (q, J = 7 Hz, 2H); δ 1,1 (t, J = 7 Hz, 3H).

3.8.5 1-BENZOYL-2-PROPIONYLETHYLENEDIAMINE (HMC 1)

An approach similar to that used for the preparation of MC 1 was used for the preparation of its hydrolysed form, HMC 1. The hydrolysed form of 2-ethylimidazoline, N-propionylethylenediamine (HMC), prepared as described in the literature by Hill and Aspinall$^{(15)}$ (see Section 3.8.1.1a) was reacted with benzoyl chloride.

Benzoyl chloride (14 g = 12 cm^3; 0,1 mole) was dripped slowly into a solution of N-propionylethylenediamine (5,8 g; 1,05 mole) in benzene (100 cm^3). The mixture was gently refluxed for 6 hours and then allowed to cool. While the mixture stood overnight, a mass of white crystals formed. These were filtered off, washed well with benzene to remove any unreacted benzoyl chloride, and then dried in a vacuum oven at 30°C. The yield was 9,8 g (94%). HPLC analysis of the crude product showed that only one product was present (4,4-min peak). This was identified by accurate ^{1}H and ^{13}C nmr spectroscopy to be the desired product: 1-benzoyl-2-propionylethylenediamine (HMC 1). ^{1}H nmr (DMSO, 80 MHz) δ 8,54 - 8,38 (broad peak, 1H aromatic amide); δ 7,91 - 7,42 (m, 5H, 1H aliphatic amide); δ 3,33 - 3,19 (m, 2 x 2 H); δ 2,08 (q, J = 7,5 Hz, 2H); δ 0,99 (t, J = 7,6 Hz, 3H). ^{13}C nmr (DMSO, 80 MHz) δ 173,15; 166,31; 134,51; 130,98; 128,13 (2H); 127,12 (2H); 39,29; 38,26; 28,50; 9,81.

Correctness of the structure was further confirmed by an accurate molecular mass determination: M^+ calculated for $C_{12}H_{16}N_2O_2$ 220,121158; found 220,12114. MS (m/z, relative intensity) 220 ($M^{+\cdot}$, 7), 191 (4), 134 (29), 105 (100), 77 (41), 57 (23), 30 (56).

3.8.6 1-BENZENESULPHONYL-2-PROPIONYLETHYLENEDIAMINE (HMC 2)

HMC 2 was found to be formed after a sample of MC 2 was left to age for approximately 6 months. The purity of such a product of HMC 2 was ascertained by HPLC analysis which revealed only one peak with a retention time of around 4,8 min.

Analysis by ^{1}H and ^{13}C nmr spectroscopy confirmed that the product was 1-benzenesulphonyl-2-propionylethylenediamine (HMC 2). ^{1}H nmr (DMSO, 80 MHz) δ 7,88 - 7,56 (m, 5H); δ 7,88 - 7,56 (2 x 1H amide, obscured by aromatic protons); δ 3,16 - 2,75 (m, 2 x 2H); δ 2,04 (q, J = 7,5 Hz, 2H); δ 0,96 (t, J = 7,6 Hz, 3H). ^{13}C nmr (DMSO, 80 MHz) δ 173,09; 140,37; 132,31 (2H), 129,14; 126,40 (2H); 42,10; 38,44; 28,37; 9,66. The mass spectrum was recorded. MS (m/z, relative intensity) 256 ($M^{+\cdot}$, 0,2), 101 (68), 77 (39), 57 (100). (HMC 2 could also be prepared by reacting HMC and benzenesulphonyl chloride according to a procedure described by Amundsen and Longley(19).)

3.9 REACTIONS OF MODEL COMPOUNDS

The following model compounds were investigated for their behaviour or reactivity under the following conditions:

Aqueous hydrolysis of:	MC, MC 1 and MC 2
Exposure to air of:	MC 1 and MC 2
Exposure to chlorine of:	MC 1, MC 2 and HMC 1
Exposure to acidic and basic conditions of:	MC 1, MC 2, HMC 1 and HMC 2.

The reactions were followed by high-pressure liquid chormatographic analyses (HPLC). The column retention times for the various model compound reagents (MC 1, MC 2, HMC 1 and HMC 2) which had already been established (see Sections 3.8.2 and 3.8.3), were specific for the column, carrier solvent, solvent ratio and solvent flow-rate (described in the experimental Section 3.1). Reaction products were therefore analysed by injecting samples into the chromatograph under the same HPLC conditions. The relative decrease in the amount of model compound reagent and appearance of any new products were recorded, as a function of their respective column retention times. The amount of any new product formed over a period of time could also be recorded. An advantage of this analytical technique was that if any new absorption peaks appeared, it might be possible to isolate and collect these fractions preparatively and then identify them by nmr or mass spectroscopy.

It is important to note that, under the conditions of HPLC analysis, only compounds which absorbed in the selected UV frequency range (254 nm, see Section 3.1) could be detected by the HPLC method described. It was established that MC and HMC gave very weak absorbance signals, at a retention time of about 3 min, under HPLC conditions. All four model compound reagents investigated (MC 1, MC 2, HMC 1 and HMC 2) could be detected in the UV range because of the presence of the substituent benzene ring.

3.9.1 HYDROLYSIS OF 2-ETHYLIMIDAZOLINE (MC)

Two separate aqueous solutions of 2-ethylimidazoline (10% and 20%) were made up in deuterium oxide (0,5 cm^3) and allowed to hydrolyse at 30°C in 5 mm nmr tubes. (Solution 1 (10%) contained 100% MC at time zero. Solution 2 (20%) contained 80% MC at time zero.) ^{1}H nmr spectra of the reaction mixtures were run at frequent intervals over the period of two days and the courses of the reactions followed. This was done by measuring the decrease in the integral of the two equivalent methylene carbons of the 2-imidazoline (amidine) structure and the increase in the integral of the two non-equivalent methylene carbons of the newly formed linear amide structure as the hydrolysis reaction proceeded.

The rate of hydrolysis for Solution 1 was $k = 2{,}07 \times 10^{-5}\ \text{sec}^{-1}$; $t_{1/2} = 9{,}3$ hours.
The rate of hydrolysis for Solution 2 was $k = 1{,}22 \times 10^{-5}\ \text{sec}^{-1}$; $t_{1/2} = 15{,}8$ hours.

During the course of the hydrolysis reaction of MC there is a large change in pH value of the solution. A freshly prepared aqueous solution of MC (2%) had a pH value of 11,56. After 144 hours, at 22°C, and upon complete hydrolysis, this had dropped to pH 9,12.

(A similar hydrolysis study was carried out on the PVAM polymer, as described in Section 4.3.4.3, where a similar hydrolysis reaction and decrease in solution pH took place but the observed rate of hydrolysis, $k = 1{,}87 \times 10^{-7}\ \text{sec}^{-1}$; $t_{1/2} = 42{,}8$ days, was very much less for the polymer containing the 2-imidazoline ring. Indications were, therefore, that the results of model compound studies showed the trend of the polymer's chemical reaction but that the rates at which processes occured differed.)

3.9.2 HYDROLYSIS OF BENZOYLATED RING-STRUCTURES

3.9.2.1 1-Benzoyl-2-ethylimidazoline (MC 1)

Two separate solutions (0,05 mol and 0,01 mol) of the benzamide model compound MC 1 (0,02 g and 0,004 g) were prepared in a water/methanol (45/55) medium (2,0 cm^3) and allowed to react over a period of 14 days at 22°C.

Solution 1 (0,05 mole/ℓ), prepared from a crude product after MC 1 synthesis, comprised 86,0% MC 1; 1,8% HMC 1 and 10,5% 1,3-Dibenzoyl-2-ethylideneimidazolidine (DBEI).

Solution 2 (0,01 mole/ℓ) was prepared from a freshly distilled sample of MC 1 and comprised 98,2% MC 1; 1,6% HMC 1 and no dibenzoylated species DBEI.

The courses of the hydrolysis reactions were followed by HPLC analyses. This involved introducing samples (0,025 cm^3) of the reaction product directly onto the HPLC column at time zero and then at various time intervals, under chosen conditions (see Section 3.1), and obtaining a print-out of the reaction product sample composition which included percentage amounts of the components in the reaction product sample at their respective retention times (min). (As the starting materials MC 1 and MC 2 were not adequately water soluble, they were allowed to hydrolyse in an aqueous methanol medium. Apart from the fact that this dissolved the materials, it was also the chosen eluting solvent for the HPLC analytical technique and so allowed the reaction samples to be introduced directly into the column.)

During the course of the hydrolysis reactions, the area under the 7-min peak in the reaction product mixtures decreased while a new peak emerged at about 4 minutes. This was expected(18,20), since the retention time for the linear amide model compound HMC 1 was about 4 min (see Section 3.8.5).

During the hydrolysis reaction of a sample of the crude benzamide model compound product MC 1 (Solution 1) there was an increase in two peaks, other than the 4-min peak, in the HPLC spectrum of the reaction product. The greater of these two peaks had a retention time of about 10 min and the lesser peak had a retention time of about 3 min. The product with the retention time of 10 min, observed earlier during the preparation of MC 1 and described in Section 3.8.2.1 was 1,3-dibenzoyl-2-ethylieneimidazolidine. It was not possible to obtain a sufficiently large sample of the 3-min peak for analytical purposes by HPLC preparative separation because of the low concentration in the reaction product mixture and its closeness to the following peak of the linear amide hydrolysis product HMC 1 (retention time 4 min), hence the lesser product was not identified.

On termination of the hydrolysis-reaction experiments the reaction products comprised the following:

Solution 1 (after 313 h): 0% MC 1; 96,0% HMC 1; 1,7% dibenzoylated species DBEI.
$k = 2{,}72 \times 10^{-5}\ \mathrm{sec}^{-1}$; $t_{\frac{1}{2}} = 7{,}1$ hours
Solution 2 (after 51 h): 20,3% MC 1; 31,2% HMC 1; 34,0% dibenzoylated species DBEI.
$k = 6{,}19 \times 10^{-5}\ \mathrm{sec}^{-1}$; $t_{\frac{1}{2}} = 3{,}16$ hours

3.9.2.2 1-Benzenesulphonyl-2-ethylimidazoline (MC 2)

Two separate solutions (0,05 mol and 0,01 mol) of the sulphonamide model compound MC 2 (0,0238 g and 0,0049 g) were prepared in a water/methanol (45/55) medium (2,4 cm^3) and allowed to react over a period of two weeks at 22°C. The course of the reactions was followed by HPLC analyses, as described in Section 3.9.2.1.

Solution 1 (0,05 mole/ℓ), prepared from a crude product after MC 2 synthesis, comprised
78,7% MC 2 and 16,0% HMC 2.
Solution 2 (0,01 mole/ℓ) comprised 89,0% MC 2 and 8,8% HMC 2.

On termination of the reactions, the reaction products comprised the following:

Solution 1 (after 312 hours): 0,5% MC 2; 88,4% HMC 2; and two unidentified lesser
products of 8% and 4% concentration at retention times
5-6 min and 2-3 min respectively.
$k = 2{,}3 \times 10^{-6}\ \mathrm{sec}^{-1}$; $t_{\frac{1}{2}} = 83{,}7$ hours.

Solution 2 (after 265 hours): 1,0% MC 2; 87,2% HMC 2; and the two lesser products and in
similar concentrations as to those described above.
$k = 9{,}56 \times 10^{-7}\ \mathrm{sec}^{-1}$; $t_{\frac{1}{2}} = 201{,}3$ hours.

3.9.3 BEHAVIOUR OF RING-MODEL COMPOUNDS MC 1 AND MC 2 UPON EXPOSURE TO AIR

Separate samples (0,2 g) of both MC 1 and MC 2 were left exposed to the air at 22°C. At various time intervals, samples of the ageing products were dissolved in a small volume of a water/methanol (45/55) solution. Sample volumes (0,025 cm^3) were then taken and injected onto the HPLC column under conditions described in Section 3.1. Any change in the composition of the exposed product compared with that of the initial composition at time zero, was observed.

The initial composition of the sample of MC 1 was: 90% MC 1; 8,2% DBEI and 1,8% HMC 1. After 144 days this had changed to: 49% MC 1, 30,4% DBEI and 19,1% HMC 1. Hydrolysis of MC 1 had taken place and the rate constant was calculated as $k = 2{,}74 \times 10^{-8}\ \mathrm{sec}^{-1}$; $t_{\frac{1}{2}} = 293$ days.

The initial sample of MC 2 was 100% pure. After 144 days, no hydrolysis of MC 2 was detected. (This indicated that the sulphonamide MC 2 was more hydrolytically stable than MC 1, as mentioned in Section 3.8.3.)

3.9.4 BEHAVIOR OF THE MODEL COMPOUNDS UPON EXPOSURE TO AQUEOUS CHLORINE SOLUTIONS

3.9.4.1 General Procedure

Samples of model compounds were allowed to react in aqueous sodium hypochlorite solutions (7,5 ppm free chlorine or 100 ppm free chlorine). Reaction media were unbuffered because of the desirability of avoiding any contamination of reaction products with species which also show absorption peaks under the conditions of the HPLC analysis and hence complicate HPLC analyses (see Section 3.9.5.1). Reactions were carried out at the alkaline pH of solutions of the model compounds in aqueous sodium hypochlorite (pH 10-11) and hence the OCl^- species would predominate. Chlorine solutions were prepared by dilution of commercial sodium hypochlorite (Jik; 3,5% NaOCl). The level of chlorine in the sodium hypochlorite solutions was determined by the DPD titration method(14) (see Section 3.6.3). Analysis of reaction products of these experiments was carried out by HPLC. Prior to injection onto the HPLC column, the reaction product samples were treated as follows: a volume (2,0 cm^3) of the reaction product suspension was passed through a C^{18} Sep-Pak cartridge filter. The organic reaction products were absorbed in the filter and extracted with methanol solvent (2,0 cm^3). An aliquot (0,020 cm^3) of this methanol solution was introduced onto the HPLC column for analysis of reaction products, in terms of the number of components in the reaction product and their retention times.

3.9.4.2 1-Benzoyl-2-ethylimidazoline (MC 1)

(i) A 1%-suspension of benzamide MC 1 (0,28 g) in an aqueous sodium hypochlorite solution (27,7 g; 7,5 ppm free chlorine) was prepared, and allowed to react in a sealed container at 22°C for 12 days.

In the control experiment; an aqueous 1%-suspension (21,5 cm^3) of benzamide MC 1 (0,215 g) was prepared, then similarly allowed to react in a sealed container at 22°C for 12 days.

Reaction products of both solutions were analysed by HPLC as described in 3.9.4.1. The final products were found to contain HMC 1 as the major product (61 and 68% respectively), the dibenzoylated species DBEI (30 and 21% respectively) and an unidentified lesser product (5 and 9% respectively). No new chlorinated products were detected. Mass spectra of the two reaction products substantiated this.

(ii) An 0,5% suspension of benzamide MC 1 (0,1 g) was prepared in an aqueous sodium hypochlorite solution (20 cm^3) containing about 100 ppm free chlorine and allowed to react over a period of up to three weeks at 22°C.

At frequent intervals, samples of the reaction product were taken, purified and analysed by HPLC for their composition as described in 3.9.4.1. No new products, due to chlorination, were detected even after exposure to this high chlorine concentration. The final product comprised HMC 1 (67%) and DBEI (22%) and an unidentified lesser product (7%).

3.9.4.3 1-Benzenesulphonyl-2-ethylimidazoline (MC 2)

A procedure similar to that described in Section 3.9.4.2(i) was followed to investigate the reaction of the sulphonamide MC 2 (0,255 g) in an aqueous suspension (1%) of sodium hypochlorite (22,5 g; 7,5 ppm free chlorine). This experiment ran for 15 days. HPLC analysis revealed that the final product comprised only HMC 2.

3.9.4.4 1-Benzoyl-2-propionylethylenediamine (HMC 1)

An 0,5% suspension of the linear benzamide HMC 1 (0,1 g) was prepared in an aqueous sodium hypochlorite solution (20 cm^3) containing 100 ppm free chlorine and was stirred in a sealed container at 20^oC over a period of 10 days. The course of the reaction was followed by HPLC, the composition of reaction product was analysed and compared to that of the starting material HMC 1 at time zero. No reaction was found to have taken place.

HPLC analysis of the product showed that the peak heights of the HMC 1 (4-min peak) were the same at the beginning and the end of the experiment. Because injection volumes of samples were kept constant, observing no decrease in peak height would mean that there was no decrease in the amount of that component present.

3.9.5 BEHAVIOUR OF MODEL COMPOUNDS IN AQUEOUS SOLUTIONS OF HIGH AND LOW pH

3.9.5.1 General Procedure

Two procedures were used during this study. Reactions of the model compounds in both buffered and unbuffered media were investigated.

(i) **In buffered medium**

In separate experiments, samples of the model compounds MC 1, MC 2, HMC 1 and HMC 2 were allowed to age in aqueous buffer solutions of pH 3,7 and 11 at 20^oC. Any changes in their composition were monitored by HPLC. For this, an injection sample had first to be prepared. This was done as follows: an aliquot of reaction product (1,0 cm^3) was taken from the reaction suspension and filtered through a C^{18} Sep-Pak cartridge to remove any inorganic components present. The organic products were then extracted from the cartridge filter with methanol (1,0 cm^3). An aliquot (0,025 cm^3) of this methanol extract was introduced directly onto the HPLC column for analysis.

The buffers used were:

pH 3: 50 cm^3 of 0,1 molar potassium hydrogen phthalate + 22,3 cm^3 of 0,1 molar HCl.
pH 7: 50 cm^3 of 0,1 molar tris (hydroxymethyl) aminomethane + 46,6 cm^3 of 0,1 molar HCl.
pH 11: 50 cm^3 of 0,05 molar sodium bicarbonate + 22,7 cm^3 of 0,1 molar NaOH.
Each solution was made up to a volume of 100 cm^3.

(The specific buffers were so chosen as to correspond to those selected for studies of the performance of PVAM/SCI tubular membranes at pH extremes, carried out during a parallel study and described in Section 4.5.2.)

Control samples of the various buffers used were analysed for any abosrbance which they might have under the chosen HPLC conditions. These analyses were done after "sample preparations", similar to those described above, had been carried out. HPLC analysis of samples of buffers pH 3 and 7 showed them to have absorption signals at retention times of about 3 min. This confused interpretation of results of experiments carried out at these pHs as any reaction products which might also have retention times of about 3 min would have been masked by the buffer and not regarded. Hence, as the use of these buffers complicated the analysis of HPLC data of hydrolysis reaction products, acid- and base-catalysed hydrolysis reactions were repeated without the inclusion of buffers and as follows:

(ii) In unbuffered medium

Samples of model compounds were mixed together with solutions of 1 HCl (1%; pH 1) or NaOH (1%; pH 12) and allowed to react at 20°C over a period of time.

The reaction products were analysed by HPLC after they had been isolated as follows: the reaction medium was neutralised (with either NaOH or HCl) followed by removal of the NaCl salt formed, by addition of methanol to the dry product mixture and then filtering off the methanol-insoluble NaCl. The methanol solution containing the reaction products was then evaporated to dryness on a rotary evaporator at about 50°C to yield the crude reaction product. A sample was then taken up in methanol and an aliquot (0,025 cm^3) of the methanol solution was then directly introduced onto the HPLC column for analysis.

Occasionally analyses were supplemented by the thin-layer chromatography (TLC) technique.

3.9.5.2 1-Benzenesulphonyl-2-ethylimidazoline (MC 2)

(i) At pHs 3, 7, 11

Samples of sulphonamide MC 2 (0,054 g) were mixed with separate volumes (10 cm^3) of buffers pH 3, 7 and 11 (0,05% concentrations). The reaction mixtures were heterogeneous, even at the low concentration, and were stirred at 20°C over a period of 15 days. Change in reaction products was monitored at frequent time intervals by HPLC analysis of product samples. Product samples were prepared as described in Section 3.9.5.1 (i) before each injection.

Because the pH 3 and pH 7 buffers had absorption peaks at the retention time of about 3 min, results reported for the hydrolysis reactions at these pHs were corrected as follows:

The recorded area under the 3-min absorption peak was subtracted from the total area recorded on the HPLC chromatogram and the recorded area under the remaining absorption peaks at 4 min, 7 min and 10 min were recalculated as percentages of the "corrected" total area calculated. The absorption peak at 3 min was therefore disregarded as being a possible reaction product peak when the results were reported. Any hydrolysis products which had a HPLC retention time of about 3 min would therefore not have been detected by this analytical method.

The HPLC results are nonetheless adequate to show the decrease in the amount of ring MC 2 (reflected as a decrease in the 7-min peak) and a corresponding increase in the linear amide HMC 2 (reflected as an increase in the 4-min peak) as hydrolysis proceeded.

The final composition of the reaction products was as follows in the different pH media:

pH 11: 26,6% MC 2; 61,4% HMC 2 and 7,2% unidentified lesser product
(HPLC retention time 2-3 min).
pH 7: 8,7% MC 2; 83,0% HMC 2 and 6,3% unidentified lesser product
(HPLC retention time 8-9 min).
pH 3: 0% MC 2; 97,5% HMC 2 and 1,1% unidentified lesser product
(HPLC retention time 8-9 min).

Results showed that MC 2 hydrolysed to form HMC 2 at the following different rates in the different pH media:

pH 11: $k = 7{,}93 \times 10^{-7}\ sec^{-1}$; $t_{\frac{1}{2}} = 10{,}1$ days
pH 7: $k = 1{,}5 \times 10^{-6}\ sec^{-1}$; $t_{\frac{1}{2}} = 5{,}2$ days
pH 3: $k = 3{,}25 \times 10^{-6}\ sec^{-1}$; $t_{\frac{1}{2}} = 2{,}5$ days.

(ii) In acidic medium (pH 0,8)

A suspension (1,0%; pH 0,82) of sulphonamide MC 2 (0,221 g) was prepared in a dilute solution of HCl (1,0 m/v; 22,9 cm^3) and stirred at 20°C for 480 h. The crude reaction product was isolated, and then analysed by HPLC and TLC as described in Section 3.9.5.1(ii).

It was found to contain 0% MC 2; 82,0% HMC 2 and 18% product with a 3-min HPLC retention time. This is proposed to be N-benzenesulphonylethylenediamine, for reasons described below.

In the attempt to identify the component responsible for this 3-min HPLC peak, the routes by which MC 2 could hydrolyse and the possible reaction products were considered. Figure 3.3 shows the possible routes by which MC 2 could hydrolyse.

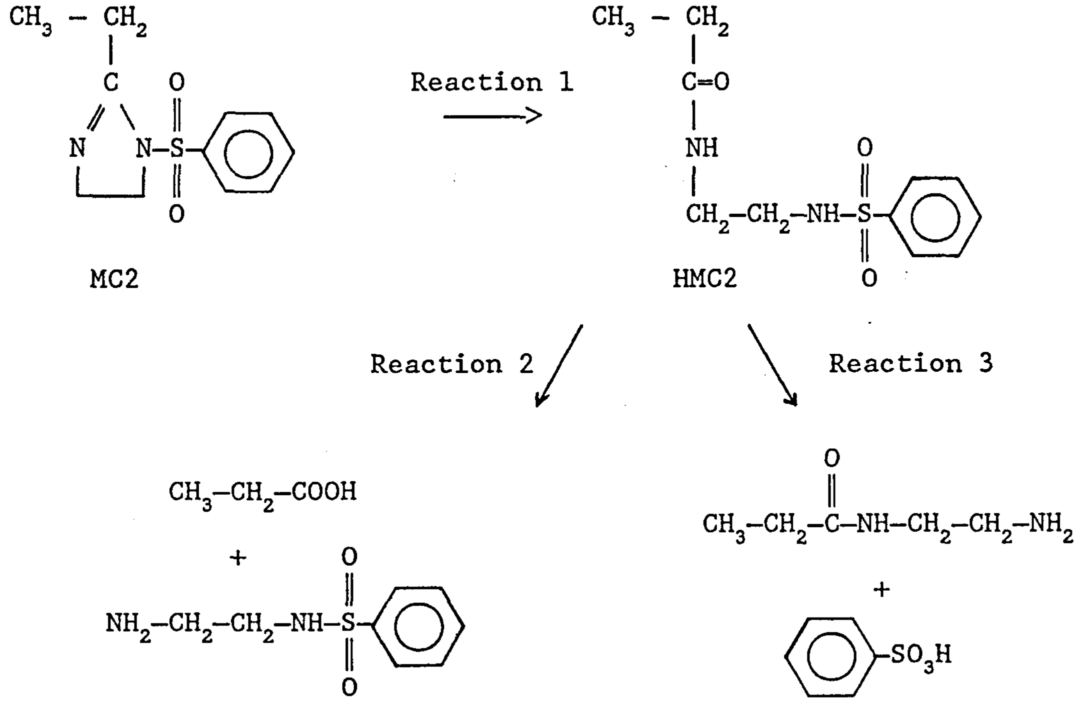

FIGURE 3.3: DIAGRAM SHOWING HYDROLYSIS REACTIONS WHICH MC 2 COULD BE EXPECTED TO UNDERGO

It was proved that reaction 1 occurred, as described in Section 3.9.2.2. The product HMC 2 has been characterized by spectroscopy (see Section 3.8.6). HMC 2 has two possible sites at which it may be cleaved i.e. at the amide bond (reaction 2) or at the sulphonamide bond (reaction 3) to yield the products shown in Figure 3.3. According to the literature, reaction 2 is the most likely one. Zienty(17) has described the reaction of N-acetyl-N'-benzenesulphonylethylenediamine under acidic conditions to form N-benzenesulphonylethylenediamine and acetic acid. Amundsen and Longley(19) have reported that the aliphatic acid and aromatic benzenesulphonyl derivative of ethylenediamine are the products of acid-catalyzed hydrolysis of a linear sulphonamide.

Propionic acid, which is also formed during reaction 2, had a HPLC retention time of around 3,5 min, close to the 3,2-min peak under consideration, but was not expected to be present in large amounts in the reaction product sample analysed by HPLC. Propionic acid forms an azeotrope with water, which has a boiling point of 99°C(21), and it is expected that this component would have been removed by rotary evaporation from the reaction product, prior to HPLC analysis, during sample preparation (see Section 3.9.5.1ii). Hence, it was deduced that N-benzenesulphonylethylenediamine contributed to the 3-min peak in the HPLC chromatogram of the reaction product. (The presence of a peak with a similar 3-min retention time was also revealed after HPLC analysis of the product of the acid-catalyzed hydrolysis of the linear sulphonamide HMC 2, as described in Section 3.9.5.5i).

A TLC chromatogram of the hydrolysis product revealed components of Rf values: 0,83; 0,75 and approximately 0,27. The linear sulphonamide HMC 2 had a Rf value of 0,74. The components with Rf values 0,83 and 0,27 appeared to be also present in the base-catalyzed hydrolysis reaction product (see Section 3.9.5.2ii). The value 0,83 was provisionally assigned to the component with the retention time of 3 min in the HPLC, namely, N-benzenesulphonylethylenediamine.

(iii) **In basic medium (pH 12,5)**

A suspension (1%; pH 12,5) of sulphonamide MC 2 (0,202 g) was prepared in a dilute solution of NaOH (1% m/v; 20 cm^3) and stirred at 20°C for 480 h. The crude reaction product was isolated and then analysed for its composition by HPLC and TLC as described in Section 3.9.5.1(ii).

The final product contained 56,3% HMC 2; 12,3% HMC 2 and 31,4% product with a 3-min HPLC retention time. The latter component was proposed to be N-benzenesulphonylethylenediamine, on the grounds of Zienty's findings that similar products are formed by both acidic or basic hydrolysis of linear benzenesulphonamides(17) and it had been established that N-benzenesulphonylethylenediamine was a product of the acidic hydrolysis of MC 2 (Section 3.9.5.2ii). (Both acid- and base-catalyzed hydrolysis of a linear benzenesulphonamide, N-acetyl-N'-(p-nitrobenzenesulphonyl)-ethylenediamine, was reported to yield the monoacyl aromatic sulphonyl derivative of ethylenediamine(17) (see Section 2.5.2.3)).

A TLC chromatogram revealed components of Rf values: 0,83; 0,65 and 0,27. The Rf value of unhydrolysed ring MC 2 had a Rf value of 0,65. The other two components were similar to those found by TLC analysis of the acid-catalyzed hydrolysis reaction product (see Section 3.9.5.2ii).

3.9.5.3 1-Benzoyl-2-ethylimidazoline (MC 1)

(i) At pHs 3, 7, 11

Samples of the benzamide MC 1 (0,05 g) were mixed with separate volumes (10 cm^3) of buffers of pH 3 and 11 (0,05% concentrations). The suspensions were stirred at 20°C over periods of 27 and 172 hours respectively. Change in reaction products was monitored at frequent intervals by HPLC analysis of products. Product samples were prepared as described in Section 3.9.5.1(i) before each injection. In the HPLC analytical results for the experiment done at pH 3, corrections were made for the buffer, as described in Section 3.9.5.2(i). The final compositions of the reaction products were as follows:

pH 3: 0% MC 1; 72,0% HMC 1; 6,8% DBEI and 16,2% unidentified product
(HPLC retention time 8 min).
pH 11: 1,3% MC 1; 69,3% HMC 1; 26,1% DBEI and 7,3% unidentified lesser peak
(HPLC retention time 3 min).

Results showed that MC 1 hydrolysed to form HMC 1 at the following different rates in the different pH media:

pH 11: $k = 7{,}72 \times 10^{-6}\ sec^{-1}$; $t_{1/2} = 24{,}8$ hours
pH 3: $k = 6{,}08 \times 10^{-5}\ sec^{-1}$; $t_{1/2} = 3{,}2$ hours.

(ii) In basic medium (pH 12,8)

A suspension (1%; pH 12,8) of benzamide MC 1 (0,257 g) was prepared in a dilute solution of NaOH (1% m/v; 25,7 cm^3) and stirred at 20°C for 20 days. The crude reaction product was isolated and then analysed for its composition by HPLC and TLC as described in Section 3.9.5.1(ii).

Three HPLC analyses were done and the average composition of the final product was found to be: 0% MC 1; 7,3% HMC 1; 9,2% DBEI; and a major product of 80,3% which had a HPLC retention time of 3 min. (In one of the three HPLC analyses this was resolved into two components, retention times of 2,9 and 3,4 min). This major product is proposed to be N-benzoylethylenediamine, for reasons described below.

Attempts to characterize the major component entailed a preparative separation of the compound showing the 3-min peak from the other reaction-product components. A ^{13}C nmr analysis of the isolated product did not reveal much information because of the smallness of the sample and a very noisy baseline. A mass spectrum was obtained of the isolated product. Major peaks occurred at 122, 105 and 77 (see Figure 2, Appendix 3).

To facilitate the identification of the 3-min HPLC peak in the hydrolysis reaction product of MC 1, the routes by which MC 1 could be expected to hydrolyse and possible reaction products were considered, as shown in Figure 3.4.

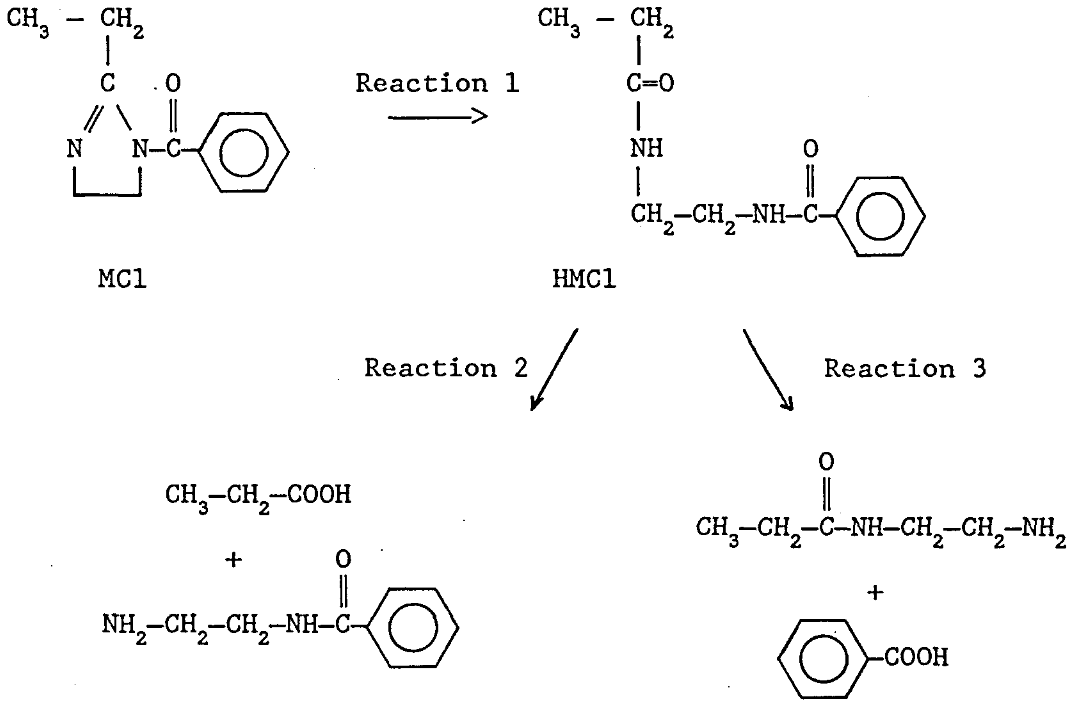

FIGURE 3.4: DIAGRAM SHOWING HYDROLYSIS REACTIONS WHICH MC 1 COULD BE EXPECTED TO UNDERGO

Reaction 1 has been proven to take place, as described in Sections 3.8.2.1 and 3.9.2.1. The product HMC 1 has been characterized by nmr spectroscopy. HMC1 has two possible sites at which it may cleave i.e. at the aliphatic amide bond (reaction 2) or the aromatic amide bond (reaction 3) to yield the products shown in Figure 3.4. In the event of reaction 3 taking place, benzoic acid would be a product. A control mass spectrum of benzoic acid (molecular mass 122) was recorded and compared with the mass spectrum of the 3-min peak. Benzoic acid's standard mass spectrum (Figure 3, Appendix 3) was not identical to that of the 3-min peak of the base-catalyzed hydrolysis reaction product, offering no proof that reaction 3 had taken place. Hydrolysis via reaction 2 was then considered. This type of reaction had been formulated by Zienty(17) and described in Section 2.5.2.2. A further mass spectrum of the isolated product with the 3-min retention time, recorded under conditions of a reduced threshold limit, showed the presence of a small peak at 164 and a base peak at 105 (see Figure 4, Appendix 3). MS (m/z, relative intensity) 164 ($M^{+\cdot}$, 0,06), 122 (86), 105 (100), 87 (23), 77 (80), 51 (43), 43 (58). This indicated the possible presence of N-benzoylethylenediamine (molecular mass 164) and pointed to the strong probability that reaction 2 did take place. Propionic acid, the other product of reaction 2, might be expected to be present as a component in the 3-min peak due to its having a retention time of about 3,2 min. After comparing a control mass spectrum of propionic acid (Figure 5, Appendix 3) with that of the isolated 3-min peak (Figure 4, Appendix 3) this possibility was excluded. There was no mass spectroscopy evidence that propionic acid was present. It was most likely that propionic acid had been removed from the reaction product by rotary evaporation during HPLC sample preparation (see experimental Section 3.9.5.1(ii). Propionic acid and water form an azeotrope which has a boiling point of 99°C(21). It was therefore deduced that basic hydrolysis of MC 1 proceeded via reactions 1 and 2, seen in Figure 3.4. These results are in agreement with what was formulated by Harnsberger(22) and what is known regarding the stability of amides i.e. it is accepted that aromatic amides are much more stable than aliphatic amides(23).

A TLC chromatogram of the hydrolysis reaction product revealed components of Rf values: 0,84; 0,17-0,29 and 0,014. The products with Rf values between 0,17 and 0,29 corresponded to those observed in the TLC analysis of the products of the acid-catalyzed hydrolysis reaction, where Rf values ranged from about 0,20 to 0,29. TLC supported the observation that practically no linear hydrolysis product (HMC 1), Rf 0,70, was present.

(iii) In acidic medium (pH 1,1)

A suspension (1%; pH 1,2) of benzamide MC 1 (0,025 g) was prepared in a dilute solution of HCl (1% m/v; 25,0% cm^3) and stirred at 20°C for 20 days. The reaction product was isolated, then analysed for its composition by HPLC and TLC as described in Section 3.9.5.1(ii).

Results showed that the final product contained: 0% MC 1; 72,7% HMC 1; 0% DBEI and 19,9% of a compound with a retention time of 2,8 min and 5,2% of a compound with a 3-min retention time. It is proposed that their latter is N-benzoylethylenediamine, for reasons given below.

N-benzoylethylenediamine was a product of the base-catalyzed hydrolysis reaction of MC 1 (Section 3.9.5.3iii). Zienty(17) and Miescher *et al.*(18) have reported on a reaction similar to that formulated by Harnsberger(22) for the base-catalyzed opening of the 2-imidazoline ring, for the acid-catalyzed hydrolysis of 1-acylated-2-substituted-2-imidazolines. It is therefore proposed that MC 1 hydrolyses according to Reactions 1 and 2 as shown in Figure 3.4 with formation of some N-benzoylethylenediamine, formed by cleavage of the linear amide HMC 1, in both acidic and basic media (see also results of HMC 1 hydrolysis in acidic and basic media, Sections 3.9.5.4 ii and iii).

A TLC chromatogram of the final hydrolysis product revealed components of Rf values: 0,70 and 0,21-0,29. The Rf value of 0,70 corresponded to that of the major hydrolysis product HMC 1, Rf: 0,70. The lesser products with Rf values in the range 0,21 to 0,29 were not identified, but indications were that they were also present in the base-catalyzed hydrolysis product of MC 1 with Rf values of approximately in the range 0,17 to 0,29 (see Section 3.9.5.3ii).

3.9.5.4 1-benzoyl-2-propionylethylenediamine (HMC 1)

(i) At pHs 3, 7, 11

Samples of the linear benzamide model compound HMC 1 (0,1 g) were made up with separate volumes (20 cm^3) of buffers pH 3, 7 and 11 (0,05% concentrations) and allowed to hydrolyse over a period of 20 days at 20° C. Samples were taken from the reaction mixtures at frequent intervals and analysed by HPLC for their compositions, as described in Section 3.9.5.1(i). All values for results of experiments have been normalised, disregarding the peak with a retention time of around 6 min which is present in amounts of < 5%. Corrections had first been made for pH 3 and pH 7 media, as described in Section 3.9.5.2. No reaction was detected to have taken place and the composition of HMC 1 in all media remained practically unchanged.

(ii) In acidic medium (pH 0,97)

A suspension (1,0%; pH 1,0) of the linear benzamide HMC 1 (0,173 g) was prepared in a dilute solution of HCl (1,0% m/v; 17,3 cm^3) and stirred at 20°C over a period of 168 h (2 weeks). The reaction product was isolated and then analysed by HPLC and TLC as described in Section 3.9.5.1(ii). The final product contained 79,6% HMC 1 and several lesser products (< 10% concentrations) which were not identified.

(iii) In basic medium (pH 12,00)

A suspension (1,0%; pH 12,00) of the linear benzamide HMC 1 (0,174 g) was prepared in a dilute solution of NaOH (1,0% m/v; 17,4 cm^3) and stirred at 20°C over a period of 168 h (2 weeks). The reaction product was isolated and then analysed by HPLC and TLC as described in Section 3.9.5.1(ii). The final product contained 91,4% unreacted HMC 1 and 5,9% lesser product with HPLC retention time of 3 min and proposed to be N-benzoylethylenediamine, as described in Section 3.9.5.3iii.

3.9.5.5 1-Benzenesulphonyl-2-propionylethylenediamine (HMC 2)

(i) In acidic medium (pH 0,95)

A suspension (1,0%; pH 0,95) of linear sulphonamide HMC 2 (0,206 g) was prepared in a dilute solution of HCl (1,0% m/v; 20,6 cm^3) and stirred at 20°C for 2 weeks. The reaction product was isolated and analysed by HPLC and TLC as described in Section 3.9.5.1(ii). The final product was found to contain 83,1% HMC 2 and 16,9% compound with 3-min HPLC retention time, proposed to be N-benzenesulphonylethylenediamine as discussed in Section 3.9.5.2(ii). Results indicate that HMC 2 hydrolyses under strongly acidic conditions. (Amundsen(19) has described this type of reaction as used to prepare N-acyl-ethylenediamines.)

(ii) In basic medium (pH 11,8)

A suspension (1,0%; pH 11,8) of linear sulphonamide HMC 2 (0,2 g) was prepared in a dilute solution of NaOH (1,0% m/v; 20,0 cm^3) and stirred at 20° C for 2 weeks. The reaction product was isolated and analysed by HPLC as described in Section 3.9.5.1(ii). The final product was similar to that of the acid-catalyzed hydrolysis reaction, and was found to comprise: 84,3% unreacted HMC 1 and 15,7% compound with 3-min HPLC retention time, proposed to be N-benzenesulphonylethylenediamine.

(As mentioned in Section 3.9.5.2iii Zienty(17) has reported that the products of both acid- and base-catalyzed hydrolysis of a linear sulphonamide, N-acetyl-N'-(p-nitrobenzenesulphonyl)-ethylenediamine, yielded a monoacyl aromatic sulphonyl derivative of ethylenediamine, as described in Section 2.5.2.3 and shown in Figure 2.8. Hence, N-benzoylethylenediamine can be expected to be a reaction product from both the acid-catalyzed and base-catalyzed hydrolysis of HMC 2.)

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

The objectives of this research were to synthesize and to study the chemistry of selected nitrogen-containing water-soluble polymers and monomeric crosslinking agents for the fabrication of ultrathin-film composite (UTF) reverse osmosis (RO) membranes.

More specifically, the polymeric precursors were to contain reactive nitrogen groups and the monomeric crosslinking agents were to be acid chlorides. The latter were to be soluble in an organic solvent which was immiscible with water and which, moreover, did not have a detrimental effect on the polysulphone support material upon which the membrane was to be formed; hexane was chosen for this purpose.

The UTF membranes were to be formed in situ by the interfacial polycondensation reaction between the nitrogen-containing precursor and a crosslinking agent upon a polysulphone support. These membranes were to be used for medium- and low-pressure desalination and preferably exhibit some tolerance to feedwaters of high and low pH levels and feedwaters containing chlorine. All membranes were to be tested for their baseline RO performance of salt rejection and permeate flux under standard conditions. Membranes showing efficient baseline RO performance were also to be evaluated for their RO performance with feedwaters considered to constitute harsh operating conditions, *i.e.* feedwaters containing chlorine and feedwaters of low and high pH.

In efforts to gain a better understanding of the chemical nature of the UTF membrane desalting barrier and of any changes which might take place at molecular level when the membrane was exposed to harsh operating conditions (with respect to feedwater composition), model compound studies were carried out on the non-polymeric analogues of poly-2-vinylimidazoline(PVAM) and the PVAM /3-chlorosulphonylbenzoyl chloride (SCl) UTF RO membrane structure. Evaluation of the membranes and the model-compound chemical studies were carried out concurrently.

In the following sections therefore, the following aspects of a novel UTF polyamide membrane, including chemicals used in its preparation, will be discussed:

(a) Choice and synthesis of multifunctional aromatic acid chloride crosslinking agents (Section 4.2).

(b) Investigation of the various synthesis techniques for, and characterization, of the water-soluble nitrogen-containing poly-2-vinylimidazoline (PVAM) material (Section 4.3).

(c) Development of PVAM/SCI flat-sheet membranes, including modifications of fabrication procedures and testing for RO performance results, leading to the stage at which the membranes were considered to be suitable to be made on larger scale in tube form and to be mathematically optimized (Section 4.4).

(This optimization comprised a study on its own and was carried out during a parallel project (1).)

(d) The chemical composition of a PVAM-FD/SCI membrane.

(e) Evaluation of the RO performance of the membranes with feedwaters containing chlorine and feedwaters of low and high pH (Section 4.5). (Some results presented have been taken from tests done on both flat-sheet and tubular membranes.)

(f) Finally, an attempt was made to ascertain whether the results obtained from model compound studies (see experimental Section 3.9) could be used to explain the behaviour of a PVAM/SCI membrane (Section 4.6).

4.2 CROSSLINKING AGENTS

4.2.1 BACKGROUND

When this study was initiated, the aromatic diacid chloride crosslinking agent isophthaloyl chloride (IPC) was being used successfully in the fabrication of the well-known UTF membranes: NS-101 of North Star(2,3) and PA-300 of Fluid Systems(3,4). These membranes were fabricated from the precursors polyethyleneimine (PEI) and an epiamine, respectively, with IPC as crosslinking agent.

Fabrication techniques as described in the literature for the preparation of NS-101 membranes(2,3) were followed in order to attain familiarity with the variables of importance and the overall technique of using interfacial polymerization, in the preparation of novel UTF RO membranes (see Section 3.4.2.1). When this initial work was completed, and when it was possible to duplicate the good results afforded by typical NS-101 membranes, the search began for new and improved crosslinking agents for use in the fabrication of novel UTF RO membranes.

According to Gregor(5), incorporation of a sulphonate group into a desalting membrane structure may offer certain advantages, including the following:

(a) Sulphonate membranes had been observed to be resistant to fouling; because of their stability in the ionized salt form, ionic binding of foulants to the surface of these membranes is lessened(6);

(b) The fixed charge of a sulphonate group could enhance salt rejection of a membrane due to the creation of an electrical field in the area of the desalting barrier;

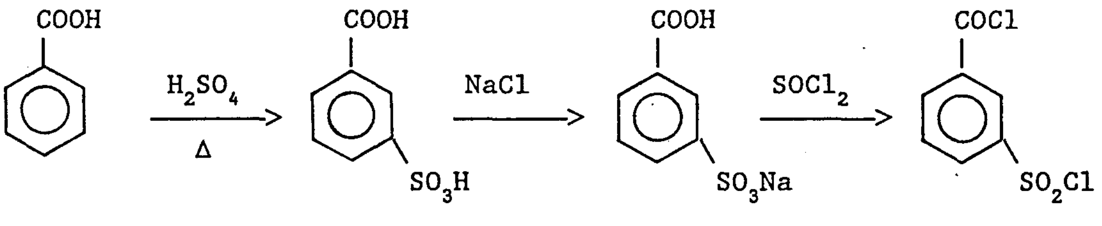
(c) Sulphonate polymers have a strong affinity for water, which could lead to greater water flux through the membrane.

The formation of sulphonamides by the condensation reaction between amines and sulphonyl chlorides is well-known and forms the basis of the well-known Hinsberg reaction(7). It was therefore decided to consider the incorporation of a sulphonic acid chloride group in a crosslinking agent. This was initially to be done by using a so-called "mixed" aromatic acid chloride crosslinking agent which was similar to IPC in that it had benzoyl chloride functionality, but which now had the extra functionality of a sulphonyl chloride group in place of one of the carbonyl chloride groups. Hence, 3-chlorosulphonylbenzoyl chloride (SCl) was prepared and used as crosslinking agent in UTF membrane fabrication. Later, the use of an aromatic trifunctional acid chloride containing sulphonyl chloride groups was investigated.

4.2.2 3-CHLOROSULPHONYLBENZOYL CHLORIDE (SCL)

4.2.2.1 Synthesis

3-Chlorosulphonylbenzoyl chloride (SCl) was synthesized in a two-step reaction(8), as described in Section 3.2.2:



SCL

The monosodium salt of 3-sulphobenzoic acid was prepared by the usual method of sulphonation of benzoic acid(9,10) and then converted into the acid chloride form with excess thionyl chloride, with DMF being used as catalyst. SCl was isolated by high-vacuum distillation in moderate yield, then characterized by mass spectroscopy and elemental analysis. This compound is hydrolytically unstable and can hydrolyse to the free-acid form in the presence of moisture. It was therefore carefully stored under dry conditions and re-distilled prior to use.

SCl appeared to be readily soluble in hexane and was used to fabricate UTF membranes as described in Section 4.2.2.2.

4.2.2.2 Membranes

(a) PEI/SCl membranes

In efforts to obtain indications as to the suitability of the newly prepared compound SCl as a crosslinking agent and whether its use held any advantage over that of the known crosslinking agent IPC, membranes were initially fabricated using the preparative technique for NS-101 membranes(2) mentioned in Section 4.2.1 and where the known crosslinking agent IPC was replaced by the new material SCl.

The chemistry of NS-101 membrane, prepared from PEI crosslinked with IPC is illustrated in Figure 4.1(3).

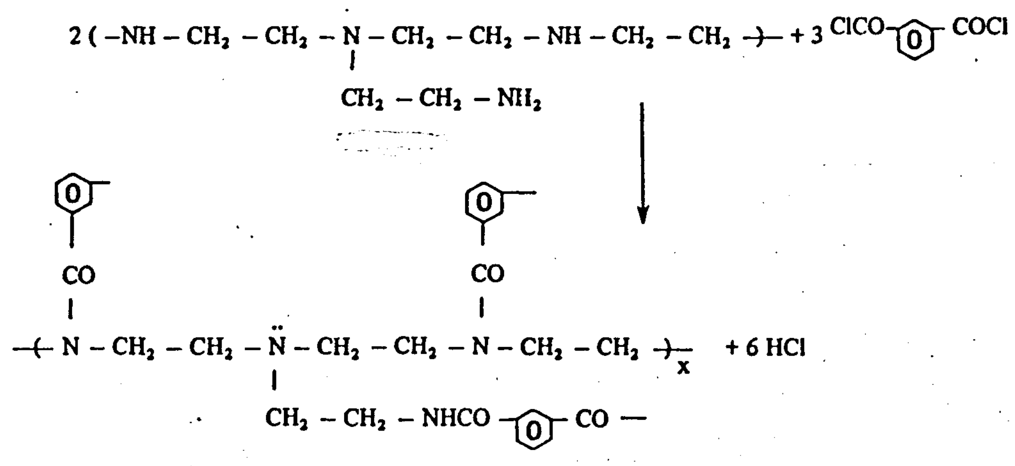


FIGURE 4.1: CHEMICAL STRUCTURE OF A NS-101 MEMBRANE(3)

The proposed chemical structure of a UTF membrane which is prepared from PEI precursor and crosslinked with SCl is illustrated in Figure 4.2.

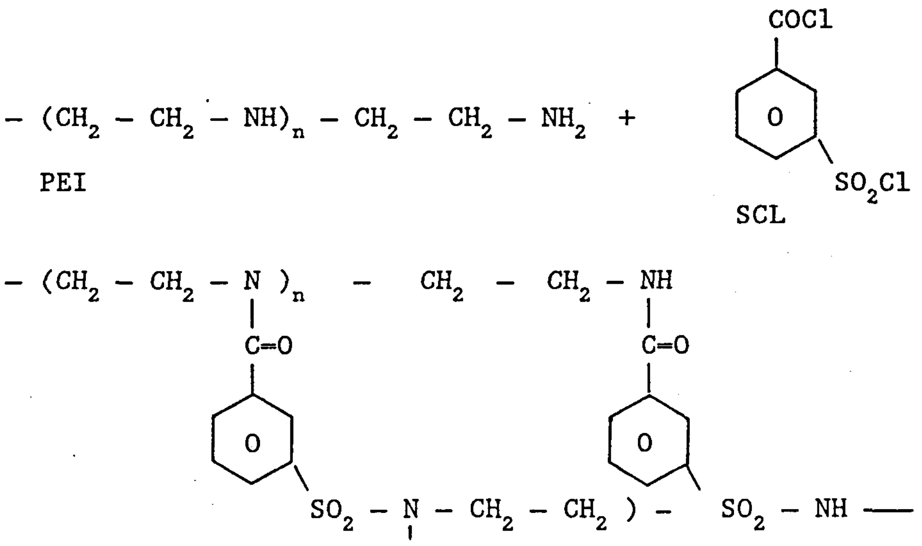


FIGURE 4.2: PROPOSED CHEMICAL STRUCTURE OF UTF MEMBRANE PREPARED FROM PEI AND SCL

The two types of membranes were fabricated under similar fabrication conditions, according to the procedure described in the experimental Section 3.5.1 and then tested under identical conditions, described in Section 4.4.2.1, and gave the following RO performances:

Membrane composition **(flat-sheet form)**	RO membrane performance
PEI/IPC	98,4% rejection; 600 lmd flux
PEI/SCl	98,7% rejection; 835 lmd flux

These initial results indicated, first, that the novel crosslinking agent SCl was indeed suitably reactive to participate in the interfacial polycondensation reaction with PEI to form a desalting barrier of high rejection and, second, its use led to the fabrication of membranes which had greater permeate fluxes. Further membranes were then fabricated with PEI and SCl under various conditions and tested for their RO performances. Results ranged from 89-95% rejection and 808-518 lmd flux, in tests done at an applied pressure of 4 MPa and 25°C for a 1% $NaNO_3$ solution (salt rejections for such solutions can be expected to be slightly lower than would otherwise be for 0,5% NaCl solutions(11)). The results of this study were the subject of South African patent(12) which covers the use of this novel crosslinking agent material in the fabrication of UTF RO membranes.

The improvement in permeate flux of membranes fabricated from PEI precursor with SCl as crosslinking agent may be ascribed to the fact that residual sulphonyl chloride groups on the membrane surface could hydrolyse to form sulphonic acid groups. Sulphonate polymers have a strong affinity for water (each sulphonate group is surrounded by many water molecules) and polymers with such groups on their surface are the most hydrophilic of known polymers(4). It is generally accepted that desalting barriers for aqueous systems applications must be hydrophilic (see Section 2.2.1), although the exact mechanism by which this affects membrane performance is not yet fully understood(13).

The use of SCl as crosslinking agent was expanded by fabricating further membranes from other novel precursor materials: polyvinylamine (PVA) and poly-2-vinylimidazoline (PVAM) with SCl as the crosslinking agent.

(b) PVA/SCl membranes

After a sample of a water-soluble polyamine material polyvinylamine (PVA) was obtained(14), two sets of flat-sheet UTF membranes were fabricated using PVA precursor: those crosslinked with IPC to form PVA/IPC membranes and those formed with SCl, namely, PVA/SCl membranes. The fabrication conditions, test conditions and the RO performances of these membranes are described in Appendix 1, Tables 1a and 1b.

The proposed chemical structure of a UTF membrane which is made from PVA precursor and crosslinked with SCl is illustrated in Figure 4.3.

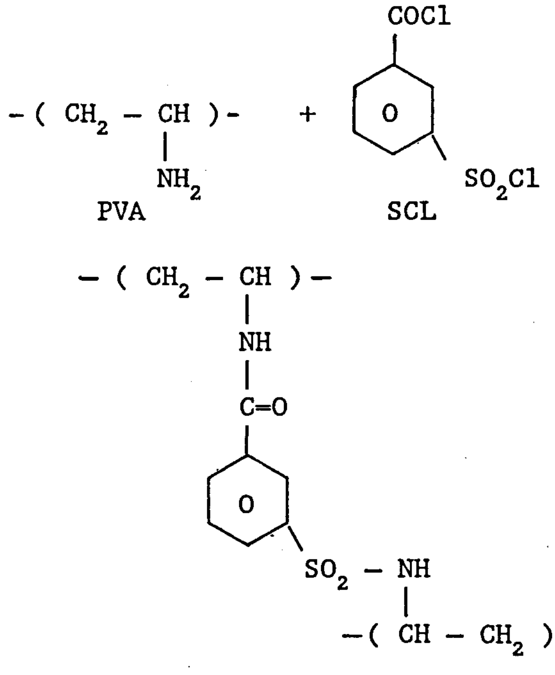


FIGURE 4.3: PROPOSED STRUCTURE OF A UTF MEMBRANE PREPARED FROM PVA AND CROSSLINKED WITH SCL

The following are average results for the RO performance of the two membrane types:

Membrane composition (flat-sheet form)	RO membrane performance
PVA/IPC	93,6 ± 0,7% rejection; 491 ± 26 lmd flux
PVA/SCl	97,4 ± 0,6% rejection; 757 ± 5 lmd flux.

Higher permeate flux and salt rejections were recorded for flat-sheet membranes fabricated with the sulphonic acid-containing crosslinking agent SCl. Similar results were obtained with tubular form PVA/SCl membranes, investigated during a parallel study[15]. In early work done on 500 mm tubular membranes, one of the experiments was designed to investigate the effects of crosslinking agent functionality and concentration on eventual membrane performance. The results indicated that better membranes were obtained from PVA/SCl rather than from PVA/IPC, when a concentration of 3 mass % crosslinking agent was used. The following average RO performance results were obtained with six tubular membranes of each of the two membrane composition types, tested with a 2000 mg/l NaCl feed solution at 2 MPa and 20°C.

Membrane composition (tubular form	RO membrane performance
PVA/IPC	86,5 ± 2,2% rejection; 720 ± 240 lmd flux
PVA/SCl	96,4 ± 0,4% rejection; 930 ± 42 lmd flux

Related investigations revealed that the concentration of the SCl crosslinking agent had a noticeable effect on PVA/SCl membrane performance. Membranes fabricated with a 1% solution of SCl showed an average performance of 93,1 ± 1,9% rejection and 860 ± 102 lmd flux, while similar membranes *fabricated with a 3% solution of SCl showed an average performance of 96,4 ± 0,4% rejection and 930 ±* 42 lmd flux[(15)]. These results are in accordance with claims, made by Riley[(16)], that variation of the concentration of a crosslinking agent in UTF membrane barrier formation has an important influence on membrane performance. The relationship between crosslinking agent concentration and charge density characteristics of a UTF membrane and the effect of the latter on membrane performance have been discussed by Riley[(17)].

(c) PVAM/SCl

Initial PVAM/SCl membranes were fabricated and tested according to conditions described in Appendix 1, Table 2, and showed good RO performance.

The evolution of this novel membrane system is described in detail later in Section 4.4.

4.2.3 1,3-BENZENEDISULPHONYL CHLORIDE (2S)

The rejection and flux of UTF membranes fabricated during this study were found to be improved by including one sulphonyl chloride group in an aromatic diacid chloride crosslinking agent, as described in Section 4.2.2. It was therefore considered to be of interest to investigate what effect the use of a similar crosslinking agent, now with two sulphonyl chloride groups (and no carboxylic acid groups) would have on RO membrane performance.

Commercially available 1,3-benzenedisulphonyl chloride (2S) was used in the fabrication of UTF membranes.

4.2.3.1 Membranes

PEI/2S:

Initial PEI/2S membranes were fabricated under conditions the same as those used in the fabrication of adequate PEI/SCl membranes[(12)] (eg. 0,7% PEI; 2,0% crosslinking agent and heat curing at 110°C/5 min.). The RO performance of these membranes was very poor, with typical results of below 20% rejection (and fluxes of up to 5 000 lmd) being recorded. In view of these results, no further membranes were prepared with 2S as crosslinking agent.

The effect of 2S as crosslinking agent on the RO performance of membranes fabricated with precursors other than PEI was not considered during this study.

The RO performance exhibited by the PEI/2S UTF membranes indicated that the desalting barrier was very inferior. This could have resulted from insufficient crosslinking during the interfacial polycondensation reaction and was initially suspected to have been caused by excessive hydrolysis of the acid chloride 2S to its free-acid form. Morgan claims that hydrolysis of an acid halide is definitely the principal interfering reaction in the interfacial polycondensation process[(18)]. The literature indicates, however, that both the aromatic sulphonyl chlorides and carboxylic acid chlorides are hydrolysed only slowly in aqueous medium. This was ascribed to their low solubility in water, which would offer protection against hydrolysis because this reaction can take place only in an aqueous medium[(18,19)]. Hence, hydrolysis of the crosslinking agent 2S could not be regarded as an adequate explanation for the formation of low-performance PEI/2S membranes. A more likely reason for the formation of inferior

PEI/2S desalting barriers was that the reaction of sulphonyl chlorides with diamines is slow compared with that of many carboxylic acid chlorides(20,21). The fabrication conditions used in the fabrication of PEI/2S membranes may have been inadequate to promote sufficient reaction. Reactivity of the sulphonyl chlorides may be improved by increasing the concentration and the time and temperature of the reaction. This should be investigated during further research, especially as 2S is commercially available.

4.2.4 3,5-DICHLOROSULPHONYLBENZOYL CHLORIDE (Cl2S)

Advances were made recently by overseas workers in the field of UTF membrane science by employing trifunctional acid chlorides, *e.g.* 1, 3, 5-Benzenetricarboxylic acid chloride (TMC), as crosslinking agents in the interfacial polycondensation reaction(22,23). In the fabrication of the NS-300- and FT-30-type membranes, it was reported that two of the acyl chloride groups of TMC were involved in the rapid interfacial polymerization reaction with an amine precursor to produce a polyamide which was, most likely, nearly linear in configuration. The third acyl chloride group could be expected to hydrolyse in an aqueous environment to an acid group, although some could react with another diamine molecule to produce chain-branching or crosslinking(24,25). It was initially believed that in the FT-30 membranes both reactions occur and that the ratio of branching to carboxyl group formation is approximately 1 : 1(24,25).

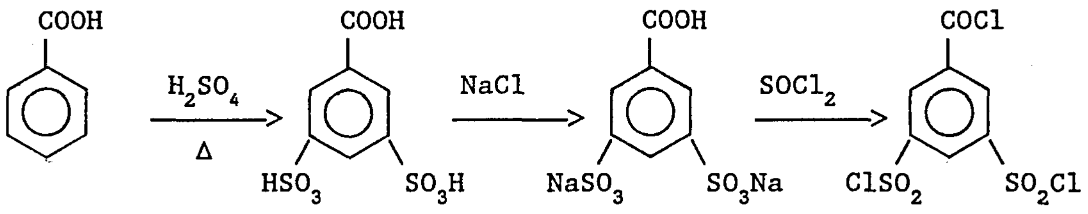
(ESCA studies later revealed that about 72% of the membrane polymer was in the crosslinked form and 28% of the membrane polymer contained the pendant free carboxylic acid group - see Section 2.3.4.5).

As PVAM/SCl membranes showing good RO performance had been obtained when the novel difunctional SCl crosslinking agent was used (Section 4.2.2) the logical next step was to investigate the effect of the use of a trifunctional crosslinking agent, with reactive groups similar to those found in SCl, on PVAM UTF RO membrane performance. 3,5-Dichlorosulphonylbenzoyl chloride (Cl2S) comprised the functionalities of two sulphonic acid chloride groups and one carboxylic acid chloride group. In the hypothetical event of no branching reaction taking place, only one of the two sulphonyl chloride groups and the one carboxylic acid chloride group were expected to take part in the interfacial polycondensation reaction with a diamine precursor to form linear chains. The reason herefore was that the reactivity of the sulphonyl chlorides with diamines is less than that of carboxylic acid chlorides(20, 21).

Hence, the more reactivity carboxylic acid chloride group was expected to react first, followed by reaction of one of the sulphonyl chloride groups. In the event of this being so, the reactive groups would be similar to those of SCl (the use of which resulted in the formation of membranes of good performance as described in Section 4.2.2.2) and not 2S (the use of which led to membranes of inferior performance, described in Section 4.2.3.1). The second sulphonyl chloride group could be expected to hydrolyse to its free acid form or react with amine precursor leading to chain branching.

4.2.4.1 Synthesis

This material was prepared in a two-step reaction, as described in experimental Section 3.2.4:



Cl2S

Benzoic acid was sulphonated at high temperature in the presence of fuming sulphuric acid to yield the difunctional sodium salt of 3-benzenesulphonic acid(26). This salt form was converted into the desired acid halide product after reaction with thionyl chloride(8) or phosphorus pentachloride(27). Experimental details are presented in Section 3.2.4.

Before an attempt was made to fabricate any membranes with this novel crosslinking agent, its solubility in hexane had to be determined. This limit was found to be about 3,2 mass %, which was considered sufficient for the fabrication of UTF membranes in flat-sheet form.

4.2.4.2 Membranes

PVAM/Cl2S

When this novel crosslinking agent became available for use, the first batches of the novel precursor material PVAM (PVAM-OD) had been synthesized. Although at this stage very little was known of the new PVAM material itself, it was nevertheless employed as precursor in the making of initial membranes which incorporated Cl2S.

PVAM-OD had already been used successfully with SCl and IPC in the fabrication of PVAM-OD/SCl and PVAM-OD/IPC membranes which exhibited salt rejections of about 70% and fluxes of about 2 000 lmd, when tested at a pressure of 4 MPa with a 5000 ppm NaCl feed solution at 20°C (see Table 2, Appendix 1). The development of PVAM membranes, including details pertaining to their fabrication and RO performance results are presented elsewhere (Section 4.4.2). The results which are mentioned here have been presented merely to justify the use of the novel material PVAM as precursor in the initial fabrication of membranes with the novel crosslinking agent Cl2S.

Membranes fabricated from PVAM-OD precursors (mol. masses PAN reagents 46 000 and 8 000) and Cl2S crosslinking agent led to the formation of barrier layers which gave the following average performances(28):

<u>Membrane composition</u>	<u>RO membrane performance</u>
PVAM-OD (PAN 46 000)/Cl2S	93,9% rejection; 1394 ± 50 lmd flux
PVAM-OD (PAN 8 000)/Cl2S	97,4 ± 0,6% rejection; 757 ± 5 lmd flux.

The RO performance of the PVAM-OD/Cl2S UTF membranes was the highest yet recorded for any membrane composition tested to date. Details of the fabrication, testing and results of these membranes are presented in Appendix 1, Table 2c.

Table 4.1 shows how the average RO performances of the PVAM-OD/Cl2S membranes compared with those of the earlier PVAM-OD/IPC and PVAM-OD/SCl membranes which were fabricated with difunctional crosslinking agents under otherwise similar fabrication conditions.

TABLE 4.1: COMPARISON OF RO PERFORMANCES OF PVAM-OD UTF MEMBRANES FABRICATED WITH VARIOUS CROSSLINKING AGENTS.

Membrane Composition	RO Membrane Performance	
	Salt Rejection [%]	Flux [lmd]
PVAM (PAN 8 000) + IPC	72,7 ± 0,4	1760 ± 58
PVAM (PAN 8 000) + SCl	84,8 ± 1,9	680 ± 58
PVAM (PAN 8 000) + Cl2S	96,4 ± 0,6	797 ± 86
PVAM (PAN 46 000) + IPC	65,2 ± 4,8	2174 ± 235
PVAM (PAN 46 000) + SCl	86,1 ± 3,0	881 ± 65
PVAM (PAN 46 000) + Cl2S	93,9 ± 1,8	1394 ± 50

The higher fluxes exhibited by the PVAM-OD/Cl2S membranes, compared with those of the PVAM-OD/SCl membranes, can be ascribed to the introduction of additional free-acid groups into the desalting barrier of the former membrane. Such groups would be formed upon hydrolysis of the unreacted third acid chloride group of the trifunctional crosslinking agent. As explained earlier (Section 4.2.4), it was envisaged that in the PVAM/Cl2S UTF membrane the free-acid group is likely to be predominantly a sulphonic acid group. This could lead to greater incorporation of bound water of hydration in the membrane surface, even with the expected enhanced degree of crosslinking achievable with a trifunctional crosslinking agent (as opposed to difunctional crosslinking agents).

(Cadotte has reported that when piperazine-isophthalamide membranes, fabricated with IPC as crosslinking agent, were modified by incorporation of the trifunctional acid halide TMC, NS-300 membranes of much higher flux performance were formed(22,25). Excellent performances were also shown by FT-30 membranes prepared from 1,3 diaminobenzene and TMC (see Section 2.3.3)(29)).

It was shown that the use of Cl2S crosslinking agent could give good membranes. Notwithstanding the apparent superiority of this crosslinking agent, its further use in the fabrication of UTF membranes did not form part of this study. Such work should, however, be done in the near future. The PVAM/SCl membrane system had been selected for thorough investigation.

4.3 POLY-2-VINYLIMIDAZOLINE (POLYVINYLAMIDINE)

4.3.1 INTRODUCTION

Considerations for the choice of poly-2-vinylimidazoline (PVAM), with its amidine nitrogen having only one reactive site, as novel polymeric precursor for UTF membrane fabrication have been discussed in Section 2.5.1.

The structure of homopolymeric PVAM is shown in Figure 4.4.

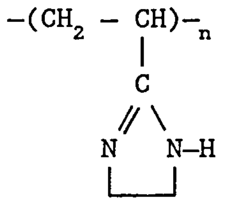


FIGURE 4.4: STRUCTURE OF HOMOPOLYMERIC PVAM

Initially, it was envisaged that the schematic structure of the crosslinked condensation product which should be formed after reaction of homopolymeric PVAM with the difunctional crosslinking agent 3-chlorosulphonylbenzoyl chloride (SCl) would be as shown in Figure 4.5. This should then represent the chemical structure of a PVAM/SCl UTF membrane's desalting barrier.

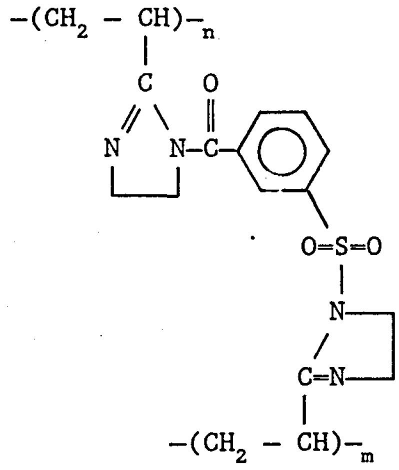


FIGURE 4.5: THEORETICAL STRUCTURE OF A HOMOPOLYMERIC PVAM/SCL UTF MEMBRANE

It will, however, be shown that there are many more structures present in a final PVAM/SCl membrane (see Section 4.4.7.2). As the synthesis and characterization of the PVAM material progressed and the synthesis of model-compounds began (Sections 3.8 and 3.9) it became apparent that the structure of PVAM shown in Figure 4.4, was, in fact, not correct. The PVAM product was a copolymeric mixture of ring-closed PVAM and its ring-opened hydrolysed form, poly-N-aminoethylacrylamide (PVAM-Hy), as shown in Figure 4.6.

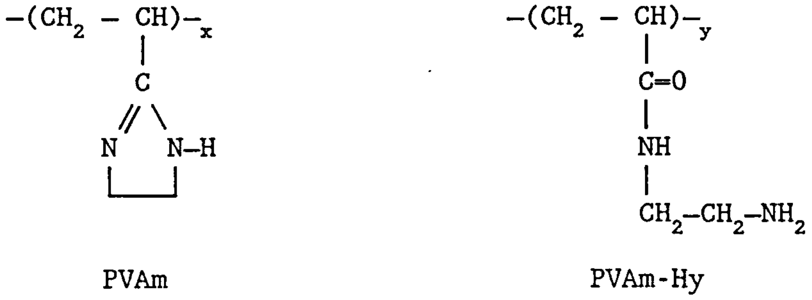


FIGURE 4.6: STRUCTURES OF THE REPEAT-UNITS OF PVAM AND HYDROLYSED PVAM (PVAM-HY)

Both the ring-closed and ring-opened repeat units of the copolymeric PVAM were expected to react with the SCI crosslinking agent in a condensation reaction and this was later confirmed by model-compound studies described in Sections 3.8.5 and 3.8.6.

PVAM was prepared by the reaction of an excess of ethylenediamine with polyacrylonitrile (PAN), in the presence of a sulphur-containing catalyst(30,31). The nitrile groups were converted to imidazoline (amidine) groups with the liberation of ammonia, as shown in Figure 4.7.

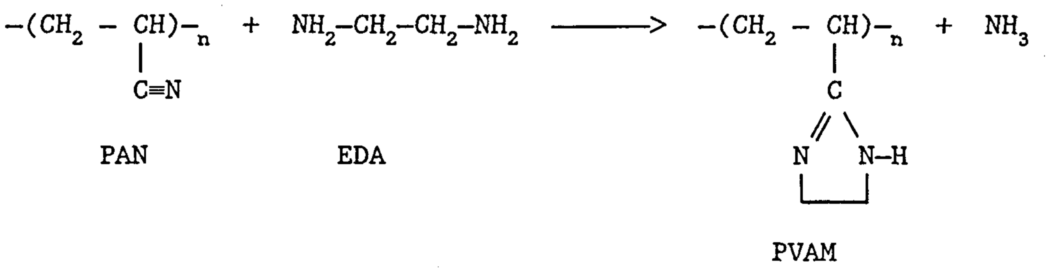


FIGURE 4.7: SYNTHESIS OF PVAM

The water-soluble product could be isolated either by precipitation in acetone, followed by drying under reduced pressure (OD method) or by freeze-drying (FD method). Details of the synthetic procedures used in the synthesis of PVAM are given in Section 3.3.2.

Prior to the synthesis of PVAM, PAN of suitably low molecular mass had to be synthesized. PAN was synthesized because the molecular masses of commercially available PAN were considered to be too high for the requirements of this study, and practical problems were encountered during the preparation of PVAM from commercial PAN (molecular mass 200 000).

This section (4.3) will include a description of the two procedures employed to modify PAN in the synthesis of PVAM and the characterization of the products, including a quantitative determination of the hydrolysed form of amidine groups in PVAM, i.e. PVAM-Hy and the ethylenediamine impurity. Mention will also be made of the fully hydrolysed PVAM material (PVAM-Hy) and an attempt made to incorporate aromaticity into the PVAM structure (in an effort to retard the spontaneous hydrolysis which polymers with amidine groups undergo).

4.3.2 POLYACRYLONITRILE

In the fabrication of the well-known NS-100-type membrane of North Star, it was found that the molecular mass of the more effective grades of polymeric precursor (PEI) ranged from 10 000-60 000(32). For the preparation of PVAM precursor of similar molecular mass, for use in membrane fabrication, it was deemed preferable that the PVAM synthesis should be carried out using polyacrylonitrile (PAN) reagent of molecular mass ranging from about 6 000-33 000. This was because the average molecular mass of a homopolymeric PVAM product was calculated to be 1,8 times that of the PAN reagent used(33), as will be described in Section 4.3.2.2. Although PVAM is not a homopolymer and this relationship is therefore not accurate, it was used as a guide.

4.3.2.1 Preparation

Acrylonitrile polymerizes readily by a free-radical mechanism(34,35). Mechanisms of polymerization have been well reviewed by Thomas(36). PAN was synthesized by solution polymerization of acrylonitrile in N,N -dimethylformamide (DMF) at about 75°C with benzoyl peroxide as initiator, over a 24 h period. The crude product was precipitated in an aqueous medium, filtered and dried, to yield a dark-brown polymer. Experimental details are presented in Section 3.3.1.2.

The colour of a PAN product is closely related to the conditions under which the polymerization is carried out, in particular the reaction temperature which, in fact, depends on the nature of the initiator. It is generally accepted that the lower the reaction temperature is, the less coloured the PAN will be(37).

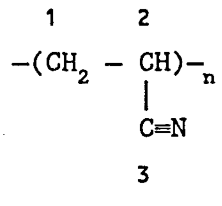
Later, an alternative method for the preparation of PAN was investigated. This involved the polymerization of acrylonitrile with a redox system initiator, in aqueous medium (see experimental Section 3.3.1.3). Selection of this polymerization method was prompted by the desire to obtain a whiter PAN product. It had further advantages in that the reaction solvent was much cheaper and safer to use and the polymerization temperature lower. An initial small-scale experiment gave a white PAN precipitate. The molecular mass of the product was later determined to be 263 000, which was too high for the requirements of this study. (If the molecular mass is controlled by use of a mercaptan regulator in the reaction, this could form an alternative route for the synthesis of PAN).

4.3.2.2 Characterization

^{13}C nmr spectroscopy:

PAN was characterized by ^{13}C nmr spectroscopy in deuterated-DMSO. Despite the dark colour of the product, there was no evidence of impurities. The ^{13}C nmr data are presented in Table 4.2.

TABLE 4.2: ^{13}C NMR DATA FOR POLYACRYLONITRILE (PAN)



$$-(CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}})-_n$$

Carbon atom	δ (DMSO)
1	32,67
2	26,73; 27,35; 27,83
3	119,56 - 120,28

The three bands for the methine carbon (C_2) are assigned to iso-, hetero- and syndiotactic triads, which is in accordance with what has been found in the literature(38). There appear to be seven pentad lines in the δ range of 119,56 to 120,28 for the nitrile carbon, indicating that atactic polyacrylonitrile is essentially a polymer with a random configuration.

Molecular mass determination

The intrinsic viscosity of PAN was determined by dilute-solution viscometry in DMF at 30°C(39). The average molecular mass of PAN could be calculated from the viscosity by using the K-constant and a - constant values for PAN(40) and the Mark-Houwinck equation:

$$[\eta]_i = kM_i^a$$
$$\therefore M_i = \frac{[\eta]_i^{1/a}}{k}$$

where η_i = intrinsic viscosity, experimentally determined
K = $33{,}5 \times 10^{-5}$
a = $0{,}72$
M_i = molecular mass

The theory governing this technique of molecular mass determination has been well described by Allcock(41).

The determination of the molecular mass of a PVAM product by dilute-solution viscometry is not easy. The required constants for substitution in the Mark-Houwinck equation do not exist. The molecular mass of homopolymeric PVAM could be determined by calculation from the molecular mass of the PAN starting material. The increase in molecular mass of polymer which occurs during the preparation of PVAM from PAN takes place according to a specific ratio. For a homopolymeric product resulting from the reaction of PAN and ethylenediamine, this factor is 1,8(33). Due to the hydrolysis of 2-imidazoline groups in PVAM, giving rise to its copolymeric structure, the determination of the molecular mass of PVAM in this manner is not accurate. In the text, an indication of the molecular mass of a PVAM precursor will be given by recording the molecular mass of the PAN reagent from which it was prepared.

During the course of the research on PVAM membranes and of later development work, more than 30 batches of PAN were synthesized. The molecular masses of the PAN products obtained under the reaction conditions used to date in this study ranged from about 8 000 to 24 000 (see Appendix 2, Table 1).

4.3.3 PVAM-OD

4.3.3.1 Preparation

The synthesis and isolation of PVAM by the so-called oven-drying method is described in the experimental Section 3.3.2.2. PVAM-OD was made in two ways, namely, by reacting PAN with ethylenediamine in DMF with thioacetamide or elemental sulphur being used as catalysts(30). The crude product was precipitated in acetone and then filtered and oven-dried under reduced pressure to yield the dark-brown product PVAM-OD. There seemed to be no difference between the courses of the two reactions, or between the appearances and yield of products of these two reactions. Sulphur was then chosen as the preferable catalyst for future use, because of its being cheaper and safer (thioacetamide is a listed carcinogen). Only later in the study, when it was established that PVAM was in fact a mixture of ring-closed and ring-opened (hydrolysed) products and that the percentage of the hydrolysed product could be quantified (Section 4.3.4.3), could a difference be seen between PVAM-OD products of.

reactions catalyzed by the two compounds. There was ^{13}C nmr spectroscopic evidence that the thioacetamide-catalyzed PVAM-OD product contained about 5% more hydrolysed product than the sulphur-catalyzed product did (see Table 4.4, Section 4.3.3.2). This further confirmed the correctness of the choice of sulphur as reaction catalyst.

The increasing demand for PVAM material for fabrication of UTF tubular membranes, carried out during a parallel project(1), soon necessitated the preparation of larger-sized batches of PVAM. When this was done, it was soon observed that during the precipitaton of the crude PVAM-OD product into acetone, if the crude PVAM was left exposed to the air and not covered by acetone, it became very tacky and difficult to handle.

4.3.3.2 Characterization

(a) Elemental Analysis

PVAM-OD products were initially analysed by elemental analysis. Typical results obtained for samples from some of the larger batches (about 300 g quantities) are presented in Table 4.3.

TABLE 4.3: RESULTS OF ELEMENTAL ANALYSES OF PVAM-OD BATCHES

$C_5H_8N_2$	Batch	% C	% H	% N	%X
Calculated		62,5	8,33	29,17	
Found	1	55,7	7,55	25,0	11,8
	2	59,5	7,95	25,65	7,1
	3	58,9	7,7	25,45	8,0
	4	59,0	8,0	26,35	6,7
	5	56,1	7,35	23,7	12,9

Review of the above results made it clear that a large percentage of elements was unaccounted for *i.e.* [100 - % (C + H + N)]. This figure has been included in Table 4.3 as % X, as at the time of obtaining these results, it was not known what elements this figure represented. (The presence of oxygen from PVAM-Hy repeat units had not been proven.)

In efforts to explain these data and to reach a clearer understanding of the chemistry of the PVAM-OD product, further chemical analyses were done.

(b) Infrared spectroscopy

Infrared spectroscopic analysis was not possible because a suitable KBr disc could not be pressed. During attempts to prepare such a disc, the PVAM-OD material again became tacky and difficult to handle.

(c) ^{13}C nmr spectroscopy

A ^{13}C nmr spectrum was obtained for one of the first PVAM-OD products. Due to the apparent complexity of the spectrum, however, no progress was made towards explaining the structure of PVAM-

OD. Only later, and after parallel research including model-compound studies on monomeric amidine-type structures (Section 3.9), was it possible to accurately interpret the nmr spectra of PVAM. This is described in more detail for PVAM-FD in Section 4.3.4.3.

It was then established that PVAM was a copolymeric mixture of ring-closed PVAM and its hydrolysed form of ring-opened poly-N-aminoethylacrylamide (PVAM-Hy). The latter could comprise up to 20% of the repeat units in PVAM, as determined from nmr data.

The following short discussion of the quantitative determination of PVAM-Hy in samples of PVAM-OD is presented here for the sake of completeness, although the work was carried out only after the investigations into the PVAM-FD material as described in Section 4.3.4.3.

Although not many ^{13}C nmr spectra have been recorded for PVAM-OD samples, the few that were available were used to determine the approximate percentage of hydrolysis product present in PVAM-OD. Results are presented in Table 4.4. The methods used in calculations were similar to those described in more detail later for similar determinations in PVAM-FD samples (Method 1, Method 2, Method i, Section 4.3.4.3.) It was not possible,however, to use the method which involved the integration of the methylene carbons (Method ii). This was due to the presence of suspected traces of unremoved reaction solvent DMF in PVAM-OD whose signals overlapped with the methylene signals of the polymer, causing the integration to be "inaccurate".

TABLE 4.4: APPROXIMATE PERCENTAGES OF PVAM-HY PRESENT IN BATCHES OF PVAM-OD, AS DETERMINED BY VARIOUS METHODS
(Calculations based on ^{13}C nmr data)

PVAM-OD Batch No.	PVAM-Hy [%]		
	M1	M2	Mi
1[a]	22,73	21,95	-
OD T[a]	21,4	22,5	14,9
OD S[b]	13,7	15,8	14,3

Legend

a - PVAM-OD prepared with thiosulphate catalyst.
b - PVAM-OD prepared with sulphur catalyst.
M1 - Method 1]
M2 - Method 2] Methods described in Section 4.3.4.3d.
Mi - Method i]

The PVAM-OD products from reactions in which thioacetamide and sulphur catalysts were used, were analysed by ^{13}C nmr spectroscopy. Results showed that these products differed in the quantity of hydrolysed product present. The sulphur-catalyzed reaction product contained about 15% of the hydrolysed form, PVAM-Hy, while the thioacetamide-catalyzed product contained about 20-22% of PVAM-Hy. (The method used for these calculations is described in Section 4.3.4.3d.)

4.3.3.3 Discussion

PVAM-OD was considered to be a very hydrophilic product[42]. This property could explain why the powdery product become tacky during prolonged handling and upon exposure to the air (conditions which were unavoidable during the experimental procedure). It could have explained also why the percentage yield of some of the PVAM-OD products from certain batches was determined to be greater than 100%. Because of the hydrophilic nature of PVAM-OD it could be expected to absorb water vapour readily upon exposure to the atmosphere and the drying conditions used in the OD-preparation method may not be sufficient to remove effectively all traces of water from the polymer. Initially, therefore, it was suspected that the unaccounted - for percentage shown by the results of the elemental analysis (% X in Table 4.4), could be ascribed to the contribution by oxygen derived from absorbed water held by the PVAM-OD. Taking this property into consideration and because of the difficulties which arose during the synthesis of PVAM by the OD-method, an alternative method for the preparation and isolation of PVAM was used. A number of UTF flat-sheet membranes and a few tubular membranes were, however, made with this PVAM-OD material; results of their RO performances are presented in Section 4.4.2.

The following section, Section 4.3.4, describes the preparation of PVAM by the FD-method, during which there was minimal exposure of the product to the atmosphere and during which no handling problems arose. PVAM-OD and PVAM-FD products are both copolymeric mixtures of PVAM and its hydrolysed form PVAM-Hy. It has been shown that PVAM-OD contains a higher percentage of the hydrolysed form than PVAM-FD does (see Tables 4.4 and 4.8).

4.3.4 PVAM-FD

4.3.4.1 Preparation

The preparation and isolation of this material is described in detail in the experimental Section 3.3.4.3. PAN was reacted with an excess of ethylenediamine under a nitrogen atmosphere, in the presence of sulphur as catalyst. Ethylenediamine acted both as reagent and solvent. On completion of the reaction, within 24 hours at reflux temperature, the product was isolated by freeze-drying[30]. More efficient drying was achieved when the crude product was divided up into smaller quantities in drying flasks for freezing which were then attatched to the freeze-dryer. The dry PVAM-FD product was a very light brown, fine powder. It looked very different from the dark-brown, sometimes coarse, PVAM-OD material. Although rather lengthy drying times were required, depending on the operating vacuum and volume of solution per flask to be dried, this method of preparation was preferred for the following reasons:

(i) no difficult handling problems arose, contrary to what happened during the PVAM-OD preparation;

(ii) only one solvent was generated as waste product, compared with the waste product from PVAM-OD synthesis which was a mixture of DMF and ethylenediamine, so that recovery or disposal was simplified;

(iii) the PVAM-FD product had a good appearance.

The following later reinforced the choice of PVAM-FD as the preferred UTF membrane precursor-material:

(i) PVAM-FD contained less of the hydrolysed form of PVAM-Hy (although it did contain some monomeric ethylenediamine impurity, as described in Section 4.3.4.3);

(ii) the first 99% salt rejection PVAM/SCI membranes were fabricated from PVAM-FD precursor, as described in Section 4.4.4.2.

During the course of the research, more than 30 batches of PVAM-FD were synthesized. For easy reference, PAN reagent batch numbers with their molecular masses and the corresponding PVAM-FD products batch numbers have been tabulated. These are presented in Appendix 2, Table 1.

4.3.4.2 Elemental Analysis

The purity of the newly synthesized PVAM-FD product was determined and compared with that of the PVAM-OD product. Elemental analysis was done for the first small-scale trial reaction product (FDO) and then for some larger-scale batches of PVAM-FD (FD1-12).

The elemental analysis results of all PVAM-FD samples analysed to date are presented in Table 4.5.

TABLE 4.5: RESULTS OF ELEMENTAL ANALYSES OF PVAM-FD

$C_5H_8N_2$	Batch	% C	% H	% N	%X
Calculated		62,5	8,33	29,17	
Found	FD 0	60,4	8,1	28,7	3,8
	1	58,1	8,25	29,05	4,7
	2	57,8	8,3	28,1	5,8
	3	59,7	8,0	28,85	3,5
	4	60,0	8,15	28,6	3,3
	5	57,5	8,0	28,7	5,8
	6	56,7	8,3	29,3	5,7
	7	58,1	8,1	29,2	4,6
	8	56,85	8,25	28,8	6,1
	9	56,1	8,25	27,7	8,0
	10	56,4	8,6	28,7	6,3
	11	56,7	8,35	28,5	6,4
	12	57,2	8,3	28,25	6,25

It was noted that the later batches of PVAM-FD (Nos 5-12) appeared to contain a slightly greater percentage of elements unaccounted for (% X) than did the earlier batches (Nos 1-4). Batches 1-4 were prepared using about 160g PAN as starting material. For batches 5-12 almost double the quantity, about 300g, of PAN was employed. It was suspected that moisture could be entering the reaction medium via the PAN starting material which may not have been sufficiently dry since ,when it was prepared, the PAN was precipitated from water.

These quantitative results indicate that the PVAM-FD products appear to be of a quality superior to that of the PVAM-OD products. The percentage of elements unaccounted for here (% X) was consistently lower than that found for the PVAM-OD samples, as seen in Table 4.3. At this stage of the research, the most likely explanation for this finding was that during that FD-method of preparation there was less opportunity for the PVAM-FD material to be exposed to the air and that water vapour and water absorption would have been reduced. Care had to be taken, however, when the dried PVAM-FD product was transferred from the drying flask to a storage vessel. Prolonged exposure led to the PVAM material becoming darker and tacky, as happened during the preparation of the OD-product. At this stage, the freeze-drying method for PVAM synthesis was considered the best technique and all further research was carried out on the PVAM product prepared by the FD-method *i.e.* PVAM-FD.

In the following Section (4.3.4.3) in which the nmr spectroscopic analysis of PVAM is described, it will be shown that it was not only water which was the cause of the difference between the calculated values and those found by elemental analysis. In the presence of moisture or water, the closed amidine ring of PVAM can hydrolyse to form a new linear ring-opened structure with an amide and terminal amine functionalities, and the amide oxygen will have affected the elemental analysis results, as would the extra two hydrogen atoms.

Ethylenediamine was also found to be present as an "impurity" in PVAM-FD (see Section 4.3.4.3c). This would also influence the analytical results.

4.3.4.3 Nuclear Magnetic Resonance Spectroscopic Analysis (nmr)

(a) Background

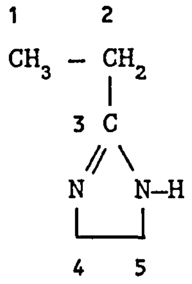
High-resolution ^{13}C nuclear magnetic resonance (nmr) spectra can be obtained of highly viscous solutions and solids$^{(43)}$. (Unfortunately, the availability of the accessory required for solid-state measurements was not available during this study. Such measurements might have greatly facilitated elucidation of the structure of the crosslinked and insoluble PVAM membrane desalting barrier. Future work should include the application of this technique of solid state nmr analysis.) A polymer chain with a high degree of stereo-regularity should exhibit a fairly simple ^{13}C nmr spectrum *i.e.* that of the polymer's single repeat unit. ^{13}C nmr spectra of PVAM samples were obtained using solutions of about 25% concentration in deuterium oxide (D_2O) solvent. The latter was added to the sample just prior to recording, to minimize interaction with the PVAM. In order to facilitate the interpretation of the PVAM spectra, extensive use was made of the ^{13}C nmr spectra of the model compounds of PVAM.

Model imidazolines and amides were prepared and characterized (Section 3.9) in order to verify the amide and imidazoline functional groups peak assignments. (A model compound is a simple monomeric compound which models the repeat unit of the polymer. An account of the choice of a PVAM/SCI UTF membrane's model compounds is presented in Section 2.5.3.)

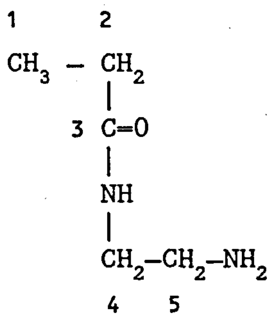
The initially proposed structure of the PVAM homopolymer (shown in Figure 4.4) would be represented by the model compound 2-ethylimidazoline (referred to in the text as MC). It was during the preparation of this monomeric compound, however, that it was realised just how highly susceptible the cyclic 2-imidazoline type structure is to hydrolysis $^{(44,45)}$. 2-Ethylimidazoline hydrolyses to form N-propionylethylenediamine (referred to in the text as HMC). Hence, the 2-imidazoline repeat units of PVAM would be expected to undergo a similar reaction. Dragan *et al.*$^{(46)}$ reported that during the reaction of PAN and diamines in aqueous medium the nitrile group undergoes an aminolysis hydrolysis transformation to form an aminoethylacrylamide group. Supportive nmr data have been presented. Hence, although the preparation of PVAM from PAN and ethylenediamine was done in an organic medium, the presence of any moisture in the system may lead to some degree of hydrolysis. These two observations suggested the probability that some hydrolysis may take place and that the PVAM material could in reality be a copolymeric mixture of ring-closed PVAM and the ring-opened hydrolysed product, poly-N-aminoethylacrylamide (Figure 4.6). This was later confirmed by ^{13}C nmr analysis, as will be discussed in this section. Copolymeric PVAM would have two model compounds: ring-closed, unhydrolysed 2-ethylimidazoline (MC) and ring-opened or linear, hydrolysed, N-propionylethylenediamine (HMC). Their chemical structures and ^{13}C nmr data are presented in Table 4.6. This will often be referred to in the discussion of the elucidation of the ^{13}C nmr spectra of PVAM.

TABLE 4.6: ^{13}C NMR DATA OF PVAM'S MODEL COMPOUNDS 2-ETHYLIMIDAZOLINE (MC) AND N-PROPIONYLETHYLENEDIAMINE (HMC)

MC



HMC



Carbon atom	MC δ (DMSO)	HMC δ (DMSO)
1	10,98	9,95
2	22,10	28,58
3	168,60	173,08
4	44,33	42,31
5	49,33	41,44

(b) Discussion

The analysis of a ^{13}C nmr spectrum of PVAM-FD and the assignment of the signals to various carbon atoms will be described here, taking PVAM-FD 8 as an example. The ^{13}C nmr spectrum of a sample of PVAM-FD (batch 8) is shown in Figure 4.8. Table 4.7 contains the data subsequently assigned to the peaks in the spectrum of PVAM FD-8.

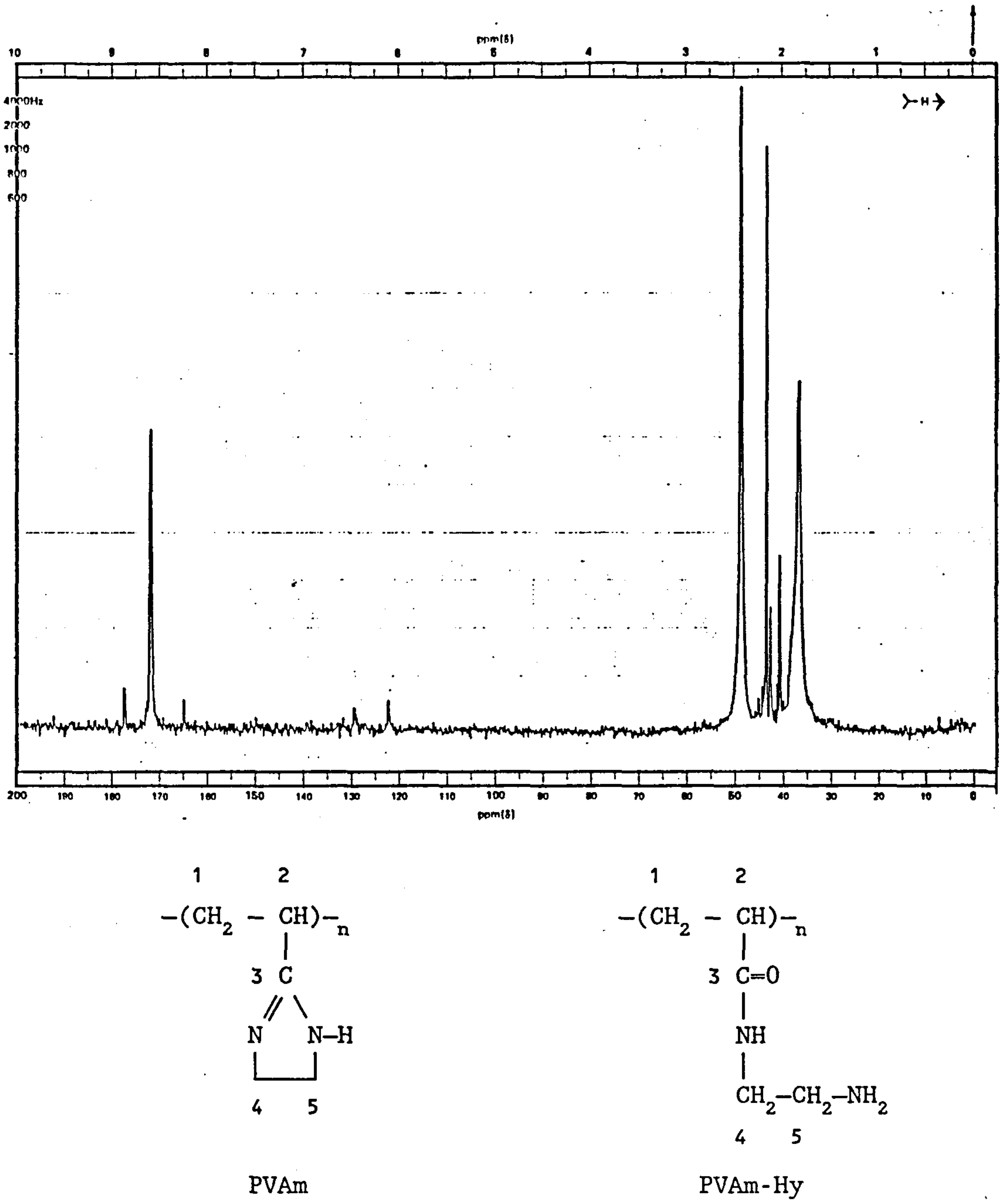


FIGURE 4.8: ^{13}C NMR SPECTRUM OF PVAM-FD 8

The expected chemical-shift values for the carbon atoms in the PVAM structure could be calculated with the aid of empirical parameters$^{(47)}$ from the model compound spectra data, presented in Table 4.6.

Consideration was given first to elucidating the originally proposed structure of PVAM in the ring-closed form (Figure 4.4) whose model compound equivalent is 2-ethylimidazoline (MC).

The methyl carbon (C_1) of MC resonates at δ 10,98. Calculation of the α-,β- and γ- shift effects showed that the corresponding methylene carbon (C_1) in the polymeric form should resonate at δ 35,98$^{(48)}$. The methylene carbon (C_2) in MC resonates at δ 22,10 and calculation of the α-,β- and γ- shift effects indicated that the corresponding methine carbon (C_2) of the polymer should resonate at δ 38,10$^{(48)}$. Both carbon atoms of the PVAM's backbone structure were thus apparently in the region of δ 35-39. The broad signal at δ 36,48 - 38,56 in the ^{13}C nmr spectrum of PVAM-FD 8 (Figure 4.8) would therefore include these two carbon atoms.

The two equivalent methylene carbon atoms (C_4 and C_5) of MC resonate at δ 49,33. This material exhibits equivalence since it is able to assume a tautomeric form. The signal at δ 48,82 in the ^{13}C nmr spectrum of PVAM-FD 8 was therefore assigned to the equivalent methylene carbons of the 2-imidazoline ring.

The -C = N group of the model compound (MC) resonated at δ (DMSO) 168,56. The signal at δ (D_2O) 172 in the polymeric form was therefore assigned to the -C = N group. The slight shift in value could have been due to a solvent effect.

The signal of the -C = N group (C_3) of the polymer under discussion (PVAM FD-8) was observed to be split into two bands (in other PVAM-FD samples this signal was split into as many as seven bands). This phenomenon is explained by the presence of the different configurations which could be formed at this site. In the spectrum of the PAN reagent, the nitrile group was also split into 7 bands. (The appearance of three bands in the noise-decoupled nitrile and methine carbon absorptions for 20% (w/v) solutions of PAN in DMSO has been reported(38). These were assigned to hetero-, iso-, and syndiotactic triads. Upon further dilution of the sample (to 5% w/v), resolution was improved and up to six pentad lines were observed. The topic of polymer configuration has been discussed by Stothers(38), Wirthlein(43) and Bovey(49)). As PVAM is prepared from PAN with reaction taking place at the nitrile carbon site, configurations similar to those described for PAN can be expected in PVAM(50).

Assignment of the remaining signals (as yet unidentified) in the spectrum under discussion was possible after consideration was given to the presence of the ring-opened hydrolysis product PVAM-Hy as mentioned in Section 4.3.4.3a.

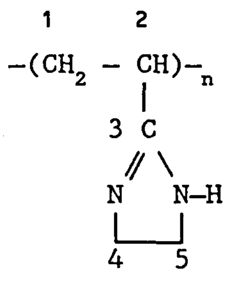
The model compound of the PVAM-Hy repeat unit is N-propionylethylenediamine (HMC). The amide carbon of HMC (C_3) resonates at δ (DMSO) 173. The position of the signal at δ (D_2O) 177 in PVAM-FD 8 is characteristic of an amide group(43). Ring-opening of the amidine-type structure would render the two methylene groups (C_4 and C_5) no longer equivalent, so that they would therefore now have different shift values. This is clear from the ^{13}C nmr spectrum of HMC in which shift values δ (DMSO) 42,31 and 41,44 were observed. Hence, the small signals at δ (D_2O) 42,59 and 40,58 in the PVAM-FD 8 ^{13}C nmr spectrum were assigned to the two now unequivalent methylene carbons of the ring-opened hydrolysis product PVAM-Hy. The assignments made for PVAM-Hy here were later verified after the ^{13}C nmr spectrum of fully hydrolysed PVAM material had been recorded (Section 4.3.5 , Figure 4.11).

A very strong signal at δ 43,41 in the ^{13}C nmr spectrum of PVAM-FD 8 remained unaccounted for. From the appearance of the signal it was suspected to be due to the presence of a monomeric species. (It may be relevant to mention that PVAM had a faint but rather unpleasant odour. As polymers should be odourless it was thought most likely that this odour was due to the presence of some monomeric impurity.) Ethylenediamine, used as the reagent in PVAM preparation, was thought to contribute to this signal (and odour) and this was investigated as described here. Ethylenediamine was added to a sample solution of PVAM in deuterium oxide, of which a ^{13}C nmr spectrum had been recorded, and the ^{13}C nmr spectrum of this mixture was recorded. Intensification of the signal at δ 43,41 (relative to the other signals) would have proved that the signal at δ 43,41 was in fact that of an ethylenediamine impurity in

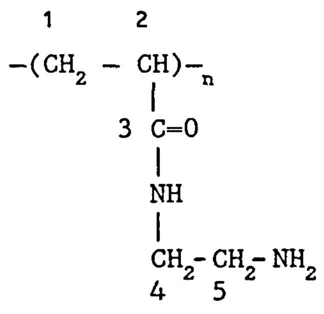
PVAM-FD 8. Adding ethylenediamine (more than was necessary) gave a very intense peak at δ 43,84. The ^{13}C nmr shift-value for pure ethylenediamine is δ (D_2O) 44,06. The closeness of these shifts to the δ 43,41 in PVAM-FD 8, indicates that ethylenediamine was present as a monomeric impurity (freeze drying was not expected to be absolutely effective in removing the solvent from a polymer). ^{13}C nmr spectra of all PVAM-FD samples showed a sharp signal at about δ 44, indicating the presence of ethylenediamine. PVAM-OD samples did not show such a distinct signal in the spectra recorded. The explanation for this apparently much lower quantity of ethylenediamine may be because during PVAM-OD synthesis, it is more effectively removed from the PVAM product by the OD-method of precipitation in acetone and filtering which forms part of the isolation procedure (see Section 3.3.2.2).

Ethylenediamine could be partly washed out of the PVAM-FD samples by an acetone extraction, as described in the experimental Section 3.3.2.4, to yield the so-called PVAM-CFD product.

TABLE 4.7: ^{13}C NMR DATA FOR PVAM-FD 8



PVAm



$$-(\mathrm{CH_2}-\mathrm{CH})_n-\quad \mathrm{CH}\!-\!\mathrm{C(=O)}\!-\!\mathrm{NH}\!-\!\mathrm{CH_2}\!-\!\mathrm{CH_2}\!-\!\mathrm{NH_2}$$

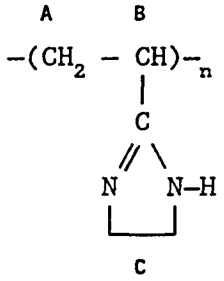
PVAm-Hy

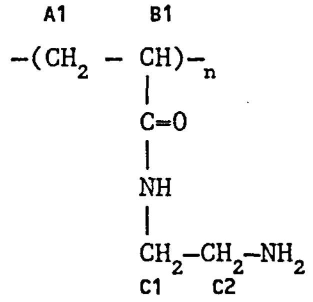
Carbon atom	δ (D_2O) PVAM	δ (D_2O) PVAM-Hy
1	36,48 - 38,56	36,48 - 38,56
2	36,48 - 38,56	36,48 - 38,56
3	172,1; 172,3	177,60
4	48,82	42,59
5	48,82	40,58

(c) **Quantitative Determination of the Ethylenediamine impurity**

The RO performance of tubular membranes fabricated from PVAM-FD batches 18 and 19, recorded during a parallel research project, were far below the expected level(51). As all fabrication variables had been kept constant, this was most probably due to the use of "below-standard" batches of chemicals. A likely cause of a batch of PVAM precursor being "inferior" would be the presence of high concentrations of ethylenediamine, which could compete with the polymeric precursor for reaction with the crosslinking agent during the in situ membrane formation reaction. This could lead to formation of an inferior membrane desalting-barrier (see Section 4.4.4.2). It therefore became necessary to be able to measure the amount of this impurity present in PVAM-FD precursors before approving their use in membrane studies. Once all the signals in a PVAM-FD ^{13}C nmr spectrum had been identified (as described in the previous Section 4.3.4.3b), the results obtained from integration of the spectrum could be used to determine the percentage of ethylenediamine present in a PVAM-FD sample. How this was to be done can best be explained by way of an example, using PVAM-FD 8.

As already described, PVAM-FD 8 comprises the two polymeric repeat-unit structures PVAM and PVAM-Hy, in addition to the monomeric impurity ethylenediamine. The polymeric structures are again presented here (see Figure 4.9), with their carbon atoms "labelled", to simplify the discussion and calculation which follow. The integrated spectrum of PVAM-FD 8 (δ 20 - 70) is shown in Figure 4.9, with identification of the various signals.





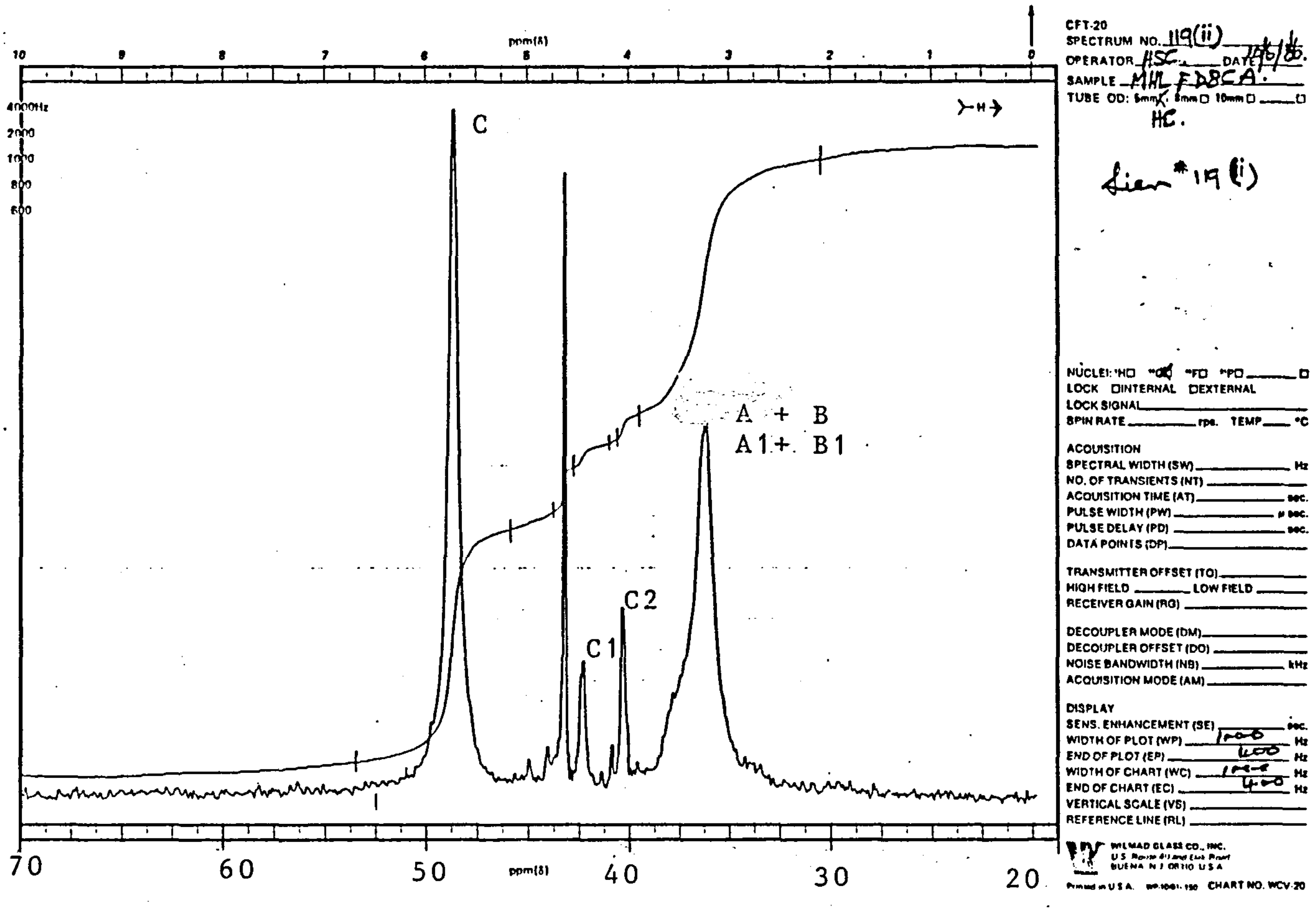


FIGURE 4.9: INTEGRATED ^{13}C NMR SPECTRUM OF PVAM-FD 8

Considering the number of carbon atoms in PVAM-FD 8 and with reference to the information contained in the integrated spectrum shown in Figure 4.9, the following was proposed:

areas under the signals: $A + B + A_1 + B_1 = C + C_1 + C_2$
then (after measuring the areas): $50 \simeq 55$
hence an area of 105 represents 4 x C atoms: $(A + B + C$ or $A_1 + B_1 + C_1 + C_2)$
hence an area of 26,25 represents 1 x C atom in the integrated PVAM-FD 8 spectrum.

In the same spectrum, the area under the signal assigned to the two equivalent carbon atoms of ethylenediamine (δ 44) was 8,5. The area under one carbon atom of ethylenediamine was therefore 4,25.

Hence, the percentage of ethylenediamine (%EDA) present in PVAM-FD 8 was calculated as follows:

$$\%\ \text{EDA} = \frac{\text{EDA}_i}{\text{EDA}_i + \text{FD}_i} \times 100$$

$$= \frac{4{,}25}{4{,}25 + 26{,}25} \times 100$$

$$= 13{,}9$$

<u>Legend</u>:

EDA_i - integration count for one carbon atom of ethylenediamine in PVAM-FD sample.
FD_i - integration count for one carbon atom of PVAM-FD in sample.

In ^{13}C nmr spectra the response of different carbon atoms may not be the same. Quantitative measurements from ^{13}C nmr spectra would depend on the relaxation times of the different carbons (polymers generally have relatively short relaxation times) and the Nuclear Overhauser Enhancement (NOE) effect (this effect comes into play when carbon atoms are protonated or near protons). For the quantitative determination of ethylenediamine by the method described above, the assumption was made that the intensities (areas under the curves) of the different carbon atoms were equivalent. This assumption was verified by running a separate nmr experiment, for PVAM FD-16, in which all the carbon atoms were allowed to relax completely in between pulses. Intensities in such a spectrum would then be quantitative. The fully relaxed spectrum was recorded on a Varian VXR-300/51 FT-NMR spectrometer. The result of the calculation for the percentage ethylenediamine from this spectrum was compared with that of the calculation from the routine high-resolution spectrum.

A relaxation time (T1) of 2,7 ± 0,12 sec had been determined for the carbon atoms of ethylenediamine in PVAM-FD 16 (see Section 4.3.4.3d). This value was used to set up the experiment for obtaining the fully relaxed spectrum of PVAM-FD 16 which included all the carbon atoms. A waiting period of 5 x T1 between pulses was selected. After integration of the fully relaxed spectrum, the new intensities were used to calculate the percentage ethylenediamine present. This was found to be 17,2% ethylenediamine. From the integrated spectrum of a sample of PVAM-FD 16 recorded under normal experimental parameters, 11,4% ethylenediamine was calculated to be present. These results indicated that the integration obtained from the fully relaxed spectrum differed from that obtained under the experimental conditions used in the recordings of the ^{13}C nmr spectra of samples of PVAM batches and from which the calculations had been made. There was evidence that the values calculated for the percentages of ethylenediamine and reported in the text are about 50% too low.

The only assumption then made which was not verified was that the Nuclear Overhauser Effect (NOE) enhancement for the protonated carbons was the same for all the protonated carbons. A relaxing agent could have been used to make the relaxation times of all the carbons equal and short, to neutralise any possible differences in the NOE factor. In practice this was not advisable due to such agents causing substantial line broadening which would confuse the integration.

When integrated ^{13}C nmr spectra of further PVAM-FD samples (batches 18, 19, 25, E4 and E6) had been obtained, the percentages of ethylenediamine present in these samples were also calculated, by the same method as described earlier for PVAM FD-8. These results are included in Table 4.8. Determination of the percentage of ethylenediamine present in PVAM-FD batches 18 and 19 (from which below-expected standard membranes had been made(51), as mentioned), showed that both batches contained more than 20% of the impurity. These results strengthened the belief that the use of a PVAM-FD precursor which contained too high a concentration of ethylenediamine resulted in the fabrication of inferior membranes. Although ethylenediamine has been seen to be present in all PVAM-FD samples analysed to date, quantities vary. The threshold value has not yet been determined accurately but certain indications have been obtained. The presence of 13,9% and 14,5% ethylenediamine in PVAM-FD (batches 8 and 25) did not have a detrimental effect on membrane performance while batches containing more than 20% ethylenediamine (batches 18 and 19) did give membranes of inferior performance(51). On the basis of the data gathered and observations made to date it is suggested that the concentration of ethylene diamine in PVAM to be used as precursor in adequate membrane fabrication should not exceed 15% (+ 50%).

PVAM-FD (batch 24, containing approximately 9,8% ethylenediamine) was washed with acetone to remove excess ethylenediamine present (see experimental Section 3.3.2.4). ^{13}C nmr analysis of the washed product (PVAM-CFD) indicated that approximately 4,8% ethylenediamine remained. The RO performance of PVAM-CFD/SCI tubular membranes, fabricated from PVAM batches which had been washed with acetone to remove excess ethylenediamine, were very good (see Section 4.4.5, Table 4.24).

(d) Quantitative Determination of PVAM-Hy in PVAM

Calculations of the percentages of hydrolysed product (PVAM-Hy) present in successive batches of PVAM-FD were initially based on the technique of comparing the peak heights (height of resonance signal) of the respective functional groups of the two different repeat units in the ^{13}C nmr spectra. The -C = N group of ring-closed PVAM-FD, resonating at δ (D_2O) 172, was compared with the -$CONH_2$ (amide) group of the ring-opened PVAM-Hy product, resonating at δ (D_2O) 177. This approach may be used on condition that it can be assumed that the relaxation times of the groups being compared, are similar. This technique had the advantage that the spectrum did not need to be integrated before calculations could be made.

Experimental nmr parameters used in the recording of accurate ^{13}C nmr spectra of batches of PVAM-FD were optimised for the polymer and carbon atoms which had relaxation times of < 1,1 sec. All recordings done were therefore quantitative for the polymers and comparisons could be made between the numerous batches. If the relaxation times of the -C=N and -CONH$_2$ groups were < 1,1 sec then it would be acceptable to use the peak heights of their respective signals to calculate the percentage of hydrolysed product PVAM-Hy present in PVAM-FD. Nonetheless, an experiment was carried out to accurately determine the relaxation times of the two functional groups under discussion$^{(48)}$. This was done on the Varian-300/51 FT-NMR spectrometer. A sample of PVAM-FD 16 was used.

The spin-inversion-recovery technique was used to determine the relaxation times. The amide groups of the PVAM-Hy repeat unit was found to have a relaxation time of 1,73 (1,73 ± 0,1) sec and the -C=N group of the PVAM repeat unit had a relaxation time of 1,63 (1,63 ± 0,39) sec. These are relatively long relaxation times for polymers and they are similar enough to justify the use of the method of quantitation under discussion, for which it was assumed that relaxation times of the -CONH$_2$ and -C=N carbons were similar. In a second determination carried out on the PVAM-FD 16 sample in D$_2$O which had undergone further hydrolysis (there were more amide groups present than in the sample used for the first determination), relaxation times were calculated to be 1,66 ± 0,09 sec for the amide group and 1,74 ± 0,07 sec for the -C=N group. During this experiment, the relaxation time for the carbon atoms of ethylenediamine impurity in PVAM-FD 16 was calculated to be 2,7 ± 0,12 sec.

Once it had been established exactly where the -C = N and amide groups resonate (*i.e.* what their chemical shift values are) their respective peak heights could be obtained: either measured manually, or taken from the listed intensities of the signals provided by the nmr apparatus. These values were substituted in the following equation to calculate the approximate percentage of hydrolysed product (% PVAM-Hy) present in a batch of PVAM:

$$\%\ \text{PVAM-Hy} = \frac{\text{peak height amide signal}}{\text{peak heights (amide + -C = N) signals}} \times 100$$

In order to arrive at a reasonably accurate value for the % PVAM-Hy, certain considerations had to be taken into account during the determination of the actual peak height values which were to be substituted in the above equation. Employing the values of peak heights as given by listed intensities (provided by the nmr apparatus) had the advantage that the baseline had been determined mechanically. Complications arose, however, in that often more than one signal intensity was listed for one carbon atom. This was due to the presence of isomers, previously referred to as triads$^{(38)}$ (see Section 4.3.2.2). It was not known then how many and which of these signals should, for practical purposes, actually be incorporated for the determination of the peak heights. Consequently, two sets of peak height values for each of the two peaks were used: obtained either by taking the sum of all the triad intensities at δ 172 and at δ 177, or by taking only the greatest intensity at δ 172 and at δ 177. Both sets of these peak height values were used separately in the calculation of the percentage of hydrolysed product, and the resultant % PVAM-Hy values were compared, as shown in Table 4.8. This was done in an attempt to obtain an indication as to which set of peak-height values should be used to enable the most realistic values for the quantity of PVAM-Hy present in PVAM samples to be calculated.

TABLE 4.8: PERCENTAGES OF PVAM-HY AND ETHYLENE DIAMINE CALCULATED TO BE PRESENT IN BATCHES OF PVAM-FD

(Calculations based on ^{13}C nmr data)

PVAM-FD Batch No.	PVAM-Hy [%]			Ethylenediamine [%]*
	M1	M2	M3	
8	11,4	11,4	6,1	13,9
11	-	-	-	
12	-	-	-	
13	11,5	11,0	18,2	
14	-	-	-	
15	14,4	13,8	8,8	
16	14,6	14,3	8,1	
18	10,3	-	-	21,05
19	11,4	12,3	6,8	22,2
20	22,1	22,7	21,6	
21	17,5	13,9	18,9	
22	12,3	13,2	12,0	
23	14,6	15,4	5,9	
24	19,5	20,5	12,2	9,8
25	15,5	18,1	16,2	14,5
E4	11,0	12,4	10,6	14,0
E6	9,7	11,0	10,7	15,5
X				
Y				

Legend:

M1 - M3 - various methods used in determination of peak height values from which calculations were made.
M1 - method 1, using peak heights of -C = N (of PVAM) and amide (of PVAM-Hy) signals, measured in millimetres.
M2 - method 2, using peak heights taken from listed intensities and using only the greatest intensity for each of the -C = N and amide peaks.
M3 - method 3, using peak heights taken as being the sum of all the listed intensities for each of the -C = N and amide peaks.
\- - no calculation possible owing to no evidence of amide signal, caused by noisy baseline.
* - these values are estimated to be too low by about 50% (see Section 4.3.4.3c, p. 132).

Method 1 is rapid and easy. When a PVAM-FD sample of low concentration had to be scanned at high resolution and gave rise to a very "noisy" baseline, the baseline was assumed to be the midline through the baseline "noise".

It was concluded, on the basis of the results presented in Table 4.8, that:

(i) there was evidence that all PVAM-FD samples which were quantified, contained approximately 10-20% PVAM-Hy;

(ii) calculations in which manually determined peak heights were employed (method 1) gave results very similar to those in which were employed the peak-height values obtained from listed intensities of which only the maximum intensity per required signal was used (method 2).

The ^{13}C nmr spectrum of some PVAM-FD samples had such a noisy baseline due to its having been recorded at high sensitivity that any evidence of an amide peak was masked. No calculation of the percentage PVAM-Hy in these samples could then be made by the methods described (methods 1-3). There was, however, evidence that there was PVAM-Hy in these samples because of the signals of the methylene carbons of the ring-opened form.

An alternative approach to calculating the approximate percentages of PVAM-Hy present in PVAM-FD samples and which was based on integration of the areas of the ^{13}C nmr spectrum signals, was considered. The lower region of the spectrum could be integrated to include the -C = N and amide groups at δ 172 and δ 177, respectively (method Mi). Alternatively, the upper region of the spectrum could be integrated to include the two equivalent methylene groups (C) of the 2-imidazoline (amidine-type) ring in PVAM-FD (δ 48,8) and the two methylene carbons (C_1 and C_2) in the open-ring amide-type structure (δ 40,6 and δ 42,6) (method Mii). See Figure 4.9.

Calculations for only two batches of PVAM-FD (E4 and E6) were done using this method. Calculations were done using both sets of integration values and according to the following equations Mi and Mii:

Mi:

$$\% \text{ PVAM-Hy in PVAM-FD} = \frac{\text{integration amide signal}}{\text{integration (amide + -C = N) signals}} \times 100$$

(based on integration of functional groups)

Mii:

$$\% \text{ PVAM-Hy in PVAM-FD} = \frac{\text{integration } (C_1 + C_2)^*}{\text{integration } (C_1 + C_2 + C)} \times 100$$

* See Figure 4.9.

Results obtained from equation Mi were very close to those obtained when methods M1 - M3, mentioned previously, were used. Results obtained from equation Mii varied rather widely from those results obtained when methods M1 - M3 were used, as illustrated in Table 4.9. This was ascribed to the difficulty in obtaining accurate integration values for the required methylene signals. This was complicated by the fact that the methylene signals appeared in a rather crowded area of the spectrum (δ 35 - 50).

This approach to the calculation of % PVAM-Hy, based on integration, was not pursued. Sufficiently accurate quantifications could be made without any need to integrate the spectrum, and by simply basing calculations on the technique of comparing peak heights (method M1) as described earlier.

TABLE 4.9: COMPARISON OF APPROXIMATE PERCENTAGES OF PVAM-HY PRESENT IN PVAM-FD, WHEN DETERMINED BY VARIOUS METHODS

(Calculations based on ^{13}C nmr data)

PVAM-FD Batch No.	PVAM-Hy [%] Method used* M1	M2	M3	Mi	Mii
E4	11,0	12,4	10,6	12,0	22,2
E6	9,7	11,0	10,7	9,2	18,5

Legend:

*	- various methods used in determination of integration- and peak height-values from which calculations for % PVAM-Hy were made.
M1	- method 1, using peak heights of -C = N (of PVAM) and amide (of PVAM-Hy) signals, measured in millimetres;
M2	- method 2, using peak heights taken from listed intensities and using only the largest intensity for each of the -C = N and amide peaks;
M3	- method 3, using peak heights taken as being the sum of all the listed intensities for each of the -C = N and amide peaks;
Mi	- method i, using integration of the -C = N signal (of PVAM) and amide signal (of PVAM-Hy);
Mii	- *method ii, using integration of the methylene carbons of the amidine (of PVAM) and amide (of PVAM-Hy) structures.*

4.3.4.4 Hydrolysis of PVAM

It had become evident that PVAM readily hydrolyses in the presence of moisture. This was proved by chemical analyses, and PVAM/SCI membrane RO performance results had pointed to the fact that an effective PVAM aqueous solution did not have a very long shelf-life. Table 4.10 contains data which illustrates this. There was a marked deterioration in performance of membranes fabricated from old aqueous solutions of PVAM.

TABLE 4.10: EFFECT OF SHELF-LIFE OF PVAM-FD PRECURSOR AQUEOUS SOLUTION ON RO PERFORMANCE OF MEMBRANES(1)

PVAM-FD Storage [days]	Salt Rejection [%]	Permeate Flux [lmd]	Solution [pH]	A^2/B^* [$x10^{-5}$]
	98,4 ± 0,2	370 ± 52	12,0	8,9
01	98,4 ± 0,3	270 ± 51	11,8	8,0
12	98,5 ± 0,1	230 ± 5	11,3	5,4
26	90,2 ± 1,0	1540 ±114	11,2	7,3

*This is a figure of merit, introduced by Lonsdale(52) and explained in Section 4.4.3.

A controlled experiment, described in Section 3.3.4.3, was then carried out to obtain an indication of how readily this hydrolysis reaction takes place in aqueous medium. This was done by following the hydrolysis of an approximately 20% PVAM-FD solution (batch 16) at 22°C in a 5mm nmr tube. At various time intervals the ^{13}C nmr spectrum was recorded and the percentage of hydrolysis product (PVAM-Hy) present calculated (by the method described in Section 4.3.4.3). Results, presented in Table 4.11, indicated that there was an initial fast hydrolysis reaction which later slowed down considerably. The rate constant for this reaction was $k = 1{,}87 \times 10^{-7}\ \text{sec}^{-1}$; $t_{½} = 42{,}8$ days.

TABLE 4.11: INCREASE OF % PVAM-HY IN AQUEOUS PVAM-FD SOLUTION AS A FUNCTION OF TIME

Time [days]	PVAM-Hy in PVAM-FD [%]
0	14,6
10	43,2
25	52,2
60	71,0
390	100,0

Another controlled experiment was carried out to determine the effect of hydrolysis on the viscosity (η) and pH of an aqueous PVAM-FD (batch 25) solution.

Results are presented in Table 4.12.

TABLE 4.12: EFFECT OF HYDROLYSIS ON THE VISCOSITY (η) AND PH OF AN AQUEOUS PVAM-FD SOLUTION, OVER A PERIOD OF TIME

Time [days]	Viscosity [η]	pH
0	0,1250	10,85
10	0,1250	10,54
29	0,1247	10,44
56	0,1090	9,76

It was concluded that as the percentage of PVAM-Hy present in an aqueous solution of PVAM increases with time (as seen in Table 4.11), there will be a corresponding decrease in viscosity (η) and pH value of the solution (as seen in Table 4.12).

Because of the nature and the reactivity of the PVAM material, careful storage under very dry conditions was necessary. Small samples were stored dry in a desiccator containing silica gel drying agent, while larger batches were stored under a nitrogen atmosphere in well-stoppered brown bottles. There appeared to be no change in the composition of the latter after 21 months' storage, as determined by ^{13}C nmr spectroscopy.

4.3.5 HYDROLYSED PVAM (PVAM-HY)

Poly-N-aminoethylacrylamide

It was considered necessary to investigate the use of the fully hydrolysed PVAM-Hy material for the fabrication of UTF membranes, to obtain indications as to what effect the hydrolysed group might have on the PVAM/SCl UTF membrane performance.

Model compound studies have shown that the model compound form of PVAM-Hy, N-propionylethylenediamine, reacted with an aromatic acid chloride and sulphonic acid chloride to form a secondary amide condensation product upon release of hydrochloric acid (Sections 3.8.5 and 3.8.6). It was therefore expected that in the event of PVAM-Hy being used as the precursor in UTF membrane fabrication with SCl crosslinking agent the structure of the resultant desalting barrier would be as shown in Figure 4.10.

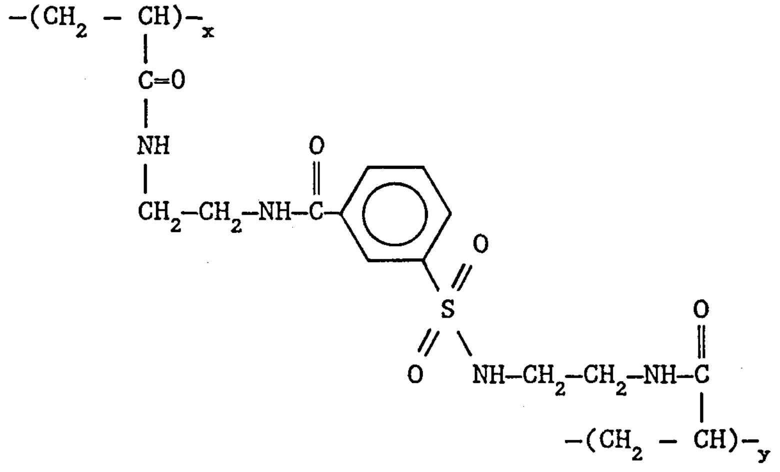


FIGURE 4.10: PROPOSED STRUCTURE OF A PVAM-HY/SCL UTF MEMBRANE

During a heat-cure step in the membrane fabrication process a further reaction may take place whereby terminal primary amine groups of adjacent PVAM-Hy chains might react with elimination of ammonia, to form a secondary amine crosslinked structure. (This is shown in Section 4.4.7.2, Structure no. XV.) A similar reaction has been reported to take place during the heat treatment of PEI in the fabrication of NS-100/1 membranes(32).

UTF membranes were fabricated using PVAM-Hy and SCl (under conditions similar to those used for optimized PVAM-FD/SCl membranes, described in Section 4.4.4.2) in order to determine what their RO performance would be, in comparison with that of PVAM/SCl membranes. In other words, an attempt was made to determine what effect the presence of PVAM-Hy repeat units in the precursor could eventually have on the RO performance of UTF membranes fabricated from copolymeric PVAM precursor. These membrane investigations are described and the results are presented in Section 4.4.6. Fully hydrolysed PVAM-FD had therefore to be prepared.

An aqueous PVAM-FD solution, with pH value of 10 to 12, could be hydrolysed by boiling overnight under reflux. Excess water was removed by rotary evaporation before drying the product on the freeze-dryer (see Section 3.3.4). This product was used in the fabrication of PVAM-Hy/SCl membranes mentioned above. A typical ^{13}C nmr spectrum of PVAM-Hy is shown in Figure 4.11. Data is given in the experimental Section 3.3.4.

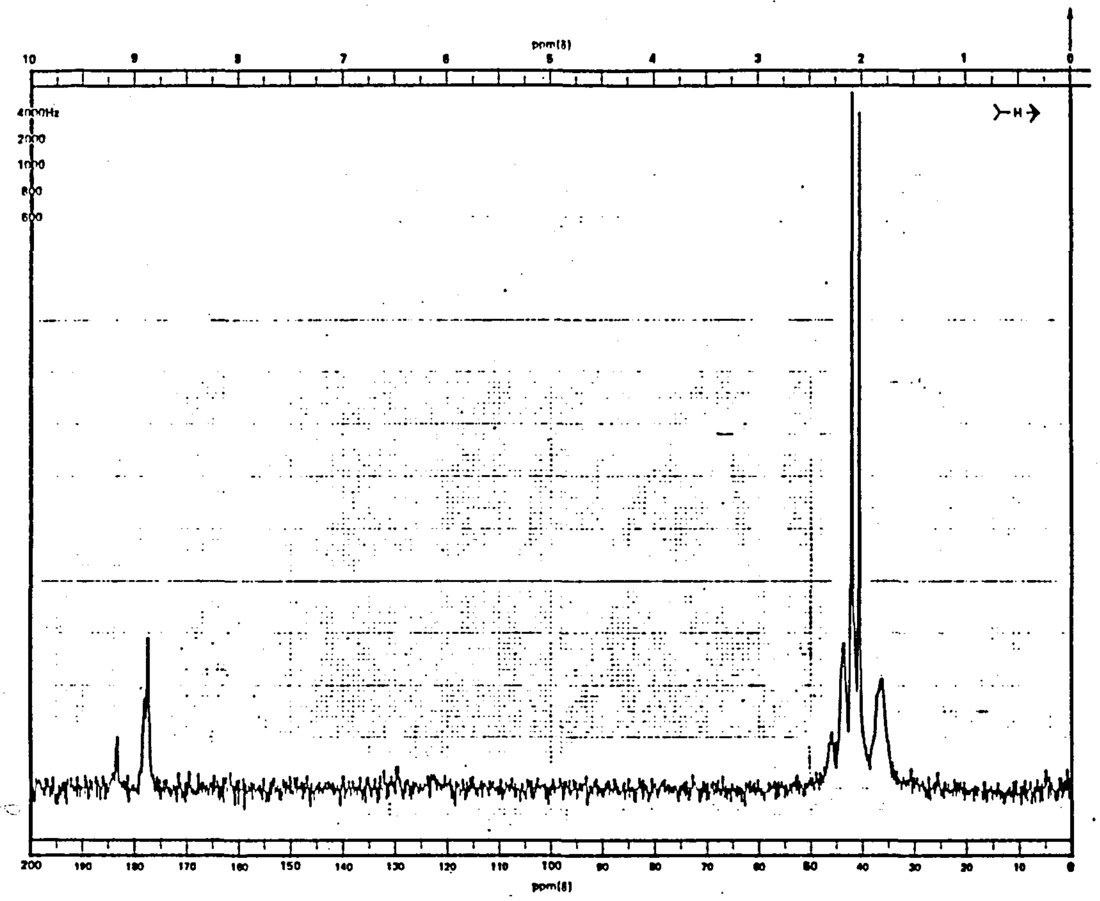


FIGURE 4.11: ^{13}C NMR SPECTRUM OF POLY-N-AMINOETHYLACRYLAMIDE (PVAM-HY)

4.3.6 AROMATIC PVAM (PVAM-AR)

4.3.6.1 Background

Consideration was given to finding an alternative precursor to PVAM which had an amidine-type structure and which would not hydrolyse as spontaneously as PVAM-OD and -FD did.

The benzimidazole compounds may be regarded as cyclic analogues of the amidines. Polybenzimidazole (PBI) membranes fabricated from the polymer poly-2,2'-(m-phenylene)-5,5'-dibenzimidazole contained such a benzimidazole-type structure(53). These membranes have been reported to have a high water flux permeability. PBI was reported to posess very good physical and chemical stability over a wide pH range(54). Attempts were therefore made to prepare a PVAM-type precursor with a cyclic aromatic-amidine type structure, which should preferably be less susceptible to hydrolysis than PVAM-OD and PVAM-FD are.

4.3.6.2 Preparation

The aromatic diamine material, 1,2-diaminobenzene, should react with PAN to yield the aromatic amidine structure PVAM-Ar, shown in Figure 4.12.

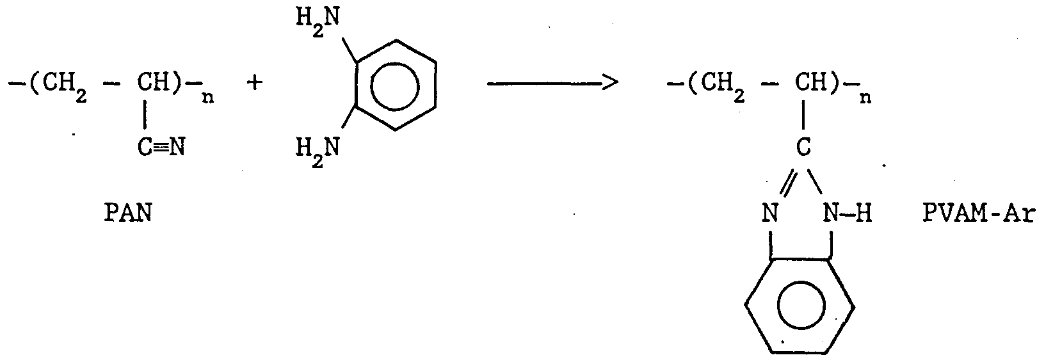


FIGURE 4.12: SYNTHESIS OF AROMATIC PVAM (PVAM-AR)

The attempted preparation of PVAM-Ar has been described in Section 3.3.3.

4.3.6.3 Results and Discussion

The very dark PVAM-Ar product was not soluble in water, and was therefore not suitable as a precursor material for the fabrication of UTF membranes by the interfacial polycondensation process which was used throughout this study. Further attempts at obtaining a water-soluble amidine-type product with some aromaticity in its structure included reacting PAN with a diamine component comprising various proportions of aliphatic ethylenediamine and aromatic 1,2-diaminobenzene. No water-soluble product could be obtained.

These investigations were terminated when it was learnt that the acylation of benzimidazoles would lead to cleavage of the imidazoline ring, especially when this reaction was carried out under aqueous alkaline conditions (Schotten-Baumann procedure)[44,55] *i.e.* conditions similar to those used during membrane fabrication by the interfacial polymerization process. No further attempts were made at modifying the PVAM structure in order to obtain an aromatic, aqueous soluble system.

4.4 DEVELOPMENT OF PVAM UTF MEMBRANES

4.4.1 BACKGROUND

PVAM was selected for use as the polymeric precursor material for the fabrication of novel UTF composite membranes by an in situ interfacial polycondensation reaction with the crosslinking agents SCl and Cl2S on the surface of a porous UF polysulphone support substrate. Research was carried out into the interfacially formed UTF RO membranes and their use in medium-pressure desalination. Membranes were initially made manually in flat-sheet form using the PVAM-OD precursor material. Later, PVAM-OD/SCl and PVAM-FD/SCl membranes were fabricated in the more advanced tube form, during a parallel research programme[1,56]. The quantity of precursor required for membrane fabrication in flat-sheet form was less than that required for the more advanced tube form, under similar fabrication conditions. This was important, especially during the early stages of the research when reactants were synthesized on only a small scale. Most of the early PVAM UTF membranes were therefore made in flat-sheet form. Fabrication of membranes in tube form did, however, have the advantage of allowing more control of the fabrication variables as was reflected in low scatter in the RO performance results.

There are very many variables pertaining to the fabrication of UTF RO membranes by the interfacial polycondensation process(32,57,58), and these have been mentioned in Section 2.3.2.1. Slight changes in many of these variables could lead to significant variations in the performance of the membranes. Morgan claimed that optimum polymerization conditions should represent the best balance of factors which affect the polymerization(58) and it was similarly envisaged that "optimum" polymeric membranes should be fabricated under the best balance of fabrication conditions. (It has also been claimed that membrane properties can be controlled(59) by using the right reaction conditions.)

During an early study, described in Section 4.4.2, numerous PVAM-OD UTF flat-sheet membranes were fabricated under a variety of conditions and then tested for salt rejection [%] and permeate flux [lmd] under standard test conditions. This study was conducted for a number of reasons:

(i) to obtain an indication as to how effective the chosen novel reagents were as membrane materials and what RO performance would be obtained by using them to fabricate novel membranes;

(ii) to determine which of the many fabrication variables had significant effects on RO performance;

(iii) to determine the fabrication conditions under which high-performance membranes could be made in flat-sheet form;

(iv) to create general guidelines for making PAM UTF RO membranes, to be used later to facilitate the selection of conditions for the fabrication of tubular PVAM UTF membranes and their mathematical optimization during a parallel research programme(1,56).

This section (4.4) describes the study of PVAM-OD and PVAM-FD UTF membranes. Fabrication conditions and variables are highlighted. Attempts to form UTF membranes from the hydrolysed form of PVAM are mentioned. The use of PVAM as base precursor to which various hydrophilic compounds were added and from which low and medium pressure membranes were formed is reported. Finally, the chemical structure of the desalting layer is discussed and the behaviour of membrane films cast on glass-slides is reported. (Experimental procedures pertaining to the fabrication of PVAM UTF membranes have been given in Section 3.4.)

4.4.2 PVAM-OD FLAT-SHEET MEMBRANES

4.4.2.1 Background to development of the membranes, and the effect of selected fabrication variables on their RO performance

The first novel PVAM UTF membranes were made by coating PVAM-OD precursor onto a polysulphone porous substrate and then allowing the precursor to react with the crosslinking agent isophthaloyl chloride (IPC). Conditions chosen for the fabrication of the first PVAM UTF membranes were similar to those used in the fabrication of the known NS-101-type membrane from polyethyleneimine (PEI) and IPC, as described by Cadotte(2,60,61). The following typical fabrication conditions were used to prepare early PVAM-OD/IPC membranes:

(i) A PS substrate was immersed in an aqueous PVAM-OD precursor solution (0,67%) for one minute; it was then drained for one minute.

(ii) The coated substrate was then immersed in a solution (0,5% by mass) of IPC in hexane for about one minute, and then allowed to drain for one minute.

(iii) The membrane was heat-cured in an oven at 110°C for 10-15 min.

The polysulphone substrates used were similar to those described by Cadotte(3,32) and prepared (as described in Section 3.4.1.1) from a 13% (w/w) solution of Union Carbide P 3500 in DMF. (Various procedures can be employed to create different PS substrates. The PS substrate is itself a variable in the formation of effective UTF membranes; this is referred to briefly in Section 4.4.2.7.)

Certain factors in the formation of membranes, considered to be sensitive to variation and which would influence membrane performance, were studied to determine how changes to them would affect PVAM UTF membrane performance. Those chosen to be investigated were:

(i) nature of the crosslinking agent;
(ii) additives to the aqueous PVAM-OD precursor solution: acid acceptors and surfactants;
(iii) heat-curing conditions;
(iv) precursor solution concentrations; and
(v) the porous polysulphone support material.

The last of these (v) emerged as a very important variable factor, but difficult to control. It was eventually included as one of the subjects of another study(1) and will therefore not be discussed further here, except to illustrate how UTF membrane performance changes with variation of the polysulphone support membrane (Section 4.4.2.7).

4.4.2.2 Effect of various crosslinking agents

A detailed account has already been given of the crosslinking agents which were used in this study (see Section 4.2). This included the motivation behind their selection, synthesis of the crosslinking agents, their use in the fabrication of UTF membranes, resultant membrane performance, and a discussion of performance results in terms of the envisaged chemical compositions of the membrane desalting barriers.

Some of the results obtained will be presented again in this section in order to describe more adequately how PVAM-OD flat-sheet membranes "evolved" from novel raw chemicals, up to the stage at which effective desalting membranes could be made from these chemicals after suitable changes had been made to the membrane fabrication variables.

(a) Isophthaloyl chloride (IPC)

Early PVAM-OD UTF membranes were made with IPC as the crosslinking agent, under fabrication conditions similar to those employed to make NS-101(2,60,61). Early batches of PVAM-OD precursor material were available in two forms, one prepared from PAN of molecular mass 8 000 and the other from

PAN of molecular mass 48 000. Each PVAM-OD was used separately to determine which was more suitable as polymeric precursor.

Initially the PVAM-OD/IPC membranes showed rejections of no more than 50% and rather low fluxes. Numerous membranes were then made by varying certain conditions, chiefly the precursor solution concentration and contact time, in attempts to obtain membranes which would give higher rejections.

The best average RO performance of sets of PVAM-OD/IPC membranes (4 in each set) arrived at and their corresponding fabrication conditions, as established by this study, are shown in Table 4.13.

TABLE 4.13: RO PERFORMANCE OF PVAM-OD/IPC MEMBRANES

Membrane fabrication conditions:

Concentration PVAM-OD		[mass %]	3
Molecular mass PAN reagent for PVAM	(a)		8 000
	(b)		48 000
Precursor contact time		[min]	60
Precursor drainage time		[min]	2
Concentration IPC		[mass %]	1
Crosslinking reagent contact		[min]	5
Post crosslink drainage time		[min]	2
Oven temperature		[°C]	100
Oven residence time		[min]	10

Membrane test conditions:

Applied pressure	[MPa]	4
Feed solution : NaCl	[ppm]	5 000
Temperature	[°C]	25
pH		6,8
Test time	[h]	70

Membrane performance:

	RO Performance	
PAN reagent for PVAM mol mass	**Salt Rejection [%]**	**Permeate Flux [lmd]**
8 000	72,7 ± 0,4	1760 ± 58
48 000	62,5 ± 4,8	2174 ± 235

These results showed that the novel PVAM-OD material showed promise as a suitable material for UTF membranes although high-rejection performance membranes had not yet been realised when used together with IPC as the crosslinking agent (under the fabrication conditions used up till that time in ths study).

(b) 3-Chlorosulphonylbenzoyl chloride (SCl)

Using the conditions established for fabrication of the aforementioned PVAM-OD/IPC membranes as guidelines, membranes were made from PVAM-OD and the novel sulphonic-group-containing crosslinking agent SCl (see also Section 4.2.2.2). RO performances of the first membranes made showed low to medium salt rejection but high permeate fluxes. This may be indicative of inadequate crosslinking having taken place. In efforts to improve salt rejection, the concentration of the crosslinking agent was increased from 1% to 2%, which gave a more highly crosslinked membrane.

The best RO performances of membranes fabricated from PVAM-OD and SCl have been approximately 85% salt rejection and 680 lmd flux, for membranes made with PVAM synthesized from PAN of mol mass 8 000, and 86% rejection and 880 lmd flux, for membranes made with PVAM synthesized from PAN of mol mass 48 000. (These membranes had been tested with a 5 000 ppm NaCl solution at 4 MPa applied pressure and 25°C). Details of the fabrication conditions and performance of these membranes are presented in Table 4.14 (Section 4.4.2.2c) along with parallel data for membranes fabricated from PVAM-OD and the trifunctional crosslinking agent Cl2S, fabricated and tested under similar conditions.

PVAM/SCl membranes made under the conditions of fabrication used up to this stage, exhibited higher salt rejections than PVAM-OD/IPC membranes although the latter gave higher fluxes. In efforts to improve further upon the RO performance of PVAM-OD membranes, the effect of using the novel trifunctional crosslinking agent Cl2S was investigated.

(c) 1,3-Dichlorosulphonylbenzoyl chloride (Cl2S)

The first PVAM-OD/Cl2S membranes were made according to conditions similar to those used for fabrication of PVAM-OD/SCl (see Table 4.14). The resulting salt rejections were 94-96% and permeate fluxes were 1400-800 lmd, when tested at 4 MPa with a 5 000 ppm NaCl solution, as shown in Table 4.14. PVAM-OD/Cl2S membranes made under the conditions of fabrication used up to this stage, exhibited higher salt rejection and fluxes than those shown by membranes made with PVAM-OD and SCl. An explanation for this has been offered in Section 4.2.4.2. It was proposed that the trifunctional crosslinking agent could enhance crosslinking and, because of a greater amount of unbound sulphonic acid groups expected in the UTF barrier layer, would allow a greater degree of water absorption and hence cause greater permeation.

TABLE 4.14: RO PERFORMANCE OF PVAM-OD/SCL AND PVAM-OD/CL2S MEMBRANES

Membrane fabrication conditions:

Concentration PVAM-OD	[mass %]	3
Molecular mass PAN reagent for PVAM-OD		8 000 46 000
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration crosslinking agent	[mass %]	2
Crosslinking agent contact	[min]	5
Post crosslink drainage time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane test conditions:

Applied pressure	[MPa]	4
Feed solution : NaCl	[ppm]	5 000
Temperature	[°C]	25
pH		6,8
Test time	[h]	45

Membrane performance:

Crosslinking agent	PAN reagent for PVAM-OD mol mass	RO Performance Salt Rejection [%]	RO Performance Permeate Flux [lmd]
SCl	14 500	84,8 ± 1,9	680 ± 58
	86 000	86,1 ± 3,0	881 ± 65
Cl2S	14 500	96,4 ± 0,6	797 ± 86
	86 000	93,9 ± 1,8	1 394 ± 50

4.4.2.3 Effect of acid acceptors

In the chemical condensation reaction which occurs when a polyamide UTF barrier is being formed, an amine precursor reacts with an acid chloride crosslinking agent to form an amide with the release of one mole of HCl per mole reactant. Acids are known to inhibit such a condensation reaction(58) by forming salts with unreacted amines. Incorporation of a base or acid acceptor in the aqueous precursor solution may therefore be necessary to neutralise the acid formed, and thus ensure continuity and a greater extent of reaction. An acid acceptor should neutralise the by-product of acid in some way while the reaction proceeds. The literature does, however, describe cases in which satisfactory membranes can be made without addition of a base, indicating that sufficient neutrality may be maintained by the polymeric amine precursor itself, which would provide for the required degree of reaction to ensure good thin-film integrity e.g. PA-300-type membrane(62).

The necessity for, and the type of, base which would be required for the fabrication of improved PVAM-OD membranes, were investigated. A tertiary amine acid acceptor, triethylamine, was the first compound to be tested for use in the fabrication of PVAM-OD membranes, as it had been used by other researchers(23) and was less basic than mineral bases. (The base-strength requirements of acid acceptors, their side reactions(63), and their uses in the preparation of both benzamides and sulphonamides(64) have been described by Morgan.) Later in the study, the use of piperazine as an acid acceptor was also investigated, although it was realised that piperazine could compete with the PVAM precursor for reaction with SCl crosslinking agent. This choice was prompted by the success of NS-300 membranes which included the use of piperazine as both precursor material and acid acceptor in their fabrication(22). The use of piperazine polyamides for RO membranes was first reported by Credali *et al.*(65).

(a) Triethylamine (TEA)

PVAM-OD/SCl membranes were fabricated with and without the use of TEA as acid acceptor and both types of membrane were evaulated for their RO performance. The results are presented in Table 4.15. The control membranes, made without the addition of TEA, were fabricated under conditions similar to those used to fabricate PVAM-OD/SCl described in the previous section (see Table 4.14, Section 4.4.2.2). When membranes were fabricated with TEA as acid acceptor, the TEA was added to the aqueous precursor solution and initially used in a concentration of 0,5%.

TABLE 4.15: RO PERFORMANCE OF PVAM-OD/SCL MEMBRANES MADE WITH AND WITHOUT TRIETHYLAMINE AS ACID ACCEPTOR

Membrane fabrication conditions:

Concentration PVAM-OD		[mass %]	3
Molecular mass PAN reagent for PVAM-OD	(a)		8 000
	(b)		46 000
Acid acceptor TEA		[mass %]	0
			0,5
Precursor contact time		[min]	60
Precursor drainage time		[min]	2
Concentration crosslinking agent		[mass %]	2
Crosslinking reagent contact		[min]	5
Post crosslink drainage time		[min]	2
Oven temperature		[°C]	100
Oven residence time		[min]	10

Membrane test conditions:

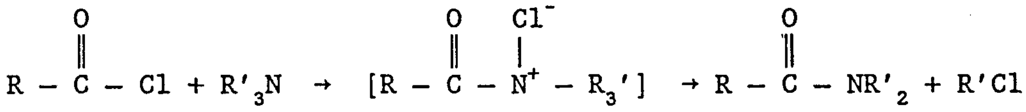
Applied pressure	[MPa]	4
Feed solution : NaCl	[ppm]	5 000
Temperature	[°C]	25
pH		6,8
Test time	[h]	117

Membrane performance:

PAN reagent for PVAM-OD mol mass	TEA conc. [%]	RO Performance Salt Rejection [%]	RO Performance Permeate Flux [lmd]
8 000	0	84,8 ± 1,9	680 ± 58
46 000		86,1 ± 3,0	881 ± 65
8 000	0,5	76,8 ± 1,0	1 096 ± 100
46 000		94,3 ± 1,2	1 096 ± 50

Similar results were reported by Cadotte for the poly-(piperazine-isophthalamide) membranes(22). It was found that when tertiary amines were used, thinner membranes which gave higher flux and lower salt rejection were obtained. This cannot be explained adequately at this stage, but consideration should be given to the reactions which TEA itself could undergo. The side reactions of amine acceptors which could be relevant during the formation of the PVAM-OD/SCl membranes are(63,64):

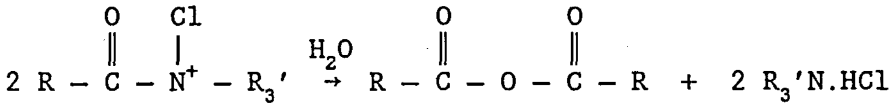
(i) TEA could react with the aromatic crosslinking agent to form a monoamide group and an alkyl halide:



$$R-\overset{\overset{O}{\|}}{C}-Cl + R'_3N \rightarrow [R-\overset{\overset{O}{\|}}{C}-\overset{\overset{Cl^-}{|}}{N^+}-R_3'] \rightarrow R-\overset{\overset{O}{\|}}{C}-NR'_2 + R'Cl$$

In a polymerization system this would be a chain-terminating reaction. The analogous reactions with sulphonyl chlorides are reported to be even faster(66) and could consequently cause greater interference. The alkyl halide may react even further with other amine group to form salts.

(ii) The reaction between an acid chloride and a tertiary amine in the presence of moisture could lead to the formation of an acid anhydride:



$$2\,R-\overset{\overset{O}{\|}}{C}-\overset{\overset{Cl}{|}}{N^+}-R_3' \xrightarrow{H_2O} R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + 2\,R_3'N.HCl$$

An anhydride group in a swollen or water-sensitive polymer would be a hydrolytically weak link and possibly undergo cleavage.

Although amine acceptors could be disadvantageous to the interfacial polycondensation reaction upon their undergoing side reactions, no difficulty should be experienced if the polycondensation reaction is fast. As a polycondensation reaction becomes slower, however, there is more interference by side reactions. This could happen especially in the crosslinking reaction of sulphonyl chlorides, because they react more slowly than benzoyl chlorides do(21).

PVAM-OD/Cl2S membranes were also fabricated with and without the use of TEA as acid acceptor and were tested for their RO performance. Results are presented in Table 4.16. The control membranes made without the use of TEA were fabricated under conditions similar to those described in the previous section (see Table 4.14, Section 4.4.2.2). When membranes were fabricated with TEA used as acid acceptor, the TEA was added to the aqueous precursor solution and initially used in a concentration of 0,5%.

TABLE 4.16: RO PERFORMANCE OF PVAM-OD/CL2S UTF MEMBRANES MADE WITH AND WITHOUT TRIETHYLAMINE AS ACID ACCEPTOR

Membrane fabrication conditions:

Concentration PVAM-OD		[mass %]	3
Molecular mass PAN reagent for PVAM-OD	(a)		8 000
	(b)		46 000
Acid acceptor TEA		[mass %]	0
			0,5
Precursor contact time		[min]	60
Precursor drainage time		[min]	2
Concentration crosslinking agent		[mass %]	2
Crosslinking agent contact		[min]	5
Post crosslink drainage time		[min]	2
Oven temperature		[°C]	100
Oven residence time		[min]	10

Membrane test conditions:

Applied pressure	[MPa]	4
Feed solution : NaCl	[ppm]	5 000
Temperature	[°C]	25
pH		6,8
Test time	[h]	117

Membrane performance:

PAN reagent for PVAM-OD mol mass	TEA conc. [%]	RO Performance Salt Rejection [%]	RO Performance Permeate Flux [lmd]
8 000	0	96,4 ± 0,6	796 ± 86
46 000		93,9 ± 1,3	1 394 ± 50
8 000	0,5	96,2 ± 0,6	863 ± 115
46 000		93,7 ± 1,8	1 444 ± 50

The results showed no significant difference between the performances of the two sets of membranes.

Similar results, showing that the addition of acid acceptor had no advantageous effect on the RO performance of UTF membranes had been reported by Cadotte for the NS-300-type membrane(23). There it was reported that the effects of acid acceptor (and surfactant) on the interfacial reaction between piperazine precursor and the trifunctional crosslinking agent trimesoylchloride (TMC) differed from that of the interfacial reaction between piperazine and the difunctional crosslinking agent isopthaloyl chloride (IPC). The most solute-retentive membrane fabricated with TMC as crosslinking agent was formed when no acid acceptor was used. In fact, the most ineffective of such membranes resulted when the stronger base, sodium hydroxide, was added. On the other hand, the reaction between piperazine and IPC required a strong base as acid acceptor such as sodium hydroxide before adequate membranes (> 96% rejection) could be fabricated.

(b) Piperazine

Successful UTF membranes, designated NS-300, have been prepared from a piperazine precursor and crosslinked with IPC and TMC. In this membrane system, piperazine can function both as a reactant and as an acid acceptor(22). In continued efforts to improve the performance of PVAM-OD UTF membranes, the use of piperazine as an additive to the aqueous precursor solution in the fabrication of such membranes was therefore investigated. Besides acting as acid acceptor, the piperazine may also take part, as a difunctional amine precursor, in the interfacial polycondensation reaction. PVAM-OD/SCl membranes were prepared with and without piperazine as additive to the precursor solution. These membranes were then evaluated for their RO performance. Similarly, PVAM-OD/Cl2S membranes were also fabricated with piperazine as additive to the precursor solution, and then evaluated. The RO performances of the best sets of membranes made under these conditions are presented in Table 4.17.

TABLE 4.17: RO PERFORMANCE OF PVAM-OD/SCL AND PVAM-OD/CL2S UTF MEMBRANES FABRICATED WITH AND WITHOUT PIPERAZINE AS ADDITIVE

Membrane fabrication conditions:

Concentration PVAM-OD	[mass %]	1
Molecular mass PAN reagent for PVAM-OD		20 000
Piperazine	[mass %]	0
		1
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration crosslinking agent	[mass %]	2
Crosslinking reagent contact	[min]	5
Post crosslink drainage time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane test conditions:

Applied pressure	[MPa]	2
Feed solution : NaCl	[ppm]	2 000
Temperature	[°C]	25
Test time	[h]	>100

Membrane performance:

Crosslinking agent	Piperazine conc. [%]	RO Performance Salt Rejection [%]	RO Performance Permeate Flux [lmd]
SCl	0	92,8 ± 0,7	272 ± 67
SCl	1,0	92,8 ± 0,9	398 ± 101
Cl2S	1,0	94,4 ± 0,4	1 030 ± 40

The incorporation of piperazine appeared to have an advantageous effect on the membrane permeate fluxes. It must be noted here that these membranes, described above, were tested at an applied pressure of 2 MPa on a new membrane testing apparatus whereas previously described membranes were tested at 4 MPa. As there exists an almost linear relationship between the applied pressure at which UTF membranes are tested, and their fluxes(68), the fluxes of the abovementioned membranes, fabricated with incorporation of piperazine could, therefore, be expected to be about double if tested at 4 MPa. Prompted by these improved RO performance results, the effect of piperazine as additive to a PVAM precursor solution on the performance of PVAM/SCl tubular membranes was later investigated during the search for adequate PVAM UTF membranes to be used in medium-pressure applications, in a parallel study. Results are presented and discussed in section 4.4.4.3. The incorporation of piperazine as additive to PVAM-FD precursor solutions and the effect on the performance of PVAM-FD/Cl2S membranes should be investigated in future work.

4.4.2.4 *Effect of surfactants*

For the fabrication of UTF membranes by interfacial polycondensation it had become customary to add a surfactant to the aqueous precursor solution. This ingredient had, in cases, led to markedly improved membrane reproducibility in machine fabrication(62). A surface-active agent may assist the transfer of both diamine and salt across the interface, and so promote the interfacial polycondensation reaction (acting as a type of phase transfer catalyst)(69). Use of such a wetting agent is believed to minimize the interfacial tension, creating conditions for better uniformity of reaction between the components of both reagent phases. Such additives could also promote better wetting of the hydrophobic polysulphone support with the aqueous precursor solution. Anionic sodium lauryl sulphate (SLS) is an example of such an agent and has been widely used(62). The effect of the addition of sodium lauryl sulphate surfactant to the PVAM-OD precursor solution on the resultant UTF membrane performance was therefore investigated. PVAM-OD membranes were prepared with and without the use of SLS surfactant and then evaluated. The membrane fabrication conditions and membrane performances are presented in Table 4.18.

TABLE 4.18: EFFECT OF THE USE OF SODIUM LAURYL SULPHATE AS SURFACTANT ON THE RO PERFORMANCE OF PVAM UTF MEMBRANES

Membrane fabrication conditions:

Concentration PVAM-OD	[mass %]	1
Molecular mass PAN reagent for PVAM-OD		20 000
Sodium lauryl sulphate surfactant	[mass %]	0 1
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration crosslinking agent	[mass %]	2
Crosslinking reagent contact	[min]	5
Post crosslink drainage time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane test conditions:

Applied pressure	[MPa]	2
Feed solution : NaCl	[ppm]	2 000
Temperature	[°C]	25
Test time	[h]	>100

Membrane performance:

		RO Performance	
Crosslinking agent	SLS conc. [mass %]	Salt Rejection [%]	Permeate Flux [lmd]
SCl	0	92,8 ± 0,7	272 ± 67
SCl	1,0	89,2 ± 1,8	164 ± 47
Cl2S	1,0	95,3 ± 0,5	257 ± 43

From these results it appears that SLS has a detrimental effect on the RO performance of the PVAM-OD/SCl membranes, reducing membrane flux. During the subsequent mathematical optimization of this membrane system in tubular form(1), the use of SLS surfactant was also found to have an adverse effect on membrane performance. Detrimental effects of anionic surfactants on some cationic UTF composite membranes have subsequently been described by Riley(70) and Leban(71). It was interesting to note that Cadotte had obtained indications that NS-300 membranes which were formed in the presence of surfactants were thicker(23). As thicker membranes are known to show lower permeate flux, this may contribute to the decrease in performance.

Since the PVAM polymeric precursor is essentially a wetting agent itself, no further investigations were carried out into the addition of surfactants in the fabrication of PVAM-OD membranes in flat-sheet form.

4.4.2.5 Effect of heat-curing temperatures

Heat-curing of the chemically crosslinked interfacial polycondensation product was believed to be necessary to effect a more complete crosslinking reaction as this would result in a more highly crosslinked polymeric structure and a more effective membrane desalting barrier(72). In the case of the NS-101 membrane (prepared from water-soluble PEI precursor), adequate heat-curing (> 100°C) caused the unreacted PEI film to become water-insoluble due to the crosslinking reaction which took place between adjacent primary amine groups, with the elimination of ammonia(32,61). Besides exhibiting fairly good RO properties itself (70-80% rejection, > 4000 lmd), the intermediate layer of insolubilized PEI plays an important role in the performance of NS-101 membranes. It serves as a gel-layer transition zone between the PS substrate and the polyamide barrier layer and provides additional support for the extremely thin desalting barrier layer(61). Because the PVAM-OD precursor material contains hydrolysed repeat units with primary amine structure, PVAM-Hy, a reaction similar to those described for the NS-101 membranes could be expected to occur during an adequate heat-cure step in the fabrication of PVAM-OD UTF membranes. The gel-layer structure of PVAM UTF membranes is discussed in Section 4.4.7.

The most favourable heat-curing temperatures reported for the NS-101 and PA-300 membranes are 110°C and 100°C, respectively(32,61,72). Heat-curing at temperatures greater than 145°C is reported to lead to deterioration of the membrane. On the basis of these figures, the heat-curing temperature of 100°C, and later 80°C, were chosen and investigated for their effects on the RO performance of PVAM-OD/Cl2S membranes. Results are shown in Table 4.19.

TABLE 4.19: EFFECT OF TEMPERATURE AND POSITION OF HEAT-CURING ON RO PERFORMANCE OF PVAM OD/CL2S UTF RO MEMBRANES

Heat curing temperature [°C]	Position	RO Performance Rejection [%]	RO Performance Permeate Flux* [lmd]
80	horizontal	96,7 ± 3,3 96,0 ± 1,5	117 ± 8 240 ± 64
100	vertical	74,7 ± 7	1 976 ± 192
	horizontal	87,7 ± 5	126 ± 25

* Quality of polysulphone support used was suspect, since tighter membranes than previously were obtained. This was the only polysulphone support available at the time.

Initial indications were that heat-curing at 80°C led to membranes with better baseline RO performance than those heat-cured at 100°C.

4.4.2.6 Effect of reduced precursor concentration and contact time

It is well known that the effective desalting barrier of a UTF membrane should be as thin as possible in order to increase permeate fluxes through the membrane(74). Salt rejection is independent of thickness, whereas transmembrane flux is inversely proportional to membrane thickness(75). The membrane fabrication variables which are considered to affect the UTF layer thickness, and hence the permeate flux, include precursor and crosslinking agent concentrations, contact times and draining times.

In continued investigations to determine favourable fabrication conditions under which improved PVAM-OD UTF membranes could be prepared, consideration was given to the effect of reducing the concentrations of the reagents which would form thinner desalting barrier layers while also ensuring a saving on the quantity of chemicals required to fabricate the membranes. Whereas at the beginning of the study a PVAM-OD concentration of 3% and crosslinking agent concentration of 2% had been used (Section 4.4.2.1), PVAM-OD/Cl2S membranes were now fabricated from dilute PVAM-OD precursor solutions of 0,5 mass % and crosslinked with a dilute Cl2S solution of 1,0 mass %. The immersion time of the PS support in the precursor solution was also reduced from 60 minutes to 10 minutes.

Fabrication conditions and RO performance of these PVAM-OD/Cl2S membranes are presented in Table 4.20.

TABLE 4.20: EFFECT OF REDUCED PRECURSOR AND CROSSLINKING AGENT CONCENTRATIONS AND IMMERSION TIME OF PS SUPPORT FILM, ON RO PERFORMANCE OF PVAM-OD/CL2S MEMBRANES

Membrane fabrication conditions:

Concentration PVAM-OD	[mass %]	0,5
Precursor contact time	[min]	60;10
Precursor drainage time	[min]	2
Concentration Cl2S	[mass %]	1
Crosslinking reagent contact	[min]	5
Post crosslink drainage time	[min]	2
Oven temperature	[°C]	80
Oven residence time	[min]	10

Membrane test conditions:

Applied pressure	[MPa]	2
Feed solution : NaCl	[ppm]	2 000
Temperature	[°C]	25
Test time	[h]	70-90

Membrane performance:

PVAM-OD contact time [min]	RO Performance Salt Rejection [%]	Permeate Flux [lmd]
60	98,9 ± 0,4	307 ± 75
10	97,4 ± 1,4	400 ± 22

These results, obtained at a pressure of 2 MPa, should be compared with those which were obtained with PVAM-OD/Cl2S membranes fabricated from more concentrated precursor and crosslinking agent solutions and which are reported in Table 4.14, Section 4.4.2.2 (RO performance of 96,4 ± 0,6% rejection and 797 ± 86 lmd flux was recorded at 4 MPa applied pressure.) Although the use of lower concentrations of reactants PVAM-OD and Cl2S did not lead to membranes with significantly improved performance, useful membranes were obtained. The precursor contact time played an important role in the fabricaton process as regards its effect on resultant membrane flux. Shorter contact times led to membranes which had higher fluxes.

4.4.2.7 Effect of polysulphone substrate membrane

UTF RO membranes are prepared by the formation of a thin permselective barrier on the surface of an asymmetric porous substrate membrane. Polysulphone (PS) and, more specifically, poly(bisphenol A sulphone), has been widely used as an RO substrate membrane(4,24,76,77). The two grades of this material which have found application as membrane-forming polymers are Udel 1700 P and the higher molecular mass 3500 P (see Section 3.4.1). PS does, however, have certain drawbacks as a microporous substrate material. These include its hydrophobic character, its strong tendency to form macrovoids during fabrication of the membrane and its high sensitivity to a broad range of solvents which can limit its usefulness in certain membrane-formation procedures. Recently, its compaction resistance was claimed to be less than was originally thought, because it had been found that compaction occurred at elevated temperature(78). An asymmetric PS substrate is made by the wet phase-inversion process in which many variables are involved(79). The important variables in the preparation and optimization of a substrate membrane include the surface-pore size and the pore distribution, both of which are determined by the composition of the casting solution and casting rate. The surface-pore distribution should be optimized to allow for maximum transport across a thin-film barrier. A porous substrate membrane is characterized by its water-permeability, or so-called "A-value"(80). Riley has claimed that the water permeability coefficient (A-value) regarded as optimal for flat-sheet UTF RO membrane fabrication is in the range 2000 to 4000 x 10^{-5} (81).

Detailed consideration has been given, as part of another parallel study(1), to the fabrication of PS substrate membranes and their incorporation in the fabrication of UTF tubular membranes and will therefore not be elaborated on here. It will merely be shown here how the eventual RO performance of UTF flat-sheet membranes was affected by the use of a few different PS substrate membranes which were made.

Four sets of flat-sheet PVAM-OD/Cl2S membranes were fabricated, using four different PS substrates prepared from four different casting-solution formulations and fabricated on a continuous casting machine. (See experimental Section 3.4.1.1).

The RO performances of these membranes are presented in Table 4.21.

TABLE 4.21: THE EFFECT OF VARIOUS POLYSULPHONE SUBSTRATES ON THE RO PERFORMANCE OF PVAM-OD/CL2S MEMBRANES

Membrane fabrication conditions:

Concentration PVAM-OD	[mass %]	3
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration SCl	[mass %]	2
Crosslinking reagent contact	[min]	5
Post crosslink drainage time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane test conditions:

Applied pressure	[MPa]	4
Feed solution : NaCl	[ppm]	2 000
Temperature	[°C]	25

Membrane performance:

PS substrate designation*	RO Performance Salt Rejection [%]	Permeate Flux [lmd]
17S 403	99,5 ± 0,1	237 ± 1
17S 207	97,4 ± 1,5	204 ± 21
17S 601	74,7 ± 10,0	186 ± 153
35S 303	17,7 ± 1,3	1 935 ± 153

***Legend:**

17S 403:	PS 1700 14%; DMF solvent 74,8%; methyl cellusolve non-solvent 10%; poly(vinyl pyrrolidone) 0,7% and sulphonated polysulphone additive 0,5%
17S 207:	PS 1700 13,7%; DMF solvent 73,5 and methyl cellusolve non-solvent 12,7%
17S 601:	PS 1700 15,0%; DMF solvent 71,5%; methyl cellusolve non-solvent 12,5% and DPT additive 1%
35S 303:	PS 3500 15,0%; DMF solvent 80% and poly(vinyl pyrrolidone) additive 5%

The adequate RO performance of the UTF membranes fabricated on polysulphone substrates 17S 403 and 17S 207 could be ascribed to the fact that the "A-values", supplied for these substrates, were 3 955 x 10^{-5} and 3 483 x 10^{-5} respectively(51). These figures were in accordance with those suggested by Riley(81) for use in adequate UTF membrane fabrication. The very poor performance of the UTF membranes fabricated from polysulphone substrate 35S 303 was ascribed to the presence of many pinholes in the substrate, which were very noticeable when the substrate was viewed on a light table. UTF membranes fabricated from substrate 17S 601 showed a wide scatter in the salt rejection values (66-86%) and fluxes were very low.

4.4.2.8 Conclusion

Although more attention could have been given to the choice of fabrication conditions from which high performance UTF RO flat-sheet membranes could be made, this was not regarded as a goal of this research. A mathematical optimization of membrane fabrication variables has formed part of a concurrent research project(1).

The development of novel PVAM UTF membranes, as described in this section, has been most successful, in that:

(i) it was shown that PVAM/SCI and PVAM/Cl2S UTF RO membranes with reasonable performance could be made;

(ii) valuable appreciation of the roles that certain variables, and their levels, played in the UTF membrane-forming process and the effects they had on membrane performance, was achieved.

4.4.3 PVAM-OD TUBULAR MEMBRANES

4.4.3.1 Background

As part of another study, equipment was designed for the fabrication of tubular UTF membranes(82) and a mathematical optimization programme was developed for the fabrication of such membranes(1). Using the membrane chemicals, PVAM precursor, SCI and Cl2S crosslinking agents (prepared as described in sections 3.3.2, 3.2.2 and 3.2.4, respectively), conditions under which the production of flat-sheet PVAM UTF membranes with good RO performance had been fabricated (see Section 4.4.2) were used to produce early PVAM tubular membranes. Reaction conditions for the fabrication of the PVAM/SCI membrane were then optimized by a mathematical routine for high rejection and flux.

To determine the efficiency of these tubular UTF membranes for brack-water desalination at medium pressure, the RO performance was determined at an applied pressure of 2000 kPa with a 2000 ppm NaCl solution at 20°C. These conditions will be referred to as "standard test conditions" for tubular membranes (see experimental Section 3.5). The mean salt rejection and flux of a set of membranes (six in each) were determined and then used in the calculation of the overall membrane performance, given by the figure of merit, that is, $A^2/B \times 10^{-5}$(52). The relationship of A^2/B was used to compare the water permeability coefficient (A) and salt permeability coefficient (B) of different membranes under similar operating conditions.

4.4.3.2 PVAM-OD/Cl2S

As the best RO performance results of PVAM UTF flat-sheet membranes had been shown by the PVAM-Cl2S membrane (see Section 4.4.2.2c) these compounds were used to fabricate the first tubular membranes; these were fabricated under conditions similar to those used for the fabrication of the flat-sheet membranes as described in Table 4.14, Section 4.4.2.2c. (PVAM-OD prepared from PAN of molecular mass 48 000 was used as precursor.)

The RO performance of initial PVAM-OD/Cl2S tubular membranes was > 90% salt rejection and 900 - 1000 lmd flux, tested at 2 000 kPa(51). These flux values for the PVAM/Cl2S tubular membranes were much higher than those for the flat-sheet membranes with similar salt-rejection performance (refer to Table 4.14, Section 4.4.2.2c). These initial results for the tubular form of PVAM-OD/Cl2S UTF membrane indicated that such membranes could be successfully fabricated in this geometric form and, furthermore, that these membranes gave higher rejection and flux than those which had been made in flat-sheet form. The closer control of fabrication and reaction variables during the fabrication of tubular membranes is a probable reason for the higher rejection and flux.

Further investigations were not made into the PVAM-OD/Cl2S tubular membrane as mentioned in Section 4.2.4.2. PVAM-OD UTF tubular membranes of adequate performance were made using SCl(1,56) and this system was selected for mathematical optimization.

4.4.3.3 PVAM-OD/SCl

PVAM-OD and SCl were used in the fabrication of PVAM-OD/SCl UTF membranes, which were then mathematically optimized, as described by Jacobs(1,56). The optimum fabrication conditions which were established for this membrane and its optimum RO performance are shown in Table 4.22.

TABLE 4.22: OPTIMUM PVAM-OD/SCL TUBULAR MEMBRANE FABRICATION FORMULATION AND RO PERFORMANCE

Concentration PVAM-OD	[mass %]	5,0
Acid acceptor (TEA)	[mass %]	1,1
Acid acceptor (TSP)	[mass %]	0,14
Precursor contact time	[min]	43,00
Precursor draining time	[min]	1,50
Concentration SCl	[mass %]	4,50
Crosslink reagent contact	[min]	3,00
Post-crosslink air dry time	[min]	10,00
Oven temperature	[°C]	95,00
Oven residence time	[min]	5,40
RO Performance	Salt Rejection	97,1 ± 0,1%
	Permeate flux	730 ± 24,1 lmd
	A^2/B value	$8{,}89 \times 10^{-5}$

Only moderately high salt rejections were realized for tubular membranes prepared with the PVAM-OD precursor material. The maximum rejection obtained in this study for a PVAM-OD/SCl UTF membrane was 98%.

4.4.4 PVAM-FD TUBULAR MEMBRANES

4.4.4.1 Background

The background to the fabrication of tubular PVAM-FD UTF membranes was covered in Section 4.4.3.1.

The PVAM-FD product was initially considered to be a chemically purer 2-imidazoline product, containing less of the hydrolysed form PVAM-Hy than the PVAM-OD product did. It was, however, established that PVAM-FD contained a rather high concentration (up to 20%) of unreacted ethylenediamine as impurity (see Section 4.3.4.3d). In the synthesis of PVAM-FD from PAN, ethylenediamine was used both as reagent and solvent. The freeze-drying process, by which PVAM-FD was isolated, should have removed the ethylenediamine satisfactorily, but apparently it did not do so.

4.4.4.2 PVAM-FD/SCI

Tubular UTF membranes were prepared from the PVAM-FD precursor and SCI crosslinking agent and mathematically optimized. The optimum fabrication conditions and resulting RO membrane performance are presented in Table 4.23.

TABLE 4.23: OPTIMUM PVAM-FD/SCL TUBULAR MEMBRANE FABRICATION FORMULATION AND RO PERFORMANCE

Concentration PVAM-FD	[mass %]	1,2
Acid acceptor (TEA)	[mass %]	0,2
Acid acceptor (TSP)	[mass %]	0,5
Precursor contact time	[min]	15,0
Precursor draining time	[min]	4,0
Concentration SCI	[mass %]	3,0
Crosslink reagent contact	[min]	6,0
Post crosslink air dry time	[min]	16,0
Oven temperature	[°C]	95,0
Oven residence time	[min]	4,0
RO Performance	Salt Rejection	98,2 ± 0,7%
	Permeate flux	560 ± 150 lmd
	A^2/B value	$10{,}9 \times 10^{-5}$

PVAM-FD was considered to be superior to PVAM-OD as a precursor, when the first PVAM UTF membrane to exhibit 99% salt rejection was a PVAM-FD/SCI membrane. A indication of the difference between the two PVAM precursor materials was that the optimum formulation designed for the one type of membrane did not apply to the other (see Tables 4.22 and 4.23). This was clear, for example, from the observation that when the optimum formulation for PVAM-OD/SCI membrane fabrication was applied to fabrication of the initial PVAM-FD/SCI membranes, the resultant membrane showed practically no permeate flux. Only after the polymer content had been reduced considerably could satisfactory membranes be fabricated.

The optimum formulation for the PVAM-FD/SCI membrane differed markedly from that for the PVAM-OD/SCI. The PVAM precursor concentration required was reduced from 5% for PVAM-OD to 1,2% PVAM-FD. It was considered that the most important reason for this difference, and which led to the need for a lower precursor concentration of PVAM-FD, was the presence of reactive ethylenediamine in the PVAM-FD precursor. During the interfacial polycondensation reaction, ethylenediamine could compete with PVAM-FD in the condensation reaction with SCI.

The ethylenediamine in PVAM-FD could, furthermore, act as an acid acceptor and explain the lower concentration of acid acceptor TEA required in the PVAM-FD solution. Hence, it emerged that the presence of ethylenediamine in PVAM batches had a significant influence on the preparation conditions and on the performance of PVAM-FD UTF membranes. This led to efforts to reduce the amount of ethylenediamine present in the PVAM-FD precursor and to determine the effect of a PVAM-FD precursor with reduced ethylenediamine content (PVAM-CFD) on membrane performance. These results are discussed in Section 4.4.5

4.4.4.3 Medium-pressure PVAM UTF membranes

With the aim of improving the flux of PVAM UTF membranes without adversely affecting their salt-rejection properties, tests were done to determine whether the addition of various hydrophilic fillers or additives to a PVAM precursor solution improved membrane performance(83). These additives were piperazine, polyvinyl alcohol (PVOH, molecular mass 72 000, 86% hydrolysed polyvinyl acetate) and AHEA-2 (a proprietary copolymer)(84).

The use of PVOH was prompted after learning that membranes made from 1,3-diaminobenzene and polyvinylalcohol had good RO performance (1 $m^3/m^2/d$; 97,1% rejection for 2 000 ppm NaCl(85)) and because of its hydrophilic nature. PVOH was not expected to compete with the PVAM precursor for reaction with SCl crosslinking agent to any great extent due to the low reactivity of hydroxyl groups with acid chlorides. It was selected to lend hydrophilicity to the desalting barrier

AHEA-2 was a hydrophilic copolymer containing about 10% acrylic acid functionality and 90% hydroxy functionality. Due to its hydrophilicity and changed nature, its use was expected to lead to membranes with increased fluxes and rejection. It is expected that this compound would be distributed throughout the membrane matrix and reaction with the SCl crosslinking agent through the hydroxy groups would be minimal.

The use of piperazine was investigated after good RO performance results were recorded for PVAM membranes prepared with the incorporation of piperazine (see Section 4.4.2.3b). Piperazine can compete with PVAM for reaction with SCl due to its much smaller size and therefore being able to diffuse quicker though the aqueous PVAM precursor solution to the organic/water interface where the interfacial polycondensation reaction takes place (assuming reaction takes place in the organic layer, as discussed in Section 4.4.7.1.).

Various membranes were prepared and tested for their salt rejection and flux. Experimental details of the composition of the precursor solution and of the membrane preparation conditions have been described in detail elsewhere(83). Membranes were tested under standard tubular-membrane test conditions (see Section 3.5.1) for 48 hours.

Test results of PVAM-FD/SCl membranes in which piperazine was used as filler material in quantities of up to 20% (on a mass to mass basis relative to PVAM-FD) are shown graphically in Figure 4.13 and Figure 4.14.

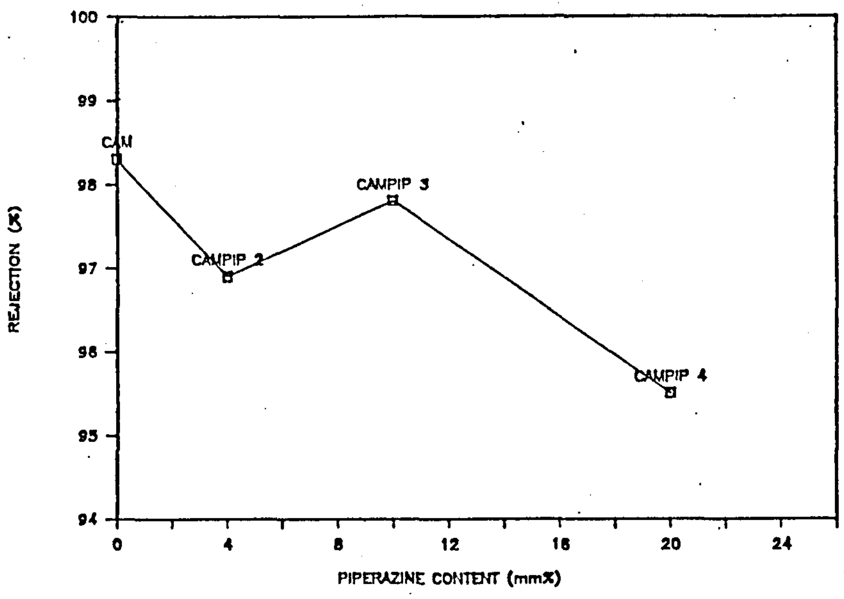


FIGURE 4.13: EFFECT OF PIPERAZINE ON THE REJECTION OF PVAM-FD UTF MEMBRANES
(piperazine content expressed as percentage ratio of PVAM-FD)

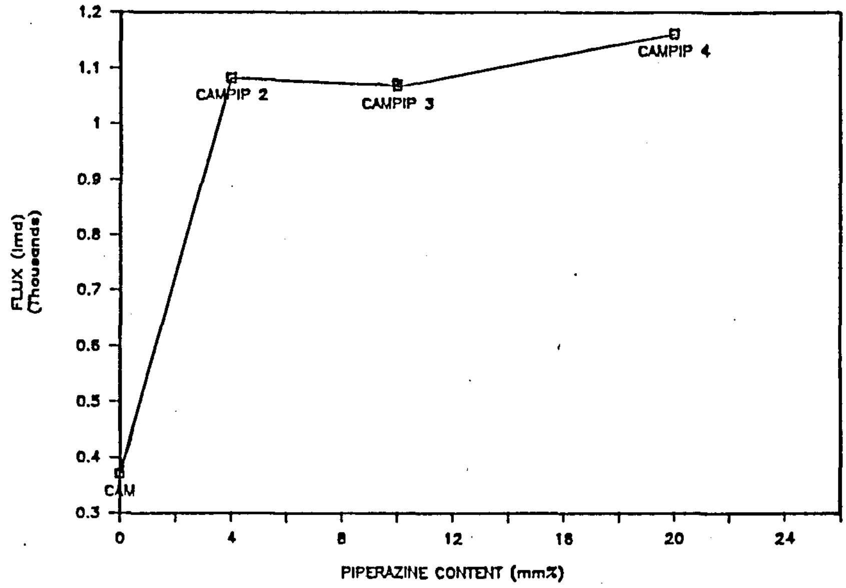


FIGURE 4.14: EFFECT OF PIPERAZINE ON THE FLUX OF PVAM-FD UTF MEMBRANES
(piperazine content expressed as percentage ratio of PVAM-FD)

Piperazine appeared to have a moderate negative influence on the salt rejection by such membranes but increased the flux significantly. (A similar increase in flux with piperazine-filled PVAM-OD/SCI UTF flat-sheet membranes had been observed previously as described in Section 4.4.2.3b).

Results of PVAM-FD/SCI membranes filled with polyvinyl alcohol are shown in Figures 4.15 and 4.16.

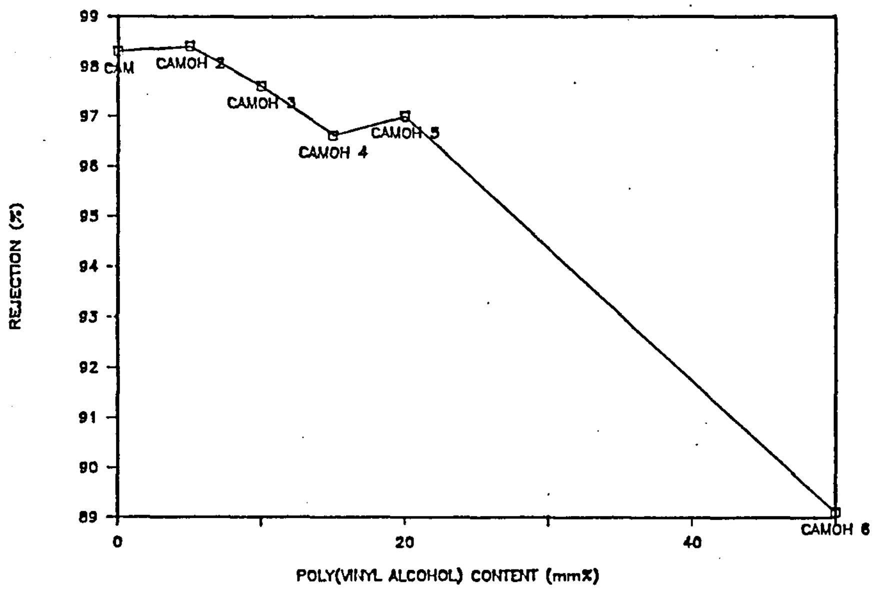


FIGURE 4.15: EFFECT OF POLYVINYL ALCOHOL ON THE REJECTION OF PVAM-FD UTF MEMBRANES
(polyvinyl alcohol content expressed as percentage of PVAM-FD)

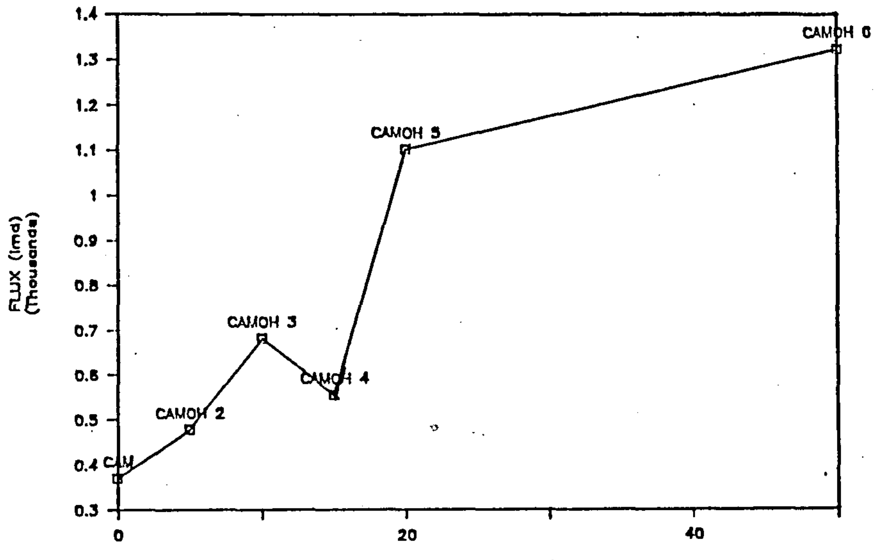


FIGURE 4.16: EFFECT OF POLYVINYL ALCOHOL ON THE FLUX OF PVAM-FD UTF MEMBRANES
(polyvinyl alcohol content expressed as percentage of PVAM-FD)

It was observed that incorporation of polyvinyl alcohol led to increased fluxes. A study of the effect of time on the RO performance of polyvinyl alcohol-filled membranes revealed a slight increase in salt rejection and flux with time, while the control PVAM-FD UTF membrane showed no real increase in salt rejection and flux with time (see Figures 4.17 and 4.18).

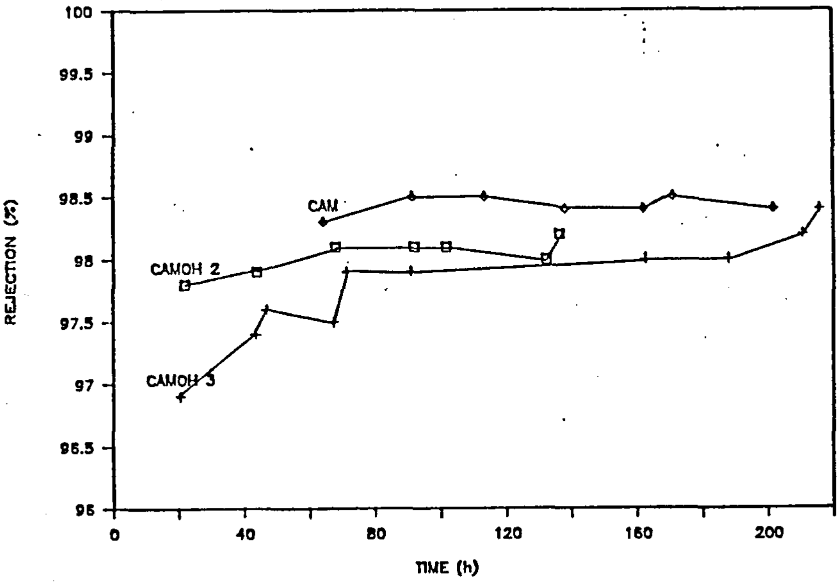


FIGURE 4.17: EFFECT OF TIME ON THE REJECTION OF POLYVINYL ALCOHOL-FILLED PVAM-FD UTF MEMBRANES

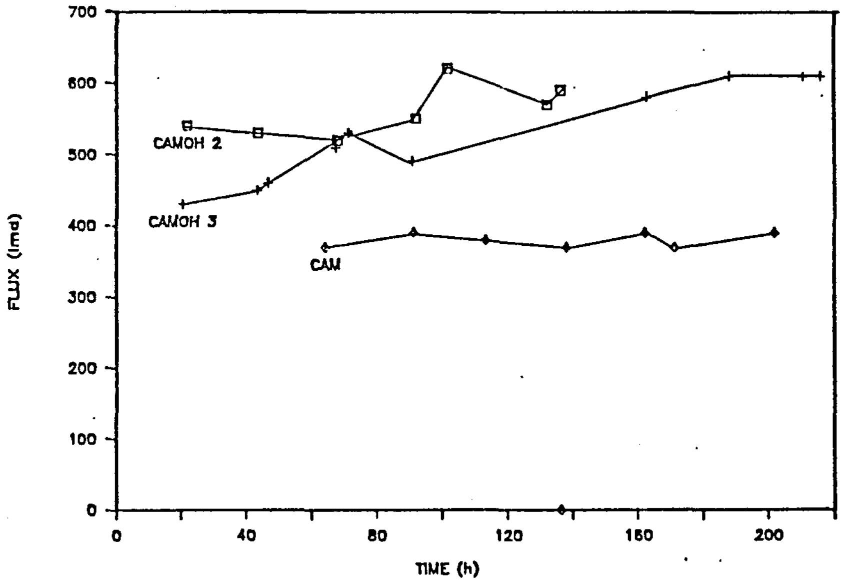


FIGURE 4.18: EFFECT OF TIME ON THE FLUX OF POLYVINYL ALCOHOL-FILLED PVAM-FD UTF MEMBRANES

The use of AHEA-2 did not appear to affect the salt rejection of PVAM-FD/SCI membranes to any great extent although one of the AHEA-2-filled membranes (CAM HA 1 precursor: 1,08% PVAM-FD + 0,12% AHEA-2) showed a flux which was much higher than that of an unfilled control membrane (CAM) (see Figure 4.19).

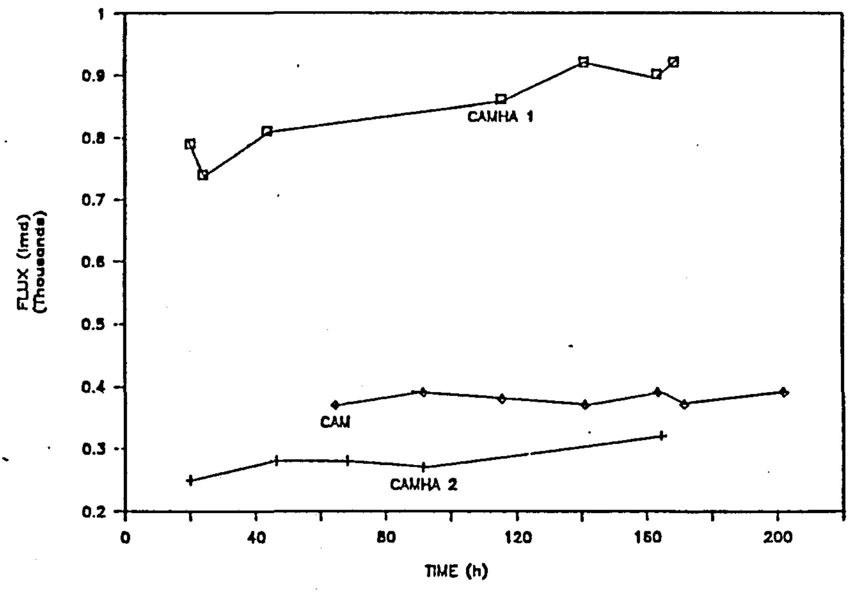


FIGURE 4.19: EFFECT OF TIME ON THE FLUX OF AHEA-2-FILLED PVAM-FD UTF MEMBRANES

As with the polyvinyl alcohol-filled membranes, the AHEA-2-filled membranes showed an increase in flux during the time period over which the membranes were tested, as shown in Figure 4.19.

Hence, early investigations have indicated that the flux of PVAM UTF membranes can be improved, without much decrease in the salt-rejecting properties of these membranes, by the use of hydrophilic additives. This suggests that some of these membranes would perform satisfactorily at operating pressures below 2 000 kPa. It further opens the field for investigation into the use and effects of filler materials other than those reported here. By incorporating various species in the precursor, a range of membranes with different performance characteristics could be created (see also Section 4.4.5.2).

4.4.5 PVAM-CFD TUBULAR MEMBRANES

4.4.5.1 PVAM-CFD/SCI

In order to ascertain what effect the presence of ethylenediamine in a PVAM-FD precursor would have on the RO performance of PVAM-FD/SCI membranes, membranes were prepared with a "cleaned" PVAM-FD precursor (PVAM-CFD), from which ethylenediamine had been partially extracted. PVAM-CFD/SCI membranes were made, using the optimum fabrication conditions established for PVAM-OD/SCI and PVAM-FD/SCI membranes, and their RO performances were compared with the performances of the PVAM-OD/SCI and PVAM-FD/SCI membranes. The PVAM precursors (PVAM-24) were all made from the same batch of PAN starting material, molecular mass 18 000, to eliminate variations in molecular mass.

A sample of PVAM-FD 24 was cleaned to remove excess ethylenediamine, as described in the experimental Section 3.3.2.4. ^{13}C nmr spectroscopy of the first PVAM-CFD product revealed evidence of the presence of about 4,8% (+50%) ethylenediamine. The mother material PVAM-FD had contained about 9,8% (+50%) ethylenediamine (as determined by ^{13}C nmr spectroscopy). The amount of ethylenediamine present in the PVAM-OD precursor was not determined because of the complexity of the ^{13}C nmr spectrum of PVAM-OD in the area where ethylenediamine signals appear (see Section 4.3.4.3c). The RO performances of PVAM-CFD/SCl, PVAM-FD/SCl and PVAM-OD/SCl tubular membranes are shown in Table 4.24.

TABLE 4.24: COMPARISON OF THE RO PERFORMANCES OF PVAM-OD/SCL, PVAM-FD/SCL AND PVAM-CFD/SCL TUBULAR MEMBRANES

Fabrication formulation	Polymeric precursor	Test time [h]	Rejection [%]	Flux [lmd]
OD	PVAM-OD	22,4	96,8 ± 0,7	256 ± 5
(see Table 4.22)		48,1	97,4 ± 0,5	296 ± 5
	PVAM-FD	22,4	60,5 ± 16,5	47 ± 8
		48,1	62,6 ± 15,0	24 ± 5
	PVAM-CFD	22,4	78,1 ± 6,9	32 ± 5
		48,1	80,3 ± 6,1	25 ± 5,5
FD	PVAM-FD	23,8	97,3 ± 1,2	340 ± 39
(see Table 4.23)		47,4	97,4 ± 1,6	417 ± 41
	PVAM-OD	23,8	94,1 ± 0,7	463 ± 24
		47,4	94,5 ± 0,3	491 ± 33
	PVAM-CFD	23,8	96,5 ± 1,1	566 ± 50
		47,4	97,0 ± 1,1	643 ± 74

Membranes prepared with PVAM-CFD precursor, using the optimum formulation for PVAM-FD/SCl membranes, showed increased RO performance. Membrane flux was higher than that of PVAM-FD/SCl membranes. The optimum formulation for fabrication of PVAM-CFD/SCl membranes has not yet been determined (due to insufficient PVAM-CFD available).

4.4.5.2 Low-pressure PVAM UTF membranes

When the RO performance of PVAM-CFD/SCl membranes was observed to be greater than that of PVAM-FD/SCl membranes (as seen in Table 4.24, Section 4.4.5.1), the use of PVAM-CFD in the fabrication of low-pressure UTF membranes was investigated. In attempts to increase the rate of water-permeation through PVAM UTF RO membranes, at operating pressures as low as 500 kPa, PVAM-CFD was used as basic precursor material to which various hydrophilic, water-soluble and non-amine containing polymeric materials were added(86). The reactive hydrophilic polymeric additives used were: polyvinyl alcohol (PVOH, 72 000 molecular mass, 86% hydrolysed polyvinyl acetate) and AHEA-1 (a proprietary copolymer(85) with acrylic acid functionality). Reasons for the use of such compounds and the effect which they have the membrane structure have been discussed in Section 4.4.4.3. Various amounts of these materials were used in admixture with PVAM-CFD to form novel precursor solutions from which UTF RO membranes were made. SCl was used as crosslinking agent throughout. Experimental details of the preparation of the tubular substrate membranes, UTF membrane preparation and membrane testing conditions have been presented elsewhere(86). Membrane fabrication conditions are given in Table 4.25.

TABLE 4.25: MEMBRANE FABRICATION CONDITIONS OF PVAM-CFD/SCL MEMBRANES, FILLED WITH AHEA-1 OR PVOH

Precursor solution composition [mm %]	**CAM 5**	**CAM 6**	**CAM 7**	**CAM 8**	**CAM 9**	**CAM 10**	**CAM 11**
PVAM-CFD precursor	1,2%	0,96	0,96	0,96	0,96	0,96	0,89
AHEA-1				0,24	0,24	0,24	
PVOH (72K, 86%)		0,24	0,24				0,22
PDA							0,09
TEA		0,2	0,2	0,2	0,2	0,2	0,02
TSP		0,5	0,5	0,5	0,5	0,5	0,5
SCl crosslinking agent	3,5%						
				Oven drying			
Oven Temperature (°C)	95	95	115	95	105	115	95
Oven Time (min)	5	5	5	5	5	5	5
	Fixed wetting and draining time [min]						
Substrate predraining	10						
Precursor contact time	15						
Precursor draining time	8						
Crosslink contact time	6						
Crosslink draining time	16						

The RO performances of PVAM-CFD/SCl membranes filled with AHEA-1 and the effect which operating pressure had on the salt rejection and flux are shown in Figure 4.20 (membranes CAM 8, 9 and 10).

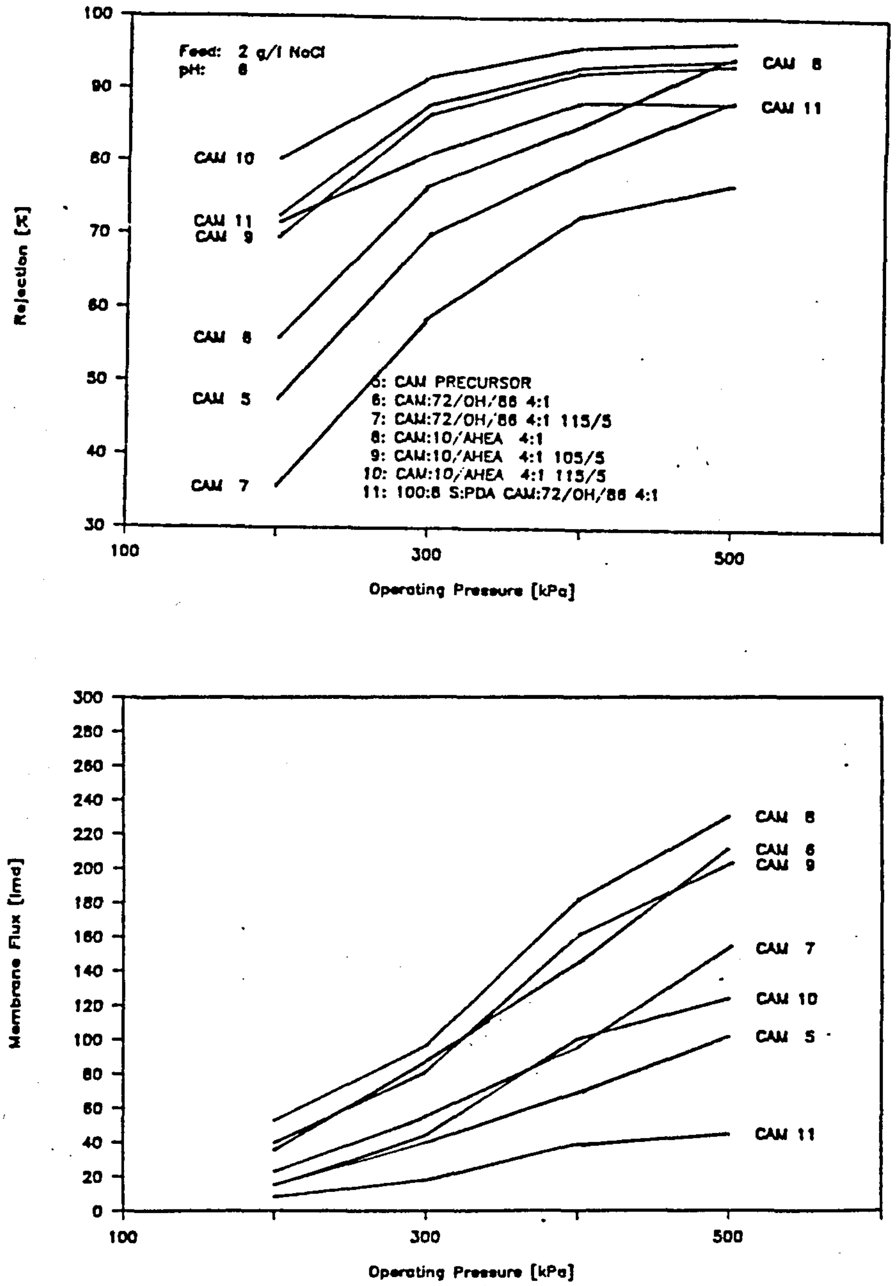


FIGURE 4.20: THE EFFECT OF OPERATING PRESSURE ON THE SALT REJECTION AND FLUX PERFORMANCE OF MODIFIED PVAM-CFD/SCL TUBULAR MEMBRANES FILLED WITH AHEA-1 OR PVOH

The membrane performance stabilities of AHEA-1-filled PVAM-CFD membranes compared with that of a PVAM-CFD membrane (CAM5) over an extended period of evaluation are shown in Figure 4.21.

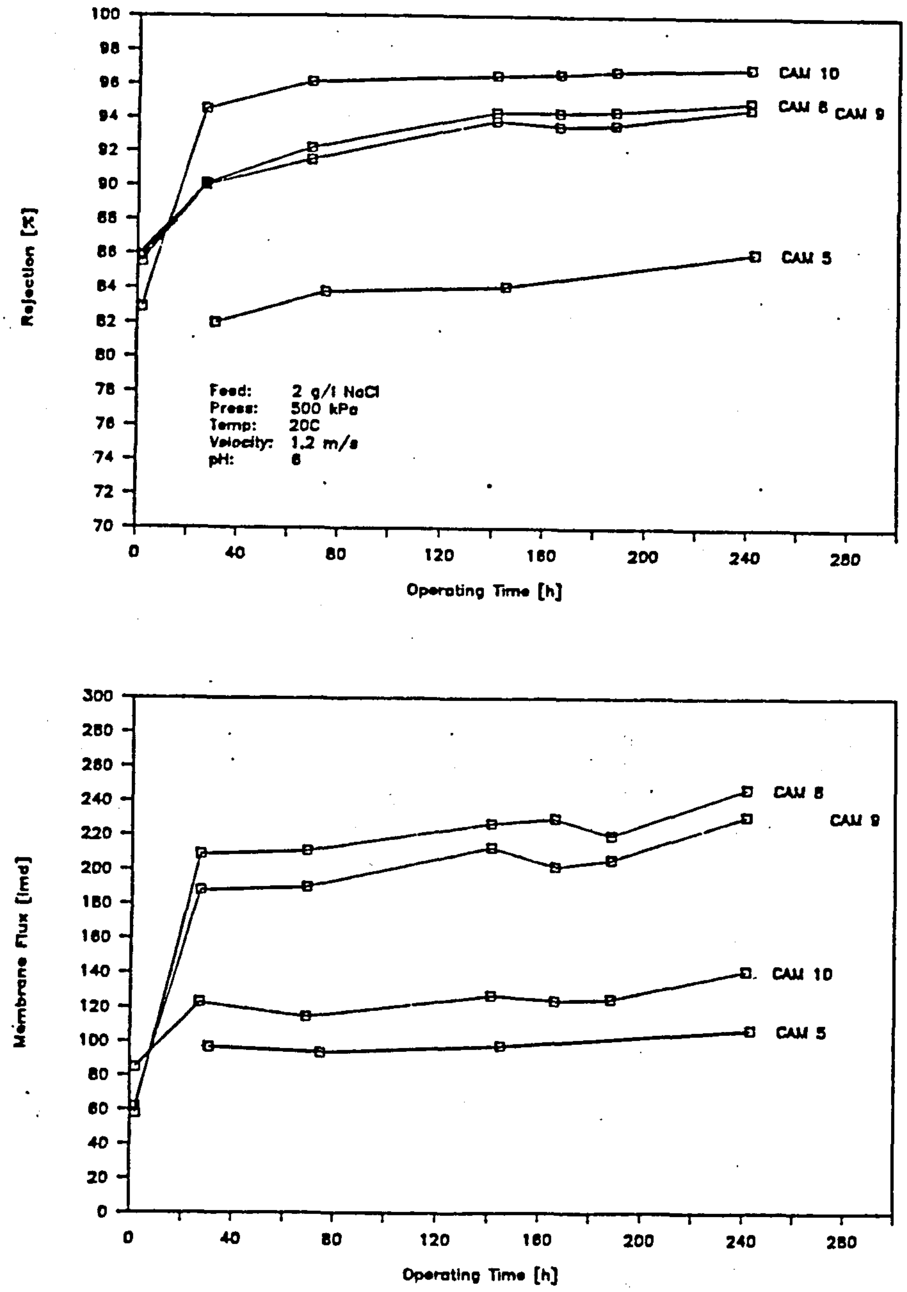


FIGURE 4.21: MEMBRANE PERFORMANCE STABILITY OF PVAM-CFD/SCL MEMBRANES CONTAINING AHEA-1 OVER AN EXTENDED PERIOD OF EVALUATION

It was evident that the set of control membranes (CAM 5) did not perform as well under a given set of operating conditions as did those membranes which had been prepared from a PVAM-CFD precursor solution containing polymeric additives. Membranes incorporating the AHEA-1 copolymer (CAM 8, 9, 10) gave a higher overall performance. The improved membrane performance could be ascribed to incorporation of greater hydrophilicity into the membrane matrix. There would also be increased freedom in the swelling capacity of the film, as was evident from the membrane's higher flux.

The RO performances of PVAM-CFD/SCl membranes filled with polyvinyl alcohol are shown in Figure 4.22.

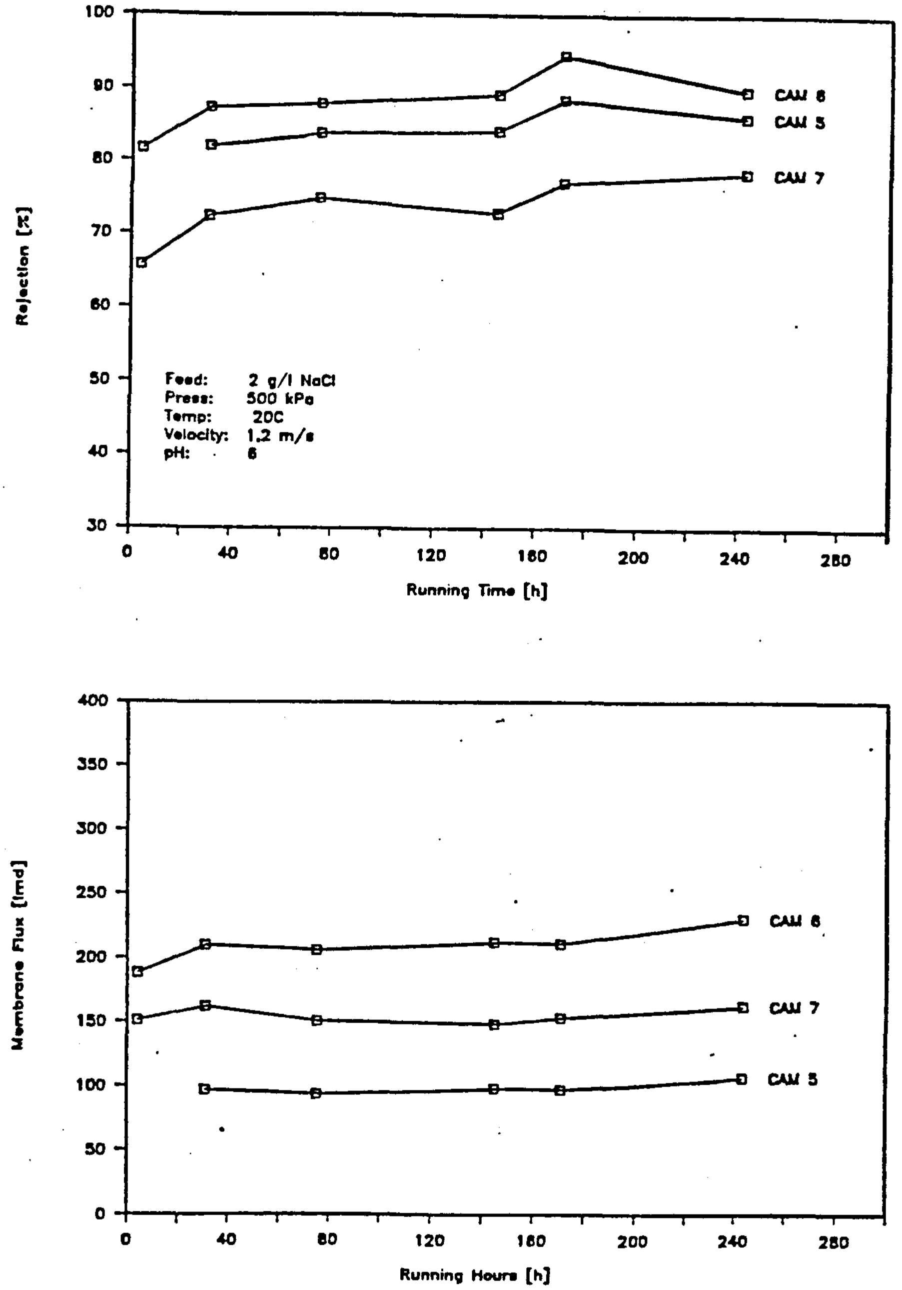


FIGURE 4.22: MEMBRANE PERFORMANCE STABILITY OF PVAM-CFD/SCL MEMBRANES CONTAINING POLYVINYL ALCOHOL OVER AN EXTENDED PERIOD OF EVALUATION

Addition of polyvinyl alcohol to the precursor solution (membranes CAM 6 and 7) did not result in such a marked increase in membrane performance. It did, however, cause some increase in the water-uptake capacity of the desalting barrier, as was reflected in the improvement in flux of membranes prepared with incorporation of polyvinyl alcohol in the precursor solution (membranes CAM 6 and 7) over that of the control membrane (CAM 5). There was no decline in the RO performance of these membranes after an evaluation period of more than 200 hours.

From the results recorded to date, it was established that stable membranes had been formed which exhibited flux performances which exceeded that of the PVAM base-polymer control membrane. Membrane fluxes greater than 200 lmd have been achieved at an operating pressure of 500 kPa.

4.4.6 FULLY HYDROLYSED PVAM MEMBRANES

4.4.6.1 Background

It had been established that the PVAM precursor material contained a significant amount of its hydrolysed form, poly-N-aminoethylacrylamide (see Section 4.3.3.2c) which would react with an acid chloride crosslinking agent e.g. SCl during formation of the membrane by the interfacial polycondensation reaction, as described in Section 4.3.5. It could furthermore be expected that heat-curing of unreacted hydrolysed repeat units would cause them to become crosslinked by elimination of ammonia from adjacent primary amine groups (as reported for the PEI precursor in the NS-101 membrane(32)). In a UTF membrane this could lead to the creation of an intermediate zone or "gel layer" which in itself could possess RO properties, while acting as a support structure within the very thin UTF membrane barrier. The importance of such a layer has been described by Cadotte(32) and Bartels(87).

To obtain an indication of the reactivity of the hydrolysed repeat unit (PVAM-Hy) during the formation of PVAM UTF membranes and to investigate the effect which this reacted group might have on the RO performance of PVAM UTF membranes, membranes were made using homopolymeric PVAM-Hy as model precursor and then tested for their inherent RO performance.

4.4.6.2 PVAM-Hy/SCl membranes

PVAM-Hy/SCl membranes were made in flat-sheet form and then evaluated for RO performance under test conditions of 2000 ppm NaCl feed solution at 2000 kPa applied pressure and 25°C. The conditions under which the initial PVAM-Hy/SCl membranes were formed (and used in experiments 1 and 2, Table 4.26) were similar to those described as the optimum formulation conditions for the PVAM-OD/SCl tubular membranes (see Table 4.22, Section 4.4.3.3). Only a few sets of PVAM-Hy/SCl membranes were made because there was a large scatter in all the RO performances results. This scatter of results was attributed to the poor quality of the polysulphone substrate, which was cast by hand. The best single PVAM-Hy/SCl UTF membrane prepared during this study, under conditions described for experiment 2, Table 4.26, gave 78,4% salt rejection and 72 lmd flux. These RO performance results indicated that, irrespective of the irreproducibility of the RO performances, this chemical structure would not form high-performance UTF RO membranes under the fabrication conditions used.

In further experiments, PVAM-Hy UTF membranes were fabricated without exposure of the PS substrate to any chemical crosslinking agent, but were heat-cured (experiments 3 and 4, Table 4.26). The RO performances of these membranes, heat-cured at 130°C, showed a salt rejection of about 22%. This indicated that, under these heat-cure conditions, PVAM-Hy can become insolubilized by intermolecular crosslinking. (PVAM-Hy films cast on glass plates and heat-cured to 110°C for 10 minutes also became insoluble, as described in Section 4.4.7.4).

Table 4.26 contains the average RO performance data for sets of PVAM-Hy UTF membranes (6 membranes in each set). PVAM-Hy precursor was either chemically crosslinked with SCl or thermally crosslinked at 130°C.

TABLE 4.26: RO PERFORMANCE OF SETS OF PVAM-HY UTF MEMBRANES FABRICATED BY CHEMICAL AND THERMAL CROSSLINKING

Exp.	Fabrication Conditions								RO performance	
No.	A	B	C	D	E	F	G	H	Rejection [%]	Flux [lmd]
1	5	30	5	6	0,15	1,1	95	6	36,5 ± 3,2	77 ± 17
2	5	43	5	3	0,15	1,1	95	5,4	27,5 ± 4,0	3039 ± 752
3	1	43	0	0	0	0	130	6	21,6 ± 6,3	6608 ± 3728
4	1	10	0	0	0	0	130	10	< 10	> 10 000

Legend:

A	PVAM-Hy concentration	E	TEA concentration
B	PVAM-Hy precursor contact time	F	TSP concentration
C	SCl concentration	G	Oven temperature
D	SCl crosslinking agent contact time	H	Oven residence time

4.4.6.3 Discussion

The PVAM-Hy/SCl membranes showed inferior performance, especially in very low permeate fluxes, when they had been fabricated under the conditions described (Section 4.4.6.2). These results indicated that the presence of hydrolysed repeat units in the PVAM precursor could have a detrimental effect on the overall PVAM/SCl membrane performance. (This may explain, at least partly, why membranes prepared by use of PVAM-FD precursor were superior to those prepared from PVAM-OD. The latter material had a higher content of hydrolysed repeat units (see Section 4.3.3.3)).

Since the RO performances showed that heat-cured PVAM-Hy membranes had some salt-rejecting capability (results of Experiment 3, Table 4.26) the indication was that PVAM-Hy repeat units could undergo thermal curing and create areas with so-called gel layer. This, in turn, could mean that PVAM/SCl membranes fabricated from PVAM precursor containing PVAM-Hy repeat units may also have possessed some gel-layer structure, created by a condensation reaction between the terminal primary amine groups of any adjacent PVAM-Hy repeat units during an adequate heat-cure step. This may be advantageous to the physical integrity of the desalting barrier, as will be discussed in Section 4.4.7.

The experiments developed to model the effect of the aliphatic repeat unit in the partially hydrolysed PVAM-OD and PVAM-FD polymers therefore indicated that there was probably an optimum balance of hydrolysed to unhydrolysed groups needed in the PVAM polymeric precursor structure. This would serve to balance rejection performance with structural integrity. There was evidence that membrane performance decreased as the percentage of PVAM-Hy groups present in the PVAM-precursor increased (see Section 4.3.4.4, Tables 4.10 and 4.11).

4.4.7 STRUCTURE OF THE PVAM/SCL UTF MEMBRANE DESALTING BARRIER

4.4.7.1 Background

Several workers have demonstrated that UTF composite membranes have a thin dense film overlying the porous substrate(88,89,90). These findings are best described by the model of Rozelle *et al.*(32) which describes the formation of an in situ polymerized UTF composite membrane. Representations of the UTF membranes, e.g. PA-300 and PEC-1000, showing schematically three zones of a progressively tighter, more crosslinked structure are shown in Figures 2.2 and 4.23, respectively. (The extent of crosslinking versus depth cannot be accurately zoned.)

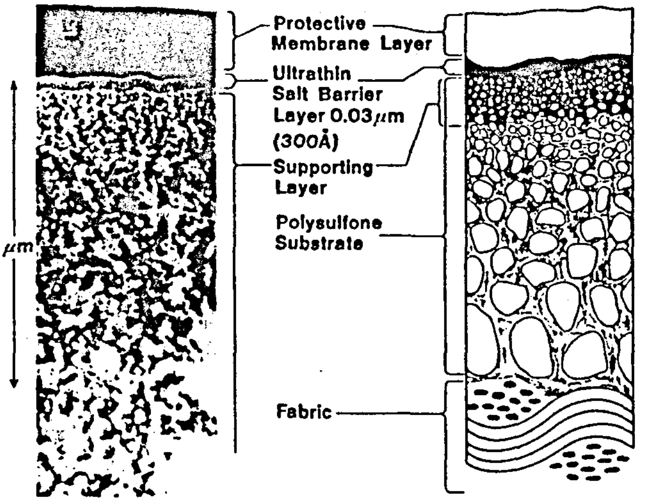


FIGURE 4.23: ELECTRONMICROGRAPH AND SCHEMATIC REPRESENTATION OF THE CROSS-SECTION OF THE UTF COMPOSITE MEMBRANE PEC-1000(90)

In the model of Rozelle *et al.*(32), which describes the NS-100 membrane, one of the main assumptions made was that growth of the interfacial film occurs predominately in the organic phase. This has been determined by Morgan(58). The unreacted PEI precursor in the membrane is thermally crosslinked during the heat-cure step of fabrication to form a distinct intermediate layer which binds the top crosslinked interfacial film to the polysulphone porous substrate. This layer is referred to as the intermediate gel layer. (Recent results of surface analysis experiments described by Bartels(87) have, however, indicated that the interfacially polymerized film penetrates the aqueous phase and that there is no distinct layer of homopolymerized PEI.) The discussion of the PVAM/SCl UTF membrane structure which follows, is based on the original model of Rozelle *et al*(32).

For the crosslinking reaction to take place in the organic layer, the polymeric PVAM precursor must migrate to the organic-phase interface. The diffusion rate of reactant species is known to be a most important factor in membrane-film formation(58). As the crosslinking reaction progresses, the migration of polymer becomes increasingly difficult and eventually stops. It is to be expected, therefore, that the crosslinked UTF membrane would have an asymmetric structure, with the crosslinking density decreasing from the aqueous/organic interface, towards the support membrane surface. The surface would show the highest degree of crosslinking and most probably an excess of acidic groups (due to hydrolysis of the acid chloride and liberation of HCl from the polycondensation reaction). Unreacted

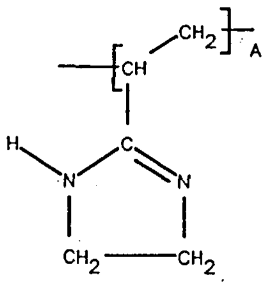
PVAM precursor could remain in the lower regons of the intermediate zone between the crosslinked layer and the porous support. Upon adequate heat-curing, adjacent primary amine groups of PVAM-Hy repeat units (see Figure 4.8) are expected to crosslink and gel formation is expected to take place. This reaction was described, referring to fully hydrolysed PVAM, in Section 4.4.6.3. The resultant structure is shown schematically in Section 4.4.7.2, Structure no. XV. The importance of the formation of some gel-layer structure in a UTF membrane is well known(32,61,87,91).

4.4.7.2 Chemical composition of the PVAM/SCl membrane

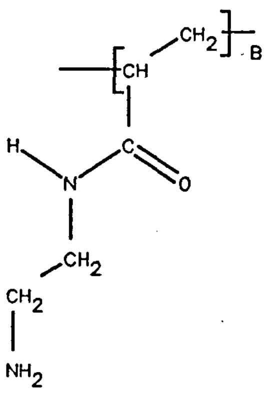
Results of model compound studies (Section 3.9) have proved most valuable in elucidating the chemistry of the PVAM/SCl membrane. The composition of the PVAM-FD/SCl membrane at the various stages during fabrication is discussed. (The contribution of the presence of ethylenediamine impurity in batches of PVAM-FD to the composition of the membrane has not been included.)

Stage 1:

Dry PVAM powder.



I



II

water ↓ Note 1
aqueous solution of PVAM

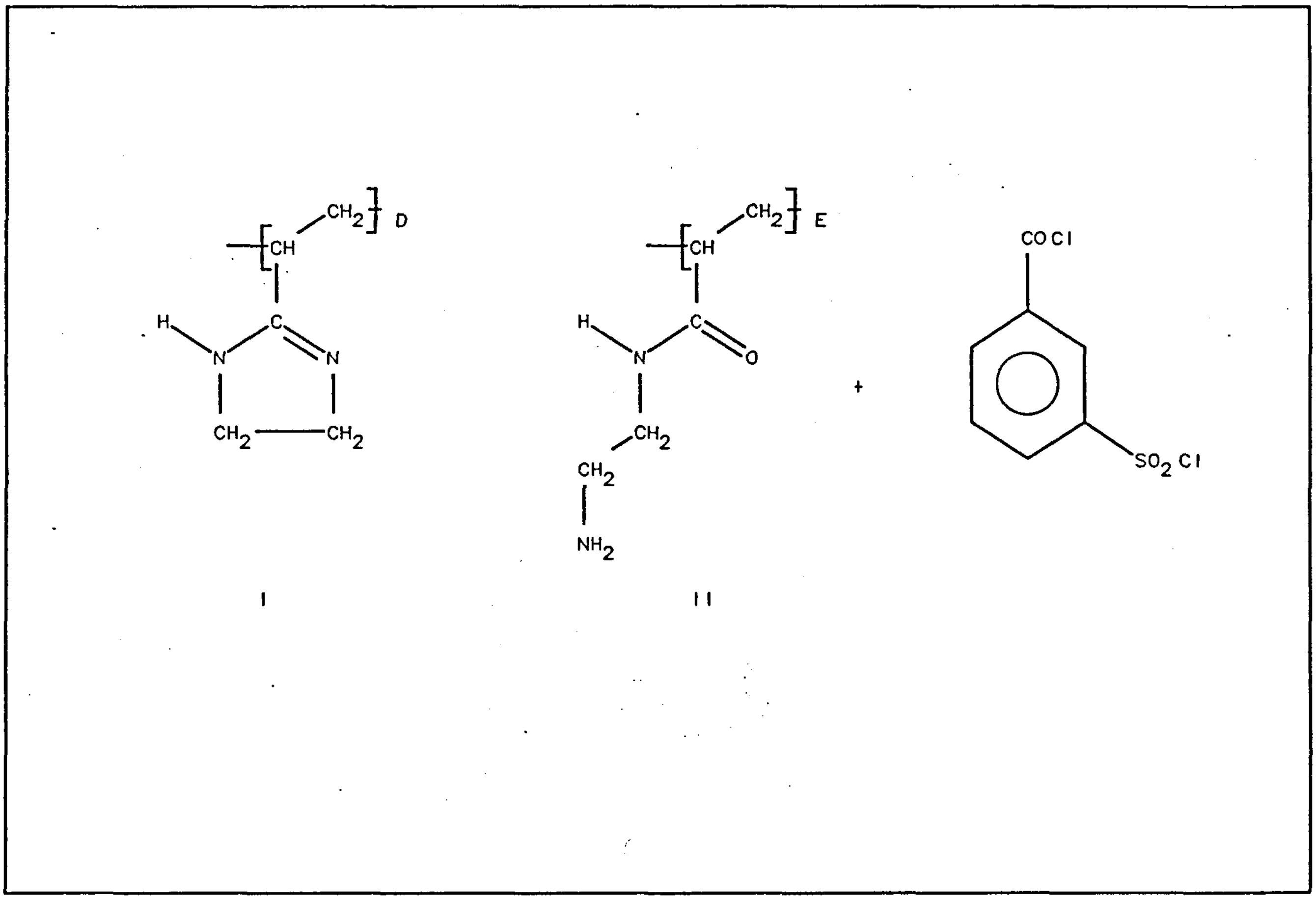
Note 1:

I : 2-imidazoline repeat unit.
II : hydrolysed form of I, linear amide repeat unit.

The composition of dry PVAM powder is approximately I:II :: 85:15. (PVAM-FD batches have been found to contain between 80 and 89% ring-closed 2-imidazoline groups. The average percentage of hydrolysed repeat units in 15 batches of PVAM-FD was calculated to be 15% (see Table 4.8, Section 4.3.4.3d)).

The composition of an aqueous PVAM-FD solution used in the making of tubular membranes (solutions all made up fresh and used within one day) would be about I:II :: 84:16. (The rate constant for hydrolysis of the 2-imidazoline groups in a PVAM copolymer is $k = 1{,}87 \times 10^{-7}$ sec^{-1}; $t_{1/2}$ 42,8 days, determined as described in Section 3.3.4.1.)

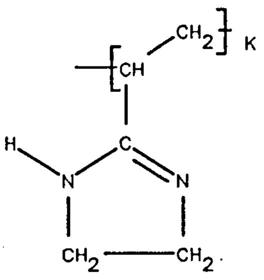
Stage 2:



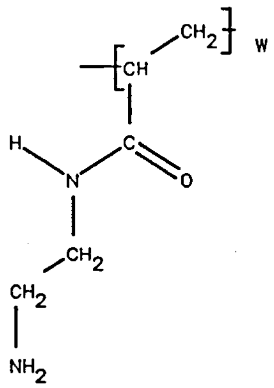
-HCl

Note 2 ↓

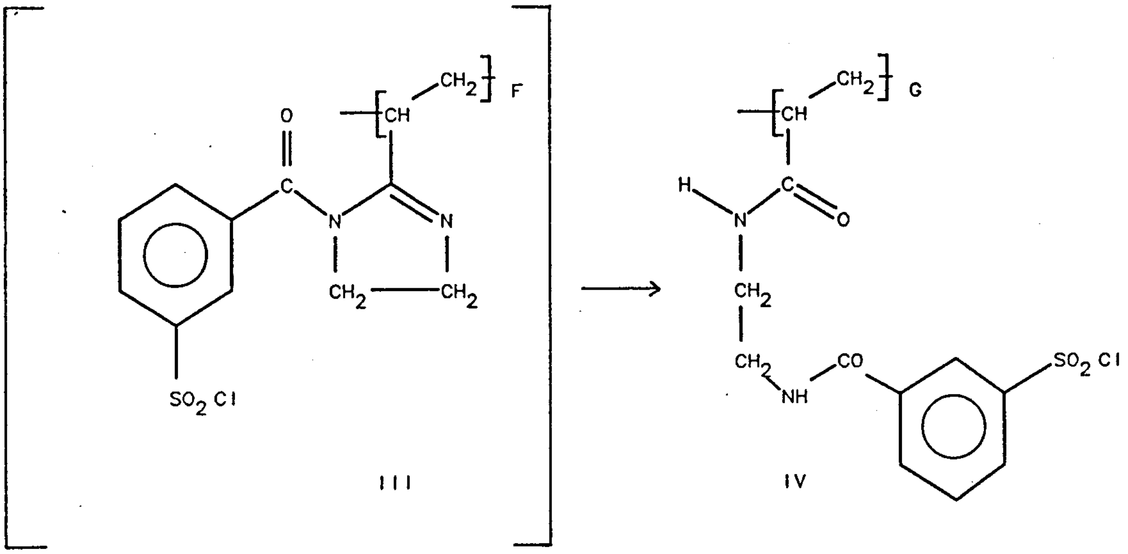
interfacial polycondensation



I

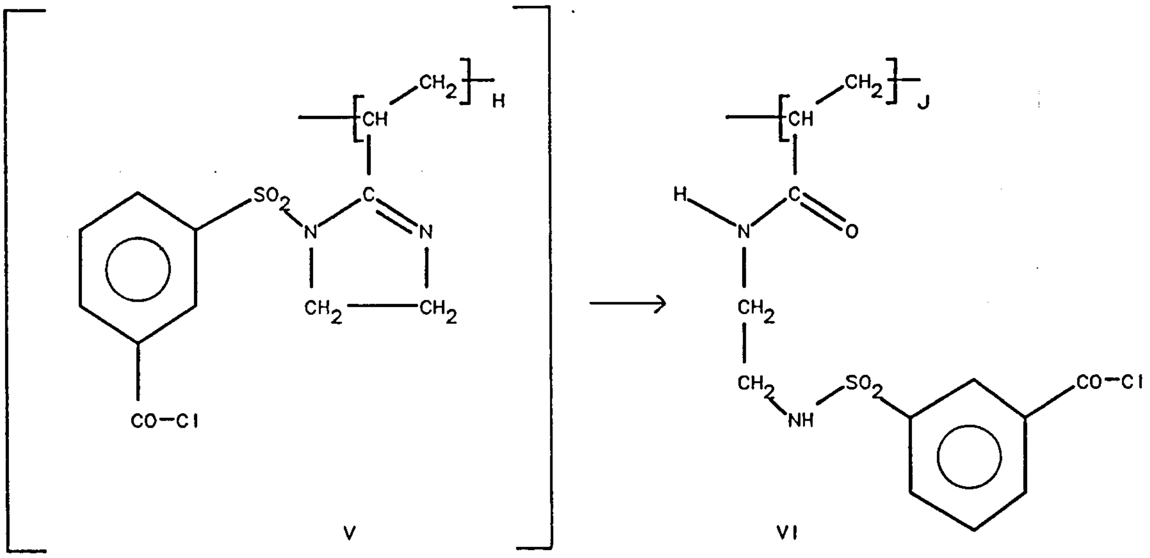


II



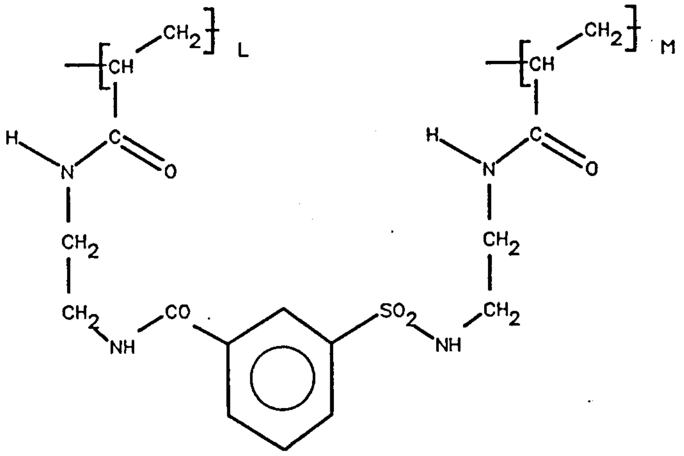
III

IV

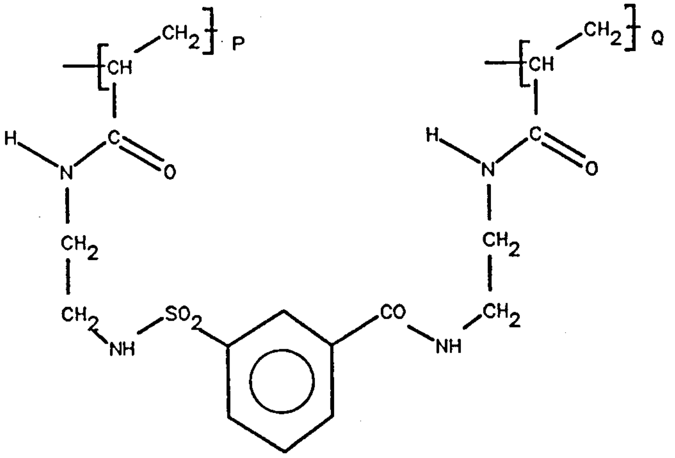


V

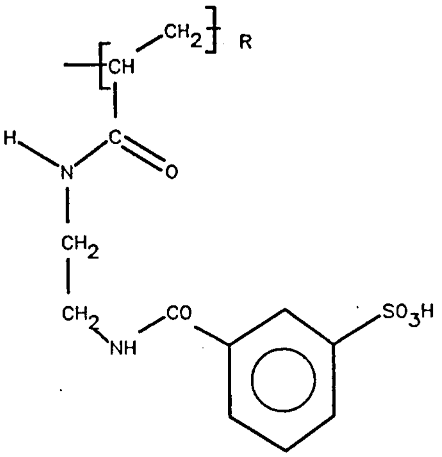
VI



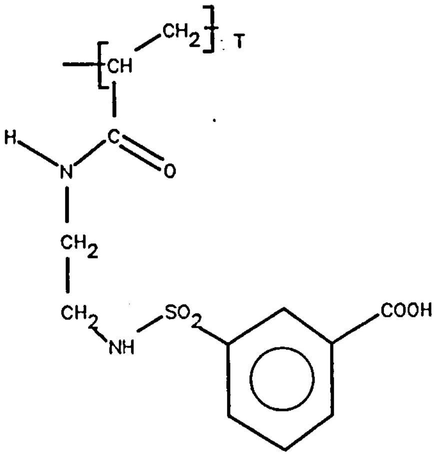
VII



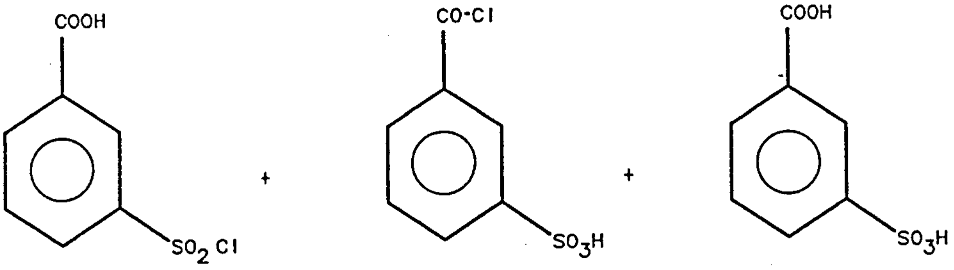
VIII



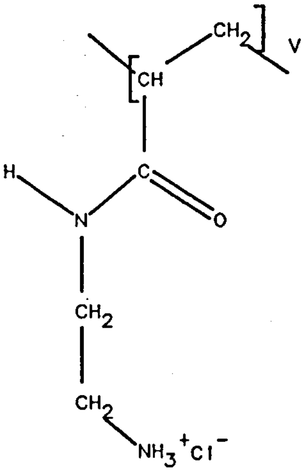
IX



X



XI XII XIII



XIV

Note 2:

(a) It is not expected that ring-closed structures III and V will be found in the membrane structure. Reaction of 2-imidazolines with benzoyl chloride and benzenesulphonyl chloride in aqueous medium leads to cleavage of the imidazoline ring (see Section 2.5.2.3).

(b) The rate of formation of the IV groups will be higher than that of the VI groups due to the higher reactivity of a carbonyl chloride group and an amine compared with that of a sulphonyl chloride group and an amine(20,21). It is therefore expected that the concentration of IV groups will be slightly higher than that of VI groups and the concentration of IX groups will be higher than that of X groups.

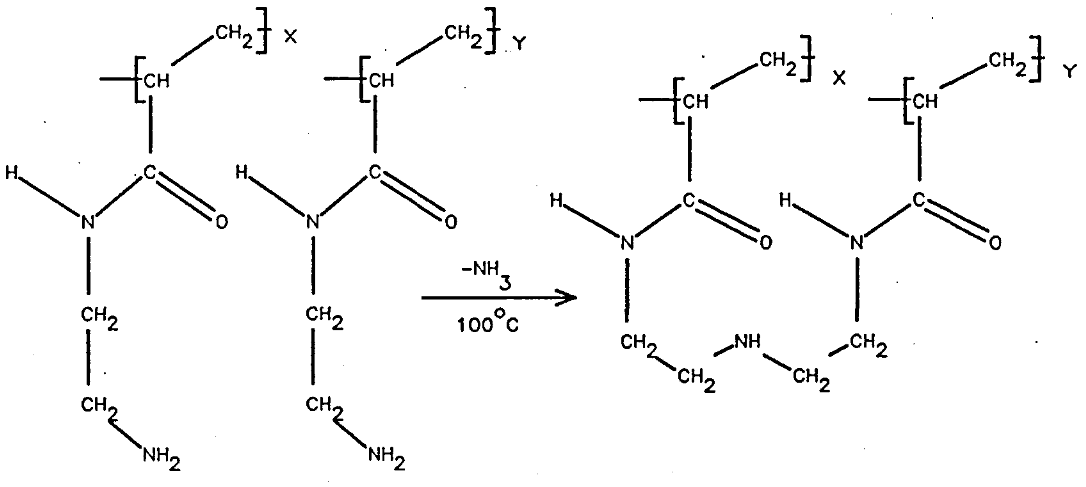
(c) Hydrolysis of some residual acid chloride groups in the structures IV and VI will take place at the water/hexane interface to form the structures with free acid groups IX and X on the membrane surface. (It was, however, reported by Morgan(18) that aromatic carboxylic acid chloride and sulphonyl chloride groups hydrolyse slowly compared with the aliphatics and can tolerate some contact with the aqueous phase.) Alternatively, these groups may be formed by the reaction of partially hydrolysed SCl (having either the -COCl or -SO_2Cl group hydrolysed) with PVAM. Hydrolysis or partial hydrolysis of SCl may take place to form structures XI, XII and XIII.

(d) Hydrochloric acid, released during the interfacial polymerization reaction, will catalyze the ring-opening hydrolysis reaction of any remaining 2-ethylimidazoline rings (reacted or unreacted), leading to a further reduction in the number of ring-closed 2-imidazoline groups in the membrane structure. (Rate constants for the hydrolysis of MC 1 and MC 2 at pH 3 are $k = 6{,}08 \times 10^{-5}$ sec^{-1}; $t_{½}$ 3,2 hours and $k = 3{,}25 \times 10^{-6}$ sec^{-1}; $t_{½} = 2{,}5$ days, respectively, determined as described in Section 3.9.5.) The salt form of unreacted structure II, structure XIV may be formed.

The acid remains present during the following heat-curing step and this will ensure complete hydrolysis.

Stage 3:

Heat-curing of membrane $\xrightarrow{\text{Note 3}}$ final PVAM-FD/SCl membrane form.



I II XV

and II + IV + VI + VII + VIII + IX + X + XI
+ XII + XIII + XIV as described earlier

Note 3:

(a) Adequate heat-curing of the membrane (100°C, see results of glass-slide studies in Section 4.4.7.4ii) could cause crosslinking in the lower layer by elimination of NH_3 from adjacent amine groups of repeat unit II, to form the proposed Structure XV. (This type of reaction was reported to take place during the fabrication of NS-100 membranes from PEI(32)).

Figure 4.24 depicts a simplification of the distribution of the various structures expected to be found throughout the PVAM-FD/SCl membrane, showing heterogenity. There exists a concentration profile of structures throughout the thickness of the membrane, between the polysulphone support and the hexane/water interface.

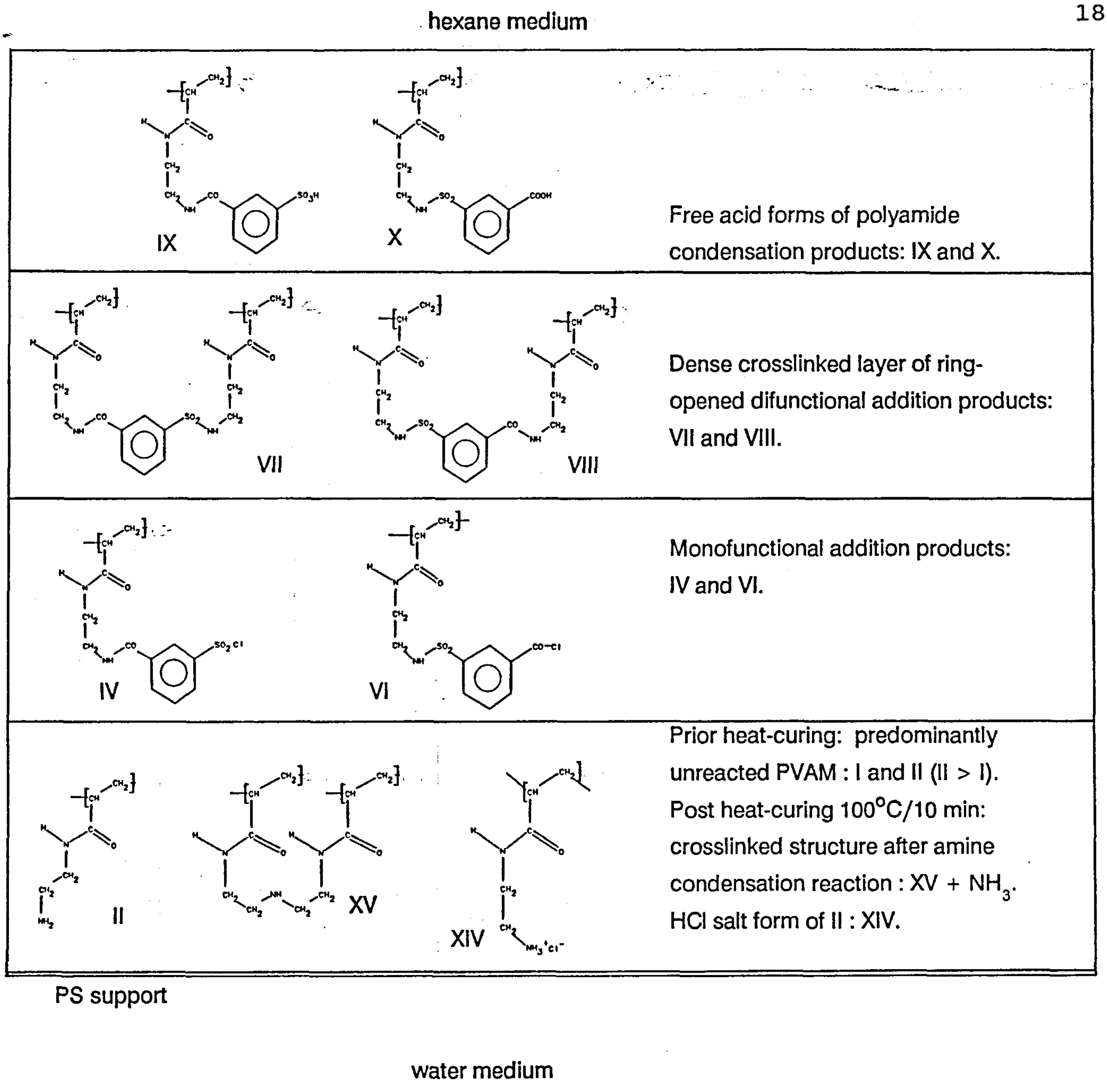


FIGURE 4.25: SCHEMATIC REPRESENTATION OF THE CONCENTRATION PROFILE OF CHEMICAL STRUCTURES THROUGHOUT A PVAM-FD/SCL MEMBRANE

4.4.7.3 Comparisons between PVAM/SCl flat-sheet and tubular membranes

Most early PVAM-OD/SCl flat-sheet membranes (see Section 4.4.2) had been thermally treated at temperatures considered to be sufficient to effect crosslinking by amine condensation (100-110°C, 10 min). During a parallel study of tubular membranes(1,56) (see Section 4.4.3.3), the final oven temperature and residence time which were determined by mathematical optimization (95°C, 5 min) were not considered to be adequate to induce any thermal crosslinking. The degree of crosslinking in tubular PVAM-OD/SCl membranes would therefore depend completely upon the chemical reaction of the amine groups of the PVAM precursor with the acid chloride groups of the SCl crosslinking agent. Hence, no intermediate gel layer was expected to be present in these tubular membranes. When tubular UTF membranes are heated to high temperatures, shrinkage of the membrane occurs which induces stress-cracking of the PVAM/SCl thin film(51).

It is inevitable, therefore, that because of the differences in heat-cure conditions used in the fabrication of flat-sheet and tubular PVAM-OD/SCI membranes, differences will result in the membrane structures of the two forms and these could affect the membranes' overall RO performances. The effect of such structural differences on the baseline RO membrane performances of flat-sheet and tubular membranes per se were not investigated. Differences in structure resulting from differences in thermal treatment during fabrication should, however, be taken into consideration when comparing the results of evaluation of both membrane forms, as will be reported in Section 4.5. It has recently been revealed by Bartels *et al.*(87) that although heat treatment can be detrimental to the performance of an UTF membrane, due to substrate densification leading to a reduction of flux, results of extensive experiments indicate that heat-curing is essential for the making of highly selective membranes. Membranes which had been heat-cured had selectivities 2 to 3 times greater than those of non-heat-cured membranes.

4.4.7.4 **Glass-slide studies**

PVAM, PVAM-Hy and PVAM/SCI films were cast on glass slides and observed for their behaviour under certain conditions of treatment. This study was done in an attempt to arrive at some understanding of the physical nature of the membrane desalting barrier structure.

(i) When a PVAM-FD film was heat-cured at 100°C/10 min and then immersed in water, the film swelled and redissolved. This indicated that no (or minimal) thermal crosslinking and insolubilization had taken place and hence no (or minimal) gel structure would have been created under these conditions. PVAM has a predominantly secondary amine structure and heat-induced elimination of ammonia from such adjacent primary amine groups cannot be expected to take place.

(ii) After a film of the hydrolysed form of PVAM, PVAM-Hy, was heat-cured at 100°C/10 min and then immersed in water, the film remained insoluble. Insolubilization due to thermal condensation had taken place, with the formation of an insoluble gel layer. This was to be expected, because of the primary amine functionality of PVAM-Hy.

(iii) A PVAM/SCI film prepared on a glass slide and then immersed in water did not dissolve, due to its being chemically crosslinked. It only swelled. Addition of a few drops of dilute acid to this film induced extensive swelling which ruptured the film. The swelling of the PVAM/SCI film in aqueous medium is attributed to the fact that the gel layer of the PVAM/SCI film was not adequately crosslinked i.e. an excess of amine functionality remained. Upon exposure of the membrane surface to acid, acid salts can form at the unreacted free-amine sites of PVAM which would further increase the water-uptake capacity of PVAM/SCI films.

High crosslinked densities are required to ensure adequate membrane rejection capabilities albeit at the cost of a reduction in water flux through the membrane. Very high crosslinking densities may, however, lead to the formation of brittle films, whereas low crosslinking densities would allow excessive swelling of the hydrophilic precursor and physical rupture of the desalting barrier.

4.4.8 SUMMARY

(a) PVAM could be used as a polymeric precursor in the fabrication of adequate PVAM/SCl and PVAM/Cl2S UTF flat-sheet RO membranes by an interfacial polycondensation reaction upon a polysulphone substrate.

Depending on the fabrication conditions the following examples of average RO performances were obtained with PVAM-OD/SCl and PVAM-OD/Cl2S membranes:

PVAM/SCl	86% rejection	880 lmd flux (at 4 MPa)
PVAM/Cl2S	94% rejection	1400 lmd flux (at 4 MPa)
PVAM/Cl2S	96% rejection	800 lmd flux (at 4 MPa)
PVAM/Cl2S	99,5% rejection	240 lmd flux (at 2 MPa)

(b) Tubular PVAM/SCl membranes, mathematically optimized during a parallel study(1,56), gave the following optimum RO performances:

PVAM-OD/SCl	97,1 ± 0,1% rejection	730 ± 24,1 lmd flux (at 2 MPa)
PVAM-FD/SCl	98,2 ± 0,7% rejection	560 ± 150 lmd flux (at 2 MPa)

(c) Use of the PVAM-FD precursor from which ethylenediamine had been partially extracted (PVAM-CFD) gave PVAM-CFD/SCl tubular membranes with higher fluxes, which were about 50% greater than those given by PVAM-FD/SCl membranes.

(d) Low-pressure membranes with fluxes greater than 200 lmd at an operating pressure of 500 kPa could be made from an admixture of PVAM-CFD and a filler material as precursor.

4.5 EVALUATION OF PVAM UTF MEMBRANES

4.5.1 CHLORINE TOLERANCE

4.5.1.1 Background

After PVAM had been synthesized (Section 4.3), suitable conditions found, and methods developed to fabricate PVAM UTF membranes which gave acceptable RO performances (Section 4.4), these novel membranes were evaluated for their tolerance to chlorine-containing feed solutions. (Degradation and subsequent failure of most polyamide RO membranes is well-known and has been widely reported in the literature(25,91,92,93), as discussed in Section 2.3.4.1.)

During this study, the following PVAM UTF membranes were exposed to chlorine-containing feed solutions and then evaluated for their RO performance:

PVAM-OD/Cl 2S	(flat-sheet)
PVAM-OD/SCl	(flat-sheet)
PVAM-OD + piperazine/SCl	(flat-sheet)
PVAM-OD/SCl	(tubular)
PVAM-FD/SCl	(tubular)

The tubular membranes were fabricated according to the mathematically determined optimum conditions given in Sections 4.4.3 and 4.4.4. The methods used for the fabrication of the various flat-sheet membranes investigated were similar to those by which membranes of acceptable RO performances had been fabricated, as described in Section 4.4.

The standard test conditions used for the determination of baseline RO performance of the membranes (performance prior to exposure to chlorine) were as described in Section 3.5. Initially, evaluation of the chlorine stability of PVAM UTF flat-sheet membranes was done by the so-called "static method". This method comprised immersion of the membranes in an aqueous NaOCl solution in a closed container for a certain time with RO performance being recorded before and after exposure to chlorine, as described in Section 3.6.1. This method was, however, soon abandoned in favour of the "in-situ" or dynamic method during which chlorine was added to the feed solution during testing of the membrane, as described in Section 3.6.2. This change was made for the following reasons:

(i) during static evaluation, membranes may be damaged when they are removed from the test rigs after initial testing for baseline performance, so that any decrease in performance which may be observed after exposure of the membranes to chlorine and their re-evaluation may be due to mechanical damage and not necessarily to degradation caused by chlorine;

(ii) the dynamic approach appeared to be more widely used by other researchers in the field (see Table 2.3, Section 2.3.4.2) so that the results of tests on PVAM membranes could be more directly compared with these;

(iii) the dynamic approach was thought to be more applicable to conditions under which commercial membranes would operate.

Certain difficulties arose in the evaluation of membranes by the dynamic method. These included:

(i) difficulty in maintaining a constant chlorine concentration in open feed-tanks due to the volatility of chlorine;

(ii) the chlorine concentration of the feed solution had to be constantly monitored during the tests, and frequent manual dosage of chlorine was required to keep level constant;

(iii) medium- to long-term chlorine evaluation tests created a shortage of test space on membrane test equipment.

4.5.1.2 PVAM-OD/Cl2S (flat-sheet membranes)

(a) Static test

PVAM-OD/Cl2S membranes were evaluated for their chlorine tolerance under static conditions. Their RO performance was determined before and after storage for 24 hours in a closed vessel containing an aqueous sodium hypochlorite solution containing approximately 20 ppm free chlorine at pH 6,3.

The baseline RO performance was 98,9 ± 0,4 % rejection and 307 ± 75 lmd flux.

The RO performance after exposure of the membrane to chlorine and a further 164 hours testing time was 98,8 ± 0,5% and 292 ± 37 lmd flux.

Details of the test results are presented in Table 1, Appendix 4. These results showed no decrease in membrane rejection and flux due to exposure to chlorine.

(b) **Dynamic test**

PVAM-OD/Cl2S membranes were evaluated for their tolerance to chlorine under dynamic conditions of approximately 10-20 ppm free chlorine in the feed solution of pH 6,5 for 24 hours. It was difficult to maintain a constant chlorine concentration throughout this experiment due to the high rate at which chlorine escaped from the solution in the open feed-tank. Details of the test results are presented in Table 2, Appendix 4.

Initial RO performance was 96,3 ± 1,0% rejection and 305 ± 79 lmd flux.

The RO performance after exposure of the membrane to chlorine-containing feed water (10-20 ppm) for approximately 10 hours (160 ppm chlorine hours) was 96,4 ± 1,9% rejection and 268 ± 133 lmd flux.

After the free-chlorine level had been allowed to fall to zero and after testing had been continued for a further 50 hours, the RO performance of the membranes was 95,2 ± 2,2% rejection and 812 ± 272 lmd flux. *These results, particularly the increase in flux value, indicated that the performance of the* membranes had been affected by the presence of chlorine.

4.5.1.3 PVAM-OD/SCl (flat-sheet membranes)

PVAM-OD/SCl flat-sheet membranes were evaluated for their tolerance to chlorine under dynamic conditions. Details of the RO performance results are presented in Table 3, Appendix 4.

Baseline RO performance was 92,8 ± 0,7% rejection and 272 ± 63 lmd flux.

After exposure of the membranes to an initial dose of chlorine (approximately 20 ppm) and after 4 hours of testing the RO performance was 94,2 ± 0,6% rejection and 251 ± 60 lmd flux.

After the free-chlorine level had been allowed to fall to zero the RO performance of the membranes was again determined and was found to be 80,3 ± 1,2% rejection and 272 ± 76 lmd flux. On reintroduction of chlorine to the feed solution (approximately 15 ppm) and after one hour of testing, the RO performance was again determined and found to have increased again to 93,7 ± 6% rejection. After the chlorine level had again been allowed to fall to zero and after 12 hours testing time the recorded RO performance had dropped to 88,0 ± 0,3% rejection and 326 lmd flux.

Two interesting points emerged from these results:

(i) initially, on addition of chlorine to the feed solution, there was an increase in membrane salt rejection;

(ii) as the level of chlorine in the feed solution decreased, membrane salt rejection decreased; it increased again when the feed solution was re-dosed with chlorine.

4.5.1.4 PVAM-OD + piperazine/SCl (flat-sheet membranes)

Fabrication of UTF membranes by the use of the monomeric secondary amine compound piperazine as precursor was prompted by the results obtained by Credali(65) who had demonstrated chlorine-resistant poly(piperazineamide) membranes in asymmetric form. In the light of this, membranes were fabricated from a precursor admixture of PVAM-OD and piperazine, as described in Section 4.4.2.3b. These membranes were evaluated for their tolerance to chlorine under dynamic test conditions. Details of RO performance are presented in Table 4, Appendix 4.

The baseline RO performance was 90,4 ± 4,2% rejection and 347 ± 99 lmd flux.

The RO performance of the membranes after exposure to a chlorinated feed solution (approximately 10 ppm) for 16 ppm chlorine hours was 96,4 ± 1,5% rejection and 273 ± 97 lmd flux.

Once the free-chlorine level had decreased to zero and after a further 12 hours of test time had elapsed, the RO performance of the membranes was 90,3 ± 0,4% rejection and 374 ± 120 lmd flux. Ideally, the evaluation should have been carried out over a longer period at a zero-chlorine level to determine whether the membrane performance would have dropped further. This should be done in future research.

From the results obtained, the trend in RO performance due to exposure to chlorine was similar to that observed for other PVAM UTF membranes (see Sections 4.5.1.2 and 4.5.1.3). When chlorine was first added to the feed solution, there was an increase in salt rejection of the membrane. As the free-chlorine level dropped, membrane salt rejection decreased.

4.5.1.5 PVAM-OD/SCl Tubular Membranes

Selected results of early studies carried out during a parallel study(56) to determine the effect of chlorine on the RO performance of PVAM-OD/SCl tubular membranes under dynamic conditions are presented in Table 4.27.

TABLE 4.27: THE EFFECT OF CHLORINE (pH 6) ON THE RO PERFORMANCE OF THREE SETS OF PVAM-OD/SCL TUBULAR MEMBRANES EVALUATED UNDER DYNAMIC TEST CONDITIONS

Baseline RO performance			Chlorine		Resultant RO performance		
Rejection [%]	Flux [lmd]	A^2/B ($x10^{-5}$)	Level [ppm]	Time [h]	Rejection [%]	Flux [lmd]	A^2/B ($x10^{-5}$)
96,4	330	3,21	1,5 2-0,2	0,5 50	97,3 95,8	260 260	3,31 2,22
84,9	1100	-	50	0,5	46,7	3690	-
90,5	1080	-	15	1,2	90,2	630	-

These results show clearly that subjection of PVAM-OD/SCl membranes to a chlorine concentration of 50 ppm has an immediate adverse effect on membrane performance.

4.5.1.6 PVAM-FD/SCl Tubular Membranes

Although short-term tests on membranes with a chlorine-containing feed solution may give an indication of the membrane's sensitivity to chlorine, long-term testing was necessary to establish the membrane's ultimate response to chlorine.

Two sets of PVAM-FD/SCl tubular membranes (6 in each set) were prepared according to the optimum condition of fabrication (Section 4.4.4.2). In two separate experiments, each set of membranes was tested under dynamic conditions for its chlorine tolerance (approximately 5 ppm chlorine, pH 6-7) over a period of 10 days. Details of evaluation conditions and test results are shown in Table 5, Appendix 4. A summary of these test results is presented in Table 4.28 to highlight some interesting effects which seem to be repeated, and which will be discussed later in Section 4.5.1.7.

TABLE 4.28: SUMMARY OF THE EFFECT OF CHLORINE (5 ppm; pH 6,3 - 6,7; 20°C) ON THE RO PERFORMANCE OF TWO SETS OF PVAM-FD/SCL TUBULAR MEMBRANES, EVALUATED UNDER DYNAMIC TEST CONDITIONS
(Results extracted from Table 5, Appendix 4)

Test time [h]	Chlorine [Σppm.h]	Salt Rejection [%]	Permeate Flux [lmd]	A^2/B $\times 10^{-5}$
Experiment 1:				
0	0	98,9 ± 0,1	897 ± 61	37,0
51,4	193,7	99,1 ± 0,1	588 ± 45	26,4
168,2	193,7	97,6 ± 0,3	767 ± 45	13,1
240,9	432,9	98,8 ± 0,2	632 ± 39	22,9
312,2	432,9	97,5 ± 0,4	892 ± 44	15,5
390,6	432,9	95,3 ± 0,6	953 ± 269	9,6
Experiment 2:				
0	0	99,3 ± 0,1	265 ± 27	14,1
52,7	193,7	99,3 ± 0,05	205 ± 29	10,5
168,2	193,7	98,2 ± 0,3	321 ± 35	6,5
240,7	432,9	98,8 ± 0,3	282 ± 38	9,1
312,2	432,9	97,3 ± 1,0	405 ± 41	5,9
390,7	432,9	91,7 ± 2,9	503 ± 39	-

These results (and the more detailed results contained in Table 5, Appendix 4) led to the following observations:

(i) On addition of chlorine to the feed solution there appeared to be an initial increase in salt rejection, and a decrease in water flux.

(ii) As the level of the chlorine in the feed solution decreased to zero, the salt rejection decreased, and water flux increased.

(iii) When the feed solution was redosed with chlorine, and membranes re-evaluated, the rejection increased whereas water flux decreased.

(iv) Once the chlorine level had dropped again and the membranes were finally evaluated after a period of 68 hours (at zero free-chlorine) an obvious drop-off in rejection was observed.

Shortage of available test space at this stage did not permit continued testing of these membranes to determine how much further their RO performance would decrease.

A further set of PVAM-FD/SCl tubular membranes was evaluated on Stellenbosch tap water (pH approximately 6,5) over a period of 20 days. Although the low chlorine content of the tap water could not be accurately determined by the DPD titration method routinely used, it was estimated to be about 0,2 ppm free chlorine as this water contained enough chlorine to exclude any biological growth in the feed tanks of the testing equipment.

At the start of the operation, the average performance of the membranes on tap water was 90,9% rejection and 580 lmd flux. After 480 hours the performance was 91,6% rejection and the flux had decreased to 280 lmd. It was suspected that the severe flux decline could be due to compaction or fouling, rather than to deterioration of the membranes due to attack by chlorine. After 1100 hours testing, no further decline in membrane performance was noted.

A further two sets of PVAM-FD/SCI tubular membranes were prepared, according to the optimum formulation conditions, and post-treated with polyvinyl alcohol. One set of membranes was evaluated for its chlorine resistance at pH 5,6 and the other set was evaluated for its chlorine resistance at pH 8, under otherwise similar dynamic operating conditions of approximately 5 ppm free chlorine at 20°C, over a period of about 2 weeks. Details of the test conditions used and the average rejection and flux results of these membranes are presented in Tables 6a and 6b, Appendix 4.

After exposure of the membranes for approximately 220 ppm chlorine hours at pH 8, there was a 3,5% drop in rejection and an almost three-fold (300%) increase in flux. Membranes exposed for approximately 160 ppm chlorine hours at pH 5,6 showed a 4% decrease in rejection and an almost 200% increase in flux. After the level of free chlorine had dropped to zero and after continued testing of the membranes, there was a further decrease in rejection and an increase in flux of membranes (see Tables 6a and 6b, Appendix 4). No major difference in the performance of PVAM-FD/SCI membranes was observed when the membranes were evaluated for chlorine stability at the acid and alkaline pHs of 5,6 and 8, respectively.

4.5.1.7 Discussion

The results of all the dynamic tests carried out on PVAM UTF membranes to determine their RO performance towards chlorinated feedwaters during this study showed similar trends. These are summarized here and some possible explanations are offered:

(i) When the membranes were first exposed to chlorine, there was a slight increase in salt rejection coupled with a decrease in water flux. Similar performance had been reported for the commercially available aromatic polyamide B9 membrane(94,95) and the FT-30 membrane(96). This was ascribed to the reaction of residual amine end-groups with chlorine which altered the transport properties of the membrane slightly, but which did not cause degradation of the polymer or membrane, as only amine end-groups were affected.
(The mechanistic study of membrane-chlorine interaction has been discussed in the theoretical Section 2.3.4.4.)

Studies on the B9 membrane which were directed at relating halogen uptake with membrane degradation included viscosity measurements of chlorinated B9 polymer solutions in attempts to detect any depolymerization or morphological changes(94,95). It was found that the viscosity of a chlorinated B9 membrane sample increased during the first 10 hours of exposure to chlorine, whereafter it decreased steadily. The initial rise in viscosity was ascribed to addition of chlorine to the polymer, accompanied by a corresponding increase in polymer mass. This finding could explain the initial tightening of the membrane and increase in salt rejection.

The initial decrease in water flux was explained by the fast N-chlorination reaction which could take place with secondary amine groups (see Section 2.3.4.4). These groups could be converted to -N-Cl-groups, thus reducing the overall extent of hydrogen bonding and the hydrophilicity of the membrane. (Chain scission, which leads to the disruption of the salt rejection barrier and an increase in flux, occurs much more slowly.)

(ii) When the chlorine level was allowed to decrease, there was a decrease in salt rejection coupled with an increase in water flux. The PA-300 and related RC-100 membranes also showed a decrease in salt rejection when the chlorine level in a chlorinated feed was decreased.

(iii) On re-introduction of chlorine to the feedwater, rejection increased and flux decreased slightly. The reasons for this performance were similar to those given in (i) above.

(iv) Membrane performance, upon exposure of the membrane to chlorine-containing feed solutions, appeared to follow the trends described in (i) to (iii) until the chlorine level fell to zero and was not increased again. After continued testing of the membranes at zero chlorine, membrane performance decreased to well below the baseline RO performance, indicating that the membranes had become degraded.

In order to be able to explain more accurately what reactions the repeat units in the PVAM membrane may undergo when exposed to chlorine-containing feedwaters, in the endeavour to determine which functual groups in the membrane are most susceptable to chlorine attack, the chemical composition of the PVAM UTF membrane required close consideration. The PVAM/SCl desalting barrier was expected to comprise the following groups, amongst others, as discussed in Section 4.4.7.2.

1. Residual 2-imidazoline groups, arising from any unreacted PVAM, Structure I. Very few of these would, however, be present due to hydrolysis.
2. Tertiary amides and sulphonamides resulting from the crosslinking reaction between PVAM and SCl, Structures III and V, respectively. Very few of these would, however, be present due to hydrolysis.
3. Primary amines, present as terminal amine sites of unreacted PVAM-Hy, Structure II.
4. Secondary amides present as unreacted groups in the PVAM-Hy, Structure II, and secondary amides or sulphonamides formed by reaction of terminal amine groups of PVAM-Hy with SCl, Structures VII and VIII, respectively.
5. Secondary amines formed after a heat-induced (> 100°C) crosslinking reaction between adjacent primary amines, Structure XV.

It is known that PVAM-FD contained a quantity of ethylenediamine as an impurity which could compete with the crosslinking agent in formation of the desalting barrier. Its influence on chlorine stability will however, not be taken into account here. It is, however, interesting to note that membranes fabricated from ethylenediamine and benzenetricarboxylic acid chloride (TMC) were reported to show good chlorine stability, better than that shown by FT-30 membranes(91). This was ascribed to their having an aliphatic amine component.

On the basis of the mechanisms of chlorine attack in polyamides, as described in Section 2.3.4.4, the susceptibilities of various functional groups, present in PVAM/SCI membranes, to attack by chlorine are proposed to be as follows:

1. Tertiary (N-alkyl substituted) amide linkages are expected to be the most stable(91,97). They do not appear to react with HOCl, presumably because of the absence of an amide proton. No mention has been found in the literature of the reaction of tertiary amides and HOCl. There are, however, very few such groups remaining in the membrane structure due to hydrolysis.

2. Secondary amines react with HOCl to undergo N-chlorination. Subsequent dehydrochlorination and hydrolysis will result in chain scission. It could therefore be expected that a polyamide membrane of high rejection should first be obtained, in which most of the amines are chemically crosslinked to amide groups, before it can possess adequate chlorine stability. Lee(91) reports that under acidic conditions, degradation of membranes containing both unreacted -NH and crosslinked -NHCO groups is caused largely by attack by chlorine on the amine group. It would seem, therefore, to be most desirable to eliminate secondary and tertiary amine groups from polyamides in order to reduce their vulnerability to chlorine attack.

3. Secondary amide linkages are reported to react primarily with an OCl^- species to form an N-chloro amide which is considered to be quite stable under neutral conditions(91). Hence, a membrane containing only secondary amide linkages may be expected to be chlorine-resistant at low pH, but unstable at high pH values.

   Mention should be made here of the correlation between the chemical structure of polyamides and their reactivity to HOCl as has been reported by Kawaguchi(98,99) (see also in Section 2.3.4.4): "Diamine components play an important role in determining the reactivity of polyamides to oxidative chlorine. Aromatic primary diamines give polyamides which are susceptible to oxidative chlorination resulting in irreversible reaction at the aromatic nucleus. Aliphatic primary diamines, on the other hand, give polyamides which react at the amide nitrogen to yield N-chlorinated amides. The N-chlorinated amide can be reversibly regenerated to the initial amide by treatment with reducing agent. Tertiary polyamides are inactive towards to oxidative chlorine."

   All the secondary amide linkages (arising from chemical crosslinking of the PVAM-Hy component in the PVAM desalting barrier) would be formed from aliphatic amine components and hence the above may be considered applicable in explaining the behaviour of the secondary amides in the PVAM-UTF membrane. These sites may, therefore, not be too susceptible to chlorine attack leading to membrane degradation.

4. Primary amines treated with HOCl yield N-chloroamines or N,N-dichloroamines(91,97). These reactions are considered to be of little relevance to polyamide membrane degradation as any primary amine site in the membrane desalting barrier will be present as a terminal group at the end of a chain. No chain scission can therefore take place and hence the integrity of the salt rejection barrier should not be detrimentally affected. Transport properties may, however, be altered.

It would appear that the site in a PVAM/SCl membrane most likely to be attacked by chlorine at high pH is a secondary amine site in the membrane substructure. Riley claims that degradation of the PA-300 membrane may occur mainly due to chlorine attack on the polyamine gel substructure (see Section 2.3.4.3).

Limited investigations into the chlorination reactions and products of chlorination of model compound materials of the PVAM-FD/SCl membrane were carried out, as described in Section 3.9.4. Under the experimental conditions used, no evidence was found to indicate the formation of any chlorinated species.

Exposure of PVAM-FD/SCl membranes, prepared under conditions described in this study, to chlorine is not advisable although brief exposure to a 5 ppm free chlorine at pH 6,5 - 8 should not seriously degrade the membrane(100).

4.5.2 pH STABILITY

Routine testing of PVAM UTF membranes for their RO performance of salt rejection and flux had been conducted at pH values of between 6 and 7 (Section 4.4). It is generally considered desirable that UTF membranes should withstand continuous operation in RO systems over a pH range of 3 to 11, at temperatures of 0 to 35°C(101). Tests were therefore carried out to evaluate the stability of the novel PVAM UTF membranes under operating conditions of low and high pH. The effect which acidic and basic environments may have on the RO performances of UTF membranes has been discussed in Section 2.3.5. (Low pH conditions usually occur during routine cleaning of membranes and certain types of deposits are removed from the surfaces of fouled RO membranes under alkaline conditions.) During this study the RO performances of the following PVAM UTF membranes were evaluated under extremes of pH conditions:

PVAM-OD/Cl2S (flat-sheets):	pH 1 (static conditions) pH 2,5 (dynamic conditions) pH 10 (dynamic conditions)
PVAM-FD/SCl (tubulars):	pH 3,6,11 (dynamic conditions) > 500 h pH 3,5,7,9,11 (static conditions)

Tubular membranes were prepared according to the mathematically determined optimum conditions given in Section 4.4.4. Methods used to fabricate the flat-sheet membranes were similar to those by which membranes of acceptable RO performance had been fabricated, as described in Section 4.4.2. Standard test conditions employed in the determination of the baseline RO performance (pH 6-7, prior to exposure of membranes to pH extremes) were as described in Section 3.5.1 (both flat-sheets and tubes were tested at an applied pressure of 2000 kPa). Results are presented and discussed in Sections 4.5.2.1 - 4.5.2.3.

In efforts to gain more information by which to explain more fully PVAM UTF membrane performance and behavior upon exposure to pH extremes, the effects of extreme pH conditions on the model compounds of the PVAM UTF membranes: MC1, MC2, HMC1 and HMC2, were investigated, as described in Section 3.9.5.

4.5.2.1 PVAM-OD/Cl2S (flat-sheet membranes)

(a) Static test at low pH (1,0)

A set of PVAM-OD/Cl2S flat-sheet membranes (6 membranes) was evaluated for RO performance after exposure to a pH 1 medium for 24 hours under static conditions (see Section 3.7.1 for experimental details). The results of this experiment are shown in Table 4.29.

TABLE 4.29: THE EFFECT OF EXPOSURE TO ACID (HCl; pH 1; 24 h; 22°C) ON RO PERFORMANCE OF PVAM-OD/CL2S MEMBRANES UNDER STATIC CONDITIONS

Test time [h]	RO performance Rejection [%]	Flux [lmd]
Baseline (165)	98,5 ± 0,5	331 ± 60
After exposure (+ 165)	97,3 ± 0,5	316 ± 85

There was a slight decrease in both the average flux and rejection of the membranes. It is uncertain, however, whether the removal of membranes from the test-rig and their replacement (procedures required by the static method of evaluation) affected the results. Future evaluations were therefore done by the dynamic method.

(b) Dynamic test at low pH (2,5)

A further set of PVAM-OD/Cl2S flat-sheet membrane was evaluated for its pH stability under dynamic conditions (see Section 3.7.2) at pH 2,5 for 200 hours. Results are shown in Table 4.30.

TABLE 4.30: RO PERFORMANCE OF PVAM-OD/CL2S FLAT-SHEET MEMBRANES UPON EXPOSURE TO ACID (HCl; pH 2,5; 200 h; 22°C) UNDER DYNAMIC CONDITIONS

Test Time [h]	pH	RO Performance Rejection [%]	Flux [lmd]
Baseline (170 h)	6,8	96,1 ± 1,3	281 ± 98
300	2,5	94,5 ± 2,0	243 ± 134
370	2,5	95,6 + 0,7	246 + 144

These results are similar to those obtained after evaluation under static conditions (4.5.2.1a); a slight drop in rejection and flux was observed.

(c) Dynamic test at high pH

A set of flat-sheet PVAM-OD/Cl2S membranes was evaluated for RO performance in an unbuffered feed solution at various alkaline pH values, under static conditions. The baseline RO performance was determined at pH 6,3. The pH of the feed solution was adjusted with sodium hydroxide to pH 9-10 and after 124 hours the RO performance was determined. The pH of the feed solution was then adjusted to pH 7-8 with hydrochloric acid, and after 24 hours the performance was again determined. Results are presented in Table 4.31.

TABLE 4.31: RO PERFORMANCE OF PVAM-OD/CL2S MEMBRANES UPON EXPOSURE TO FEED SOLUTION OF ALKALINE pH UNDER DYNAMIC CONDITIONS

Test Conditions		RO Performance	
pH	Time [h]	Rejection [%]	Flux [lmd]
6,3	95	92,4 ± 1,3	501 ± 242
9-10	219	95,2 ± 1,2	709 ± 108
7-8	243	94,4 ± 3,0	678 ± 75

These early results indicated that the RO performance of the PVAM-OD/Cl2S membranes peaked at a pH value of between 9 and 10. Increases in rejection and flux values were observed at this pH.

4.5.2.2 PVAM-FD/SCl
(tubular membranes)

(a) Dynamic tests at low and high pH

The following observations were made during early parallel studies(102) on PVAM-FD/SCl tubular membranes:

(i) A set of membranes was subjected to a series of pH changes, ranging from pH 2 to pH 10 for short periods of time, without drastic changes in performance when evaluated under standard test conditions (given in Section 3.5). The PVAM UTF membranes did, however, appear to act as a hydrogen-ion pump and at low feed-pH, the pH of the permeate was usually found to be lower than that of the feed solution, and vice versa, at feed solution pH values above 6,5. Conductivity was used as a measure of rejection (see Section 3.5.2) so that the calculated rejection decreased, at pHs below 6,3.

(ii) During another experiment, it was observed that there was a steady flux decline as pH changed from high to low values, with the salt rejection going through a maximum at pH 6-7(51). At pH 3 the recorded salt rejection was lowest, peaking at about pH 6-7 and decreasing again above pH 8,5. The baseline RO performance of membranes (prior to exposure to pH extremes) returned, however, upon testing of the membranes under standard conditions. These observations were similar to those made after the following controlled study:

Three similar sets of PVAM-FD/SCl membranes (6 in each) were subjected to feed solutions of pHs 3,6 and 11 (unbuffered) under dynamic conditions for extended periods of time (6 weeks) and then evaluated for their RO performances. These membranes were fabricated under the mathematically determined optimum conditions for PVAM-FD/SCl tubular membranes, described in Section 4.4.4.2.

RO performances were determined at various time intervals at the inherent pH of the feed solution until, on completion of this trial, the pH of the feed solution was readjusted to the standard pH 6,5. A summary of the rejection and flux results obtained, is presented in Table 4.32.

TABLE 4.32: THE EFFECT OF PH ON THE RO PERFORMANCE OF PVAM-FD/SCL TUBULAR MEMBRANES EVALUATED UNDER DYNAMIC CONDITIONS

			RO Performance	
Exp	Feed Solution pH	Total Test Time [h]	Salt Rejection [%]	Permeate flux [lmd]
Experiment 1:				
pH 3	6,6	24	97,7 ± 1,3	384 ± 27
	6,5	168	98,6 ± 0,8	416 ± 23
	3,06	171	76,6 ± 0,6	466 ± 43
	3,08	193	76,9 ± 0,7	478 ± 23
	3,08	246	72,0 ± 0,8	568 ± 50
	3,05	285	74,2 ± 0,8	468 ± 94
	3,06	356	78,6 ± 0,8	724 ± 35
	3,05	407	77,5 ± 0,9	804 ± 39
	3,03	429	82,1 ± 1,8	835 ± 47
	3,19	531	82,0 ± 0,8	878 ± 44
	3,08	796	82,1 ± 0,9	964 ± 38
	3,08	944	82,5 ± 0,5	1034 ± 61
	6,51	1024 (after 52 h @ std pH)	95,0 ± 0,6	772 ± 30
	6,52	1044 (after 72 h @ std pH)	94,9 ± 0,7	746 ± 34
Experiment 2:				
pH 6	6,5	24	97,4 ± 0,2	793 ± 66
	6,54	747	97,4 ± 0,6	667 ± 34
	6,49	792	97,2 ± 0,8	662 ± 38
	6,50	887	96,7 ± 1,2	657 ± 44
	6,58	947	97,3 ± 0,6	652 ± 34
	6,55	1035	97,2 ± 0,6	648 ± 29
Experiment 3:				
pH 11	6,61	24	98,4 ± 0,5	250 ± 39
	6,46	463	98,7 ± 0,2	353 ± 12
	10,95	466	87,2 ± 0,4	445 ± 22
	11,06	532	85,2 ± 0,3	522 ± 10
	11,0	796	83,8 ± 0,4	593 ± 8
	11,05	943	83,9 ± 0,5	635 ± 8
	10,97	963	80,6 ± 0,4	660 ± 11
	6,53	1014 (after 51 h @ std pH)	97,4 ± 0,4	613 ± 12
	6,54	1034 (after 71h @ std pH)	97,3 ± 0,4	608 ± 12

These results indicated that the membranes were not significantly degraded upon exposure to pH 3 or pH 11. There was, however, some drop in baseline rejection performance after more than a month (40 days) exposure time, coupled with a sharp increase in permeate flux. At pH 3 membranes showed a drop of 4% rejection and almost a doubling in flux. At pH 11 membranes showed a drop of only 1% rejection and more than a doubling in flux value.

(b) Static tests at low and high pH

Tests were carried out on sets of PVAM-FD/SCl tubular membranes to evaluate their RO performances after they had been exposed to buffered solutions of pHs 3, 5, 7, 9 and 11 in closed containers under static conditions for various periods of time(56). Membranes were prepared under conditions identical to those used to prepare the membranes which were evaluated for their stability under dynamic conditions (see Section 4.5.2.2.a). Compositions of the buffers are described in the Section 3.9.5.1. The composition of the pH 5 buffer was 50 cm^3 of 0,1 molar potassium hydrogen phthalate + 22,6 cm^3 of 0,1 molar NaOH. The composition of the pH 9 buffer was 50 cm^3 of 0,1 molar tris(hydroxy-methyl) aminomethane + 5,7 cm^3 of 0,1 molar HCl. Each solution was made up to a volume of 100 cm^3. After exposure of the membranes for various time intervals they were removed from the buffer solutions, rinsed with distilled water and evaluated for their RO performances. Membranes were tested under the standard conditions described in Section 3.5. Results are shown in Table 4.33.

TABLE 4.33: THE EFFECT OF pH AND TIME ON THE RO PERFORMANCE OF PVAM-FD/SCL TUBULAR MEMBRANES, EVALUATED UNDER STATIC CONDITIONS

		RO Performance		
pH	Days stored	Rejection [%]	Flux [lmd]	A^2/B (x 10^{-5})
3,05	0	97,2 ± 1,7	205 ± 40	2,6
	1	98,0 ± 0,4	590 ± 60	11,9
	2	93,3 ± 1,0	1030 ± 115	6,3
	7	56,8 ± 5,8	2000 ± 230	1,4
5,07	0	98,4 ± 0,8	245 ± 41	5,6
	1	99,0 ± 0,1	380 ± 52	14,2
	2	98,8 ± 0,3	470 ± 74	15,7
	7	97,9 ± 0,3	510 ± 92	9,5
7,00	0	99,0 ± 0,2	232 ± 39	8,5
	1	97,9 ± 0,6	210 ± 16	3,7
	2	98,6 ± 0,2	230 ± 11	6,4
	7	98,8 ± 0,1	240 ± 10	7,4
9,20	0	99,1 ± 0,03	260 ± 50	11,0
	1	99,2 ± 0,3	210 ± 17	9,5
	2	99,1 ± 0,2	240 ± 34	10,2
	7	99,2 ± 0,1	330 ± 45	16,0
11,2	0	98,4 ± 0,3	330 ± 20	7,5
	1	99,3 ± 0,2	340 ± 28	18,7
	2	99,3 ± 0,2	400 ± 19	20,1
	7	99,1 ± 0,3	540 ± 88	24,9

(Note: *No control experiment was conducted to determine whether the various chemicals used to make up the buffer solutions affected the membranes in any way.)*

Storage of PVAM-FD/SCl tubular membranes at pH 3 had a detrimental effect on their RO performance. This was evident after only two days of exposure when rejection showed a decline and there was an almost linear increase in flux. The membranes which were stored at pH 5 showed a slower decline in rejection, while the flux increase was not as marked as it had been at pH 3. The performance of the membranes stored at pH 7 remained virtually constant. Storage at higher pH values did not seem to affect the membrane rejection. There was, however, a slight linear increase in the flux of the membranes stored at pH 9 and which was more pronounced at pH 11.

The salt-rejection performance of the membranes was affected by storage at low pH (< 7) within only seven days. Storage at high pH (> 7) over the same period of time did not affect rejection. The flux of membranes, resulting from their exposure to solutions of high pH, remained stable i.e. their fluxes did not increase, over a evaluation period of 8 days, when they were tested under standard conditions of pH 6,5 to 7.

4.5.2.3 **Discussion**

It emerged that the PVAM-FD/SCI tubular membranes could be used over a pH range 4,5 - 8,5 without any effect on membrane integrity(100). Membrane performance peaked at pH values of 6,5 to 7. The overall membrane performance, given by the A^2/B value (see Section 4.4.3.1) over the pH range of 3,5 to 10,5 is shown in Figure 4.25. The rejection performance of the membrane over the same pH range is shown in Figure 4.26.

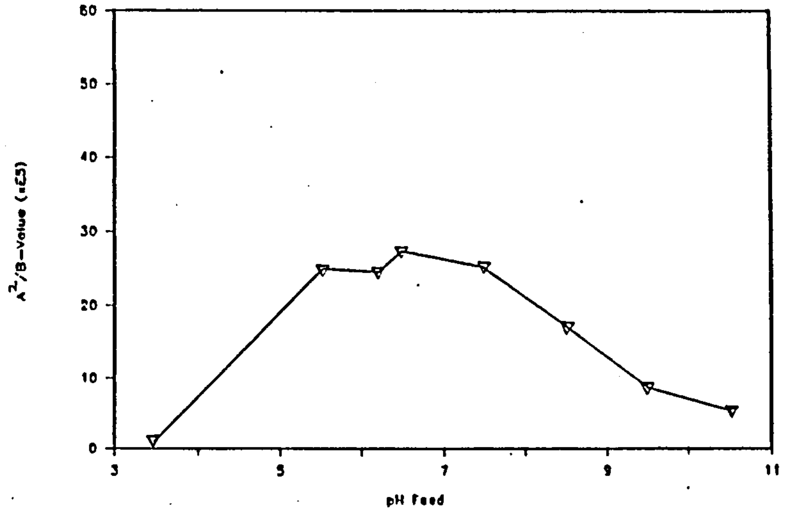


FIGURE 4.25: A^2/B-VALUE OF PVAM-FD/SCL TUBULAR MEMBRANES VS pH FEED SOLUTION

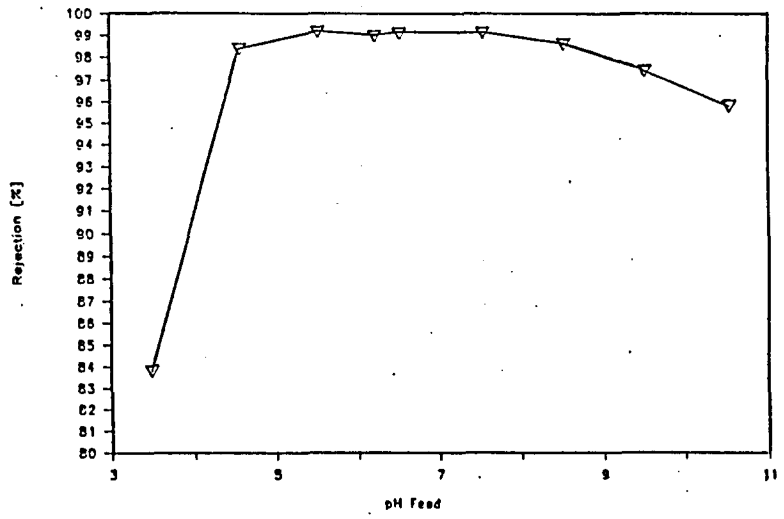


FIGURE 4.26: REJECTION PERFORMANCE OF PVAM-FD/SCL TUBULAR MEMBRANES VS pH FEED SOLUTION

Although the membrane performance declined sharply towards the ends of the pH range, it recovered when the feed solution was neutralised.

There was evidence that the PVAM-FD/SCl membranes deteriorated rapidly and drastically upon exposure to low pH environments under static conditions (see Table 4.33), whereas exposure to low pH environments under dynamic conditions did not have such a marked degrading effect. This may be attributed to a high degree of swelling which could take place within the hydrophilic PVAM UTF membrane at low pH. In a low-pH, acidic environment, the polyamine of the intermediate layer may have been converted from the amine form to the acid salt. As a result, the intermediate layer of the membrane would swell and expand. This had in fact been observed during examination of a PVAM-FD/SCl film sample on a glass slide as described in Section 4.4.7.4. Upon addition of a drop of acid to such a film (similar to that representing the membrane's desalting barrier), the film was seen to swell markedly. Riley(103) has reported that under static conditions membrane swelling could take place unchecked, leading eventually to mechanical break-up of the membrane's desalting barrier. It is expected that under dynamic conditions, however, the operating pressure exerted on the desalting barrier would serve to hold any excessive swelling in check, so preventing the mechanical rupture of the membrane barrier. The mechanical integrity of a PVAM UTF membrane might be improved by increasing the degree of crosslinking, which should then reduce the swelling capacity of the desalting matrix. This should be investigated in future research.

Unlike acids, bases would not be expected to cause the strongly alkaline intermediate layer of PVAM to swell so that the transport properties should not be adversely affected by strongly basic feed solutions. There was indeed no deterioration in PVAM-FD/SCl membrane rejection performance at high feed pH. There was, however, a flux increase after membrane exposure to a feed solution of pH 11. The explanation for this is not apparent at this stage.

The results obtained from concurrent investigations into the stability of the membrane's model compounds in acid and basic media is presented in Section 3.9.5.

4.5.3 TEMPERATURE STABILITY

Although UTF composite membranes are reported to be able to withstand exposure to high water temperatures quite successfully (see Section 2.3.6), the combination of exposure to feedwaters of high temperature and to high RO operating pressure conditions can result in irreversible lowering of the membrane flux due to creep behaviour of the materials used to fabricate the membranes(104).

Two different sets of flat-sheet PVAM UTF membranes PVAM-OD/SCl and PVAM-OD/Cl2S were evaluated for the effect which a feed-solution temperature of 40°C would have on their RO performances. Membranes were tested at 2 MPa applied pressure. These results are presented in Table 4.34.

TABLE 4.34: RO PERFORMANCE OF PVAM-OD UTF MEMBRANES AS A FUNCTION OF OPERATING TEMPERATURE

Membrane Composition	Temperature [°C]	RO Performance Salt Rejection [%]	Flux [lmd]
PVAM-OD/Cl2S	25	94,2 ± 3,4	132 ± 4
	40	95,6 ± 3,1	233 ± 10
PVAM-OD/SCl	25	98,8 ± 0,3	100 ± 25
	40	98,9 ± 0,3	181 ± 44

A significant increase in the membrane flux at the higher operating temperature, coupled with no loss in salt rejection, was observed. Due to test-system limitations the membranes were not evaluated under operating conditions at temperatures above 40°C.

The effect of altering both the operating feed-pressure and temperature on the performance of PVAM-FD/SCl tubular membranes has been investigated(51), and the results are shown graphically in Figures 4.27 and 4.28. Membrane flux was seen to be a linear function of the applied pressure. This was in accordance with what was reported in the literature(67,68).

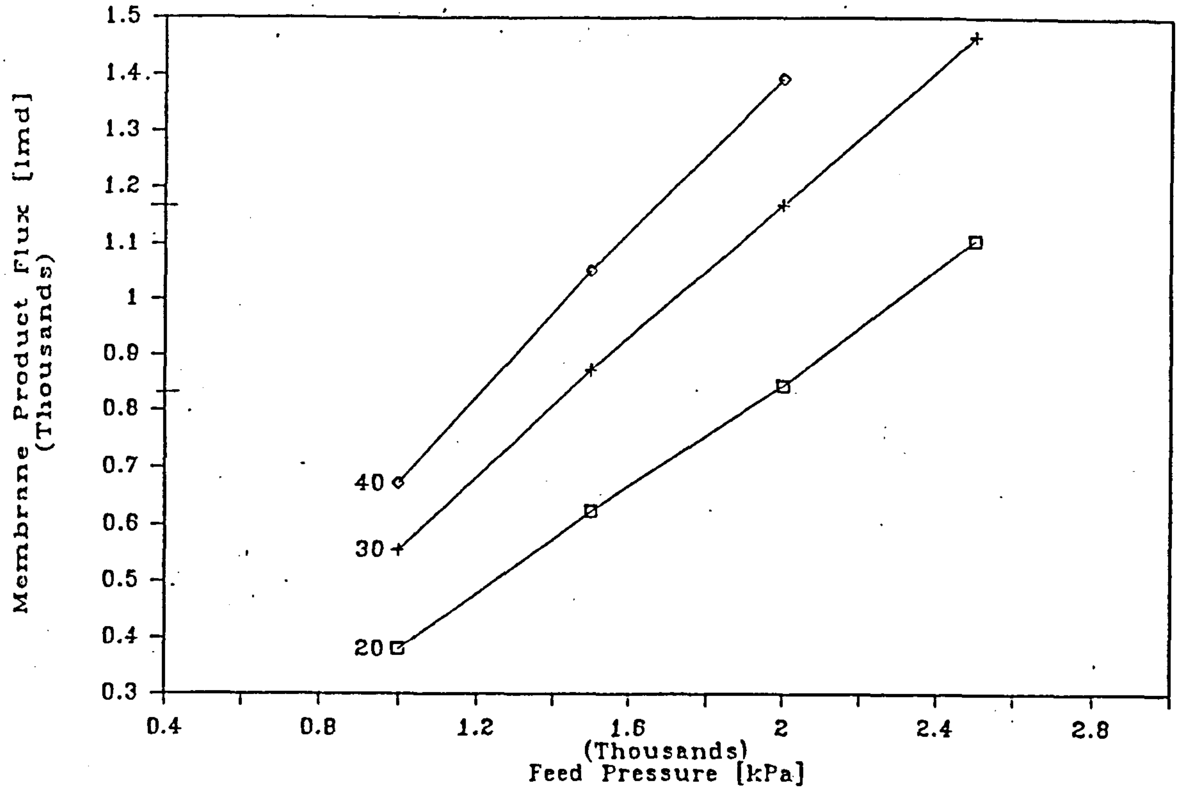


FIGURE 4.27: THE EFFECT OF FEED-SOLUTION PRESSURE AND TEMPERATURE ON THE FLUX OF OF PVAM-FD/SCL TUBULAR MEMBRANES

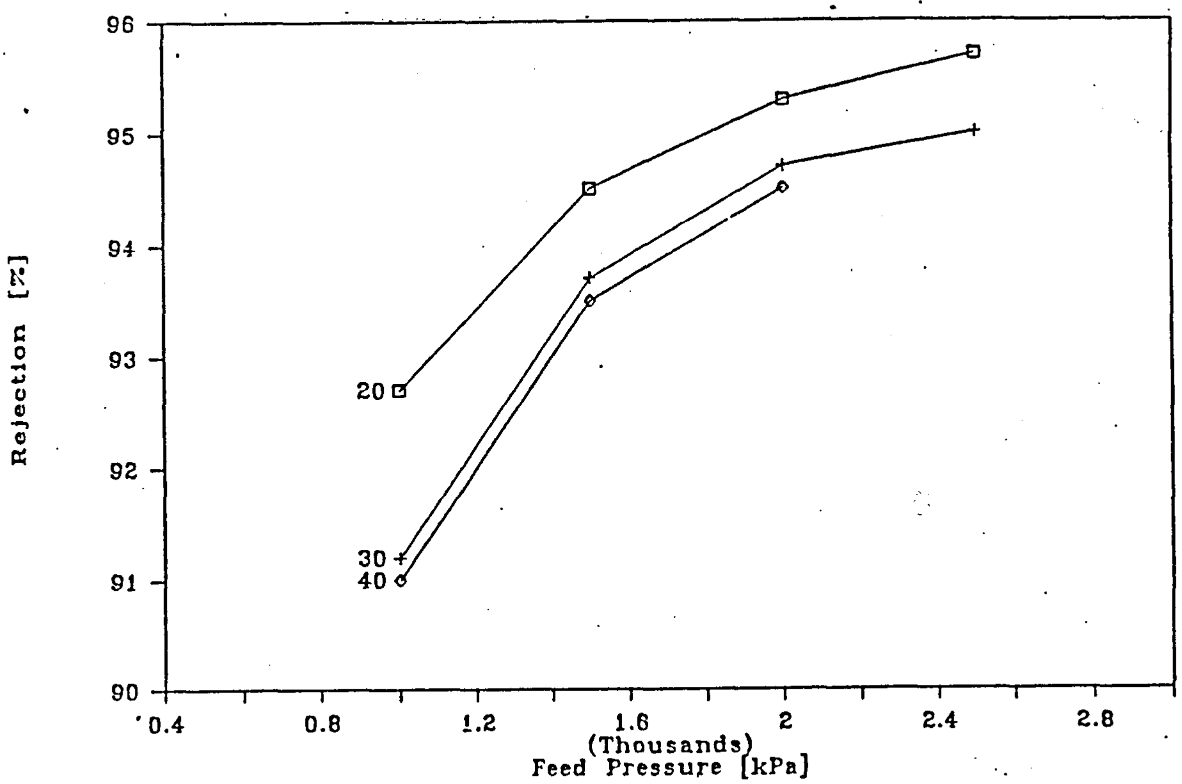


FIGURE 4.28: THE EFFECT OF FEED-SOLUTION PRESSURE AND TEMPERATURE ON THE REJECTION OF PVAM-FD/SCL TUBULAR MEMBRANES

4.5.4 Stability upon storage under atmospheric conditions

PVAM-FD/SCl tubular membranes, dry-stored and open to the atmosphere for two weeks, prior to testing, have been reported (during a parallel project(1)) to exhibit below-standard RO performance(51).

Two possibilities emerged as explanations for the inadequate dry-stability of these membranes:

(a) The presence of acid groups on the membrane surface. Acid groups remain on the membrane surface after the interfacial polycondensation fabrication process, during which HCl is formed as a condensation product. The disadvantage of this emerged from the following observations:

  (i) membrane performance generally declined after exposure of the membrane to acidic feed solutions (Section 4.5.2)

  (ii) PVAM/SCl films created on glass slides swelled and ruptured upon addition of acid (Section 4.4.2.4).

  It was therefore suggested that PVAM/SCl membranes may require a neutralization step after the standard fabrication process used. (Petersen *et al.*(96) also observed a decline in the RO performance of FT-30 membranes after dry storage. They attributed this to residues of acyl chlorides which were left on the membrane surface after the interfacial polycondensation reaction. These residues produced localized regions of high acidity which hydrolysed the polyamide barrier layer at those sites.)

(b) The geometry of the tubular membrane may be unsuitable for dry storage; water in a tubular membrane structure acts as a plasticiser and as the polysulphone substrate tube dries out upon storage, it will shrink in three dimensions as water is lost. Because the deposited PVAM/SCl desalting barrier is very thin and brittle, it could become physically damaged upon shrinkage of its substrate. In tubes, therefore, a build-up of stress in an already stressed skin area could be expected to take place upon drying of the membrane. In this case, therefore, membrane deterioration would have a physical cause.

  (It should be mentioned here that these tubular membranes had not been heat-cured sufficiently to produce any thermal condensation products, as was discussed in Section 4.4.7.3. Any adverse effect which this may have had on the dry-storability of PVAM UTF membranes is not known. It is, however, known that a weak gel layer in a membrane desalting barrier is most disadvantageous.)

Early flat-sheet PVAM-OD/SCl membranes were not stored prior to their being tested, so that the question of dry storability did not arise. It would, however, have been more difficult to assess the dry-stability of flat-sheet membranes because of the large scatter of the results of the RO performance tests.

During a parallel study(1), various approaches were tried in attempts to arrest the deterioration of the PVAM/SCl tubular membranes. These met with only limited success. Much uncertainty still surrounds the problem of the limited dry-storage of the tubular PVAM-FD/SCl membranes and future work should be directed at explaining and solving this problem.

4.5.5 SUMMARY

Operating specifications suggested for the optimized PVAM-FD/SCl tubular membranes are the following$^{(100)}$:

Feed pressure	2 MPa
Feed temperature	40°C (upper limit unestablished)
Chlorine	Preferably nil
pH range	4,5 to 8,5 (the membranes have been operated at pH values outside this range)
Optimum pH	6 to 7
Salt rejection	98 to 99% (2 000 mg/l NaCl)
Membrane flux	500 to 800 lmd

4.6 THE RELATIONSHIP BETWEEN MODEL COMPOUND STUDY RESULTS AND THE PVAM PRECURSOR, PVAM-FD/SCL MEMBRANES AND THEIR BEHAVIOUR

4.6.1 PVAM PRECURSOR

During early attempts to synthesize the model-compound material 2-ethylimidazoline (MC 1), the ease with which a 2-vinylimidazoline (amidine) ring hydrolyses became obvious. This cast doubt upon the validity of the initially proposed structure of the homopolymeric PVAM precursor (shown in Figure 4.4, Section 4.3.1), leading to the hydrolytic stability of PVAM being investigated. PVAM was found to undergo a ring-opening hydrolysis reaction, with formation of the so-called PVAM-Hy product, comprising a linear amide group and a terminal primary amine. This reaction was similar to that reported and observed for the model compound monomeric form of homopolymeric PVAM, 2-ethylimidazoline (MC 1), but took place much more slowly (compare hydrolysis reaction rate constants, Section 3.9.1). The PVAM precursor was regarded as existing as a copolymeric mixture of a 2-imidazoline ring (unhydrolysed) and linear amide (hydrolysed) repeat units (see Figure 4.5, Section 4.3.1).

The ^{13}C nmr spectra of the two model compounds of copolymeric PVAM, 2-ethylimidazoline (MC) and N-propionylethylenediamine (HMC) were very useful in the accurate assignment of peaks in the spectrum of polymeric PVAM. This in turn made feasible the quantitative determination (based on calculations from ^{13}C nmr data) of the ratio of hydrolysed (ring-opened) to unhydrolysed (ring-closed) groups present in PVAM, and the amount of ethylenediamine inpurity present in PVAM-FD batches (see Section 4.3.4.3).

Model compound studies therefore proved to be very beneficial to the more accurate analysis of the PVAM precursor material.

4.6.2 PVAM/SCL MEMBRANES

The functional groups of both repeat units of the PVAM copolymeric precursor: the amidine nitrogen with its one reactive site and the terminal primary amine of PVAM-Hy, could be expected to react with SCl crosslinking agent in the crosslinking reaction during membrane formation, as indicated by the reactions of the model-compound forms of PVAM and PVAM-Hy, MC and HMC, with both benzoyl chloride and benzenesulphonyl chloride (see Sections 3.8.2, 3.8.3, 3.8.5 and 3.8.6).

In the event of crosslinking being complete, the membrane desalting barrier would theoretically comprise two benzamide and two sulphonamide functionalities, shown in Section 4.4.7.2 as Structures III, IV, V, VI. These would be represented by the model-compound materials MC 1, HMC 1, MC 2 and HMC 2, respectively, as discussed in Section 2.5.3. Indications were that the secondary amide group of the hydrolysed repeat unit PVAM-Hy (Structure II) remained unreacted during reaction with an aromatic acid chloride. No evidence of any reaction at this site was found during model-compound studies when HMC was reacted with benzoyl chloride or benzenesulphonyl chloride (see Sections 3.8.5 and 3.8.6).

In the more likely event of the crosslinking reaction being incomplete, the following additional functionalities would theoretically be present in the membrane desalting barrier: the unreacted -NH-group of unhydrolysed PVAM repeat units (Structure I) and the unreacted termial primary amines of PVAM-Hy repeat units (Structure II). Additional secondary amine structures may be formed by a condensation reaction between primary amine groups on adjacent PVAM-Hy repeat units upon adequate heat-curing of the membranes (Structure XV), as discussed in Section 4.4.6.

It is accepted, however, that reaction of 2-imidazolines with carboxylic- or sulphonic-acid chlorides proceeds with cleavage of the imidazoline ring (see Sections 2.5.2.3 and 4.4.7.2). It is therefore most likely that all reacted imidazoline groups in the membrane desalting barrier are in their ring-opened form, Structures IV and VI.

Linear amide (benzamide and sulphonamide) groups in the PVAM/SCl membrane could be formed by:

(i) reaction of benzenesulphonyl chloride or benzoyl chloride with hydrolysed (linear amide) repeat units of copolymeric PVAM and/or

(ii) rearrangement taking place during reaction of the 2-imidazoline groups of PVAM with acid chlorides and sulphonic acid chlorides.

4.6.3 PVAM/SCL MEMBRANE BEHAVIOUR

4.6.3.1 Upon exposure to chlorine

PVAM/SCl membranes exhibited sensitivity to chlorinated feedwaters, resulting in a decrease in RO performance (see Section 4.5.1). Model-compound studies, carried out in an attempt to obtain an understanding of the reactions and changes which could be expected to occur within the membrane upon exposure to chlorine and which would cause a decline in performance, were not successful. No chlorinated species or new products were detected under the severity of the laboratory conditions. No evidence was obtained to permit an explanation, at molecular level, of how PVAM/SCl membranes deteriorated upon exposure to chlorine.

4.6.3.2 Upon exposure to acidic and basic environments

Investigations into the stability of the ring model-compounds MC 1 and MC 2 in acidic and basic media had shown marked differences in the products of their hydrolysis reactions, depending on whether the reactions were acid- or base-catalyzed. Table 4.35 contains a summary of the HPLC analytical data on the composition of the reaction products after MC 1 and MC 2 were hydrolysed under strongly acidic (pH 1) and basic (pH 12) conditions (3 weeks; 20°C).

TABLE 4.35: RESULTS OF HPLC ANALYSES SHOWING DIFFERENCES BETWEEN PRODUCTS FROM ACID- AND BASE-CATALYZED HYDROLYSIS REACTIONS OF MC 1 AND MC 2

Reagent	Reaction Medium	Time	Percentage area under absorption peaks of various components at their specific retention times				
			2,8 min[a]	3,3 min[b]	4 min[c]	7 min[d]	10 min[e]
MC 1	Acid	Begin	0	0	1,7	85,8	11,7
		End	19,9	5,2	72,7	0	0
	Base	Begin	0	0	1,7	85,8	11,7
		End	18,3	60,5	7,6	0	10,6
			3 min[f]	4 min[g]	7 min[h]		
MC 2	Acid	Begin	0	0,3	99,7		
		End	18,0	82,0	0		
	Base	Begin	0	0,3	99,7		
		End	31,4	12,3	56,3		

Legend:

a One of the two peaks represent N-benzoylethylenediamine,
b the identity of the other peak is unknown.
c Linear amide: 1-benzoyl-2-propionylethylenediamine: HMC 1
d Ring: 1-benzoyl-2-ethylimidazoline: MC 1
e Dibenzoylated species: 1,3-dibenzoyl-2-ethylideneimidazolidine
f N-benzenesulphonylethylenediamine
g Linear amide: 1-benzenesulphonyl-2-propionylethylenediamine: HMC 2
h Ring: 1-benzenesulphonyl-2-ethylimidazoline: MC 2

Table 4.36 contains a summary of the HPLC analytical data of the composition of the reaction products after HMC 1 and HMC 2 were allowed to react in strongly acidic (pH 1) and basic (pH 12) media (3 weeks and 2 weeks, respectively, at 20°C).

TABLE 4.36: HPLC ANALYSES RESULTS SHOWING DIFFERENCES BETWEEN PRODUCTS FROM ACID- AND BASE-CATALYZED HYDROLYSIS REACTIONS OF HMC 1 AND HMC 2

Reagent	Reaction Medium	Reaction Time	Percentage area under absorbtion peaks of various components at their specific retention times				
			2,7 min[a]	3,3 min[b]	4,4 min[c]	6,4 min[d]	8,7 min[d]
HMC 1	Acid	Begin	0	0	95,1	2,2	1,9
		End	2,6	1,9	79,6	7,6	8,2
				2,9 min[e]			
	Base	Begin		0	95,1	2,2	1,9
		End		5,9	91,4	2,8	0
				3,2 min[f]		4,5 min[g]	
HMC 2	Acid	Begin		1,7		98,3	
		End		16,9		83,1	
	Base	Begin		1,7		98,3	
		End		15,7		84,3	

Legend:

a b	One of the two peaks represents N-benzoylethylenediamine, the identity of the other peak is unknown.
c	Linear amide: HMC 1
d	Unknown lesser products
e	N-benzoylethylenediamine
f	N-benzenesulphonylethylenediamine
g	Linear amide: HMC 2

The following observations were made from Tables 4.35 and 4.36:

(i) Hydrolysis of both benzamide and sulphonamide ring model compounds, MC 1 and MC 2, takes place more readily in acidic media and hydrolysis is complete. The major products from the acid-catalyzed hydrolysis of the ring 2-imidazolines are the linear amides HMC 1 and HMC 2, respectively.

(ii) The major products from the base-catalyzed hydrolysis of the ring 2-imidazolines MC 1 and MC 2 are not the linear amides, although they are present in small quantities. The major products, which show retention times of about 3 min in HPLC analyses, were N-benzoylethylenediamine and N-benzenesulphonylethylenediamine, respectively.

(iii) The linear amides HMC 1 and HMC 2 themselves undergo some hydrolysis in strongly acidic and basic media. Hydrolysis of HMC 1 led to the formation of a mixture of lesser products which were not identified. Hydrolysis of HMC 2 led to the formation of only one product, besides the unreacted HMC 2, which was concluded to be N-benzenesulphonylethylenediamine.

The relevance of the results of the model-compound study in explaining membrane performance in acidic and basic media was considered.

The RO performance of PVAM-FD/SCI tubular membranes after exposure to acidic and basic environments under both static and dynamic conditions has been discussed in Sections 4.5.2.2a and 4.5.2.2b, respectively.

The effects of storage of membranes in buffer solutions of different pHs, under static conditions for up to 7 days, were:

(i) storage at pH 3 had a rapid and drastic effect on membrane performance resulting in a decline in salt rejection and increase in water-permeability after only two days' exposure;
(ii) the performance of membranes stored at pH 7 remained constant;
(iii) storage of the membranes at a higher pH of 11 did not result in a decrease of the salt rejection but membrane flux increased substantially.
(Summary made from Table 4.33, Section 4.5.2.2b)

Less dramatic effects of storage at pH extremes of 3 and 11 under dynamic conditions were observed:

(i) after exposure of the membrane to a standard feed solution of pH 3 for approximately 1 000 h, there was a slight decrease in salt rejection (3%) and increase in permeate flux (almost double) upon re-evaluation under standard test conditions;
(ii) the performance of membranes after exposure to a solution of pH 7 remained constant;
(iii) after exposure of the membranes to a standard feed solution pf pH 11 for approximately 1 000 h, salt rejection was slightly decreased (1%) but membrane flux increased drastically (more than doubled).
(Summary made from Table 4.32, Section 4.5.2.2a)

It is most likely that the membrane desalting barrier comprises chiefly ring-opened or hydrolysed structures, represented by HMC 1 and HMC 2, as mentioned in Section 4.6.2. After observing the slow reactions which these model compounds underwent in acidic and basic media, compared with the changes in RO performance of membranes, especially in acidic medium, it was concluded that the behaviour of PVAM-FD/SCI membranes in acidic and basic media could not be adequately explained, at molecular level, by the results of model-compound studies.

The RO performance of membranes in both acidic and basic media was subsequently attributed to physical changes which could take place within the membrane. This has been discussed Section 4.5.2.3.

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CHAPTER 5

CONCLUSIONS

The study has resulted in an overall appreciation of the many variables pertaining to, and difficulties coupled with, the formation of novel UTF membranes. Highlights of the achievements of this study are:

1. Poly-2-vinylimidazoline (PVAM) can be used as precursor material in interfacial reactions to make efficient RO membranes. These could be made in flat-sheet and tubular forms. Two different polymer products, termed PVAM-OD and PVAM-FD, were obtained by using two different sets of reaction conditions. PVAM was characterized by ^{13}C nmr spectroscopy and found to be a copolymer, comprising ring-closed (imidazoline) and its hydrolyzed form of ring-opened (amide) repeat units. PVAM-CFD was obtained after partial purification of PVAM-FD.

   The use of PVAM, with its nitrogen atoms being pendent to the hydrocarbon chain, resulted in some increase in chlorine-tolerance of the membranes. This chlorine-tolerance was greater than that of membranes made with the aliphatic polymeric precursor PEI (NS-100/1 membranes), but not as great as that of membranes made from the aromatic precursor phenylenediamine (FT-30 membranes).

2. The use of aromatic crosslinking agents containing sulphonyl chloride groups; in addition to carboxylic acid chloride groups, illustrated the importance of the chemical nature of the reactive groups and of the effect which the structure of the reactants has on membrane structure, as reflected in the RO performance of the membranes. In terms of membrane performance, the use of the crosslinking agents 3-chlorosulphonylbenzoyl chloride (SCl) and 3,5-dichlorosulphonylbenzoyl chloride (Cl2S) gave flat-sheet membrane RO performances better than those of membranes prepared with the more generally used reagent, isophthaloyl chloride (IPC). For example:

   (a) Use of SCl instead of IPC gave PEI UTF membranes which gave higher flux and rejection, as illustrated by the following RO performances:

PEI/IPC membranes	:	98,4% rejection; 600 lmd flux
PEI/SCl membranes	:	98,7% rejection; 835 lmd flux

   (Membranes were tested with 5 000 ppm NaCl solution at 4 MPa)

   (b) Use of SCl instead of IPC gave early PVAM UTF membranes which gave higher rejection, as illustrated by the following RO performances by flat-sheet membranes:

PVAM/IPC membranes	:	72,7% rejection; 1 760 lmd flux
PVAM/SCl membranes	:	84,6% rejection, 680 lmd flux

   (Membranes were tested with a 5 000 ppm NaCl solution at 4 MPa)

(c) Use of the trifunctional reagent Cl2S gave PVAM UTF membranes which gave higher rejection and flux than those of membranes prepared with SCl, as illustrated by the following results:

PVAM/SCl membranes : 84,6% rejection; 680 lmd flux
PVAM/Cl2S membranes : 96,4% rejection; 800 lmd flux
(Membranes were tested with a 5 000 ppm NaCl solution at 4 MPa)

3. Numerous fabrication variables were found to be important in the preparation of efficient PVAM UTF membranes; slight variations led, in some cases, to large variations in membrane performance. Of the variables studied, those considered most important were: polysulphone (PS) substrate, chemistry of the crosslinking agent, concentration of crosslinking agent and of precursor, addition of acid acceptor to the precursor solution and heat-cure temperature.

The best RO performance results obtained for PVAM-OD/SCl membranes in flat-sheet form were:

94,3 ± 1,2% rejection; 1 096 ± 50 lmd
(tested for 5 000 ppm NaCl at 4 MPa)

97,4 ± 1,4% rejection; 400 ± 22 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

The optimum RO performances of PVAM-OD/SCl tubular membranes (developed during a parallel study) were:

97,1 ± 0,1% rejection; 730 ± 24,1 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

The optimum RO performances of PVAM-FD/SCl tubular membranes (developed during a parallel study) were:

98,2 ± 0,7 rejection; 560 ± 150 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

4. Exposure of PVAM UTF membranes to chlorine is not advisable. It is, however, proposed that exposure of PVAM-FD/SCl membranes to 5 ppm chlorine at pH 6 to 7 for a short period of time would be tolerated. Prolonged exposure to chlorine results in irreversible decline in rejection.

Maximum performance of PVAM-FD/SCl tubular membranes has been recorded in the pH 6,5 to 7 range. These membranes can be safely used over a pH range of 4,5 to 8,5.

Exposure of membranes to solutions of pH 3 over a period of one month under dynamic conditions, led to a drop in baseline rejection performance and increase in flux. Under similar conditions at pH 11, the membranes showed only a slight drop in rejection but an almost doubling in flux.

After static storage of membranes at pH 3 there was a rapid and irreversible decline in membrane performance. Similar storage of membranes at pH 11 caused no decrease in salt rejection but an almost doubling in flux.

Flat-sheet PVAM/SCl membranes may be operated at temperatures of up to 40°C. Compared with the performance of membranes operated at 25°C, the salt rejection by membranes operated at 40°C was unaffected, but fluxes were almost doubled.

5. The use of model compounds to study the effect of external variables on groupings typical of those found in a PVAM/SCl ultrathin films revealed the problems associated with hydrolytic stability which could arise in the UTF membrane: during synthesis of the PVAM precursor, during formation of the PVAM UTF membrane and during operation of the membrane. Model compound studies proved to be very valuable in characterizing batches of PVAM by ^{13}C nmr spectroscopy. However, the results of the studies of the reactions of the PVAM/SCl membranes model compounds could not adequately explain changes, at the molecular level, in the membranes performance under harsh operating conditions. It is nonetheless suggested that model compound studies should be carried out in parallel with chemical studies on any future novel UTF membrane system development.

6. By incorporation of various hydrophilic additives into a PVAM-precursor solution, UTF membranes were obtained which were adequate for low-pressure (500 kPa) applications.

IDEAS FOR FUTURE RESEARCH

1. PVAM/Cl2S membrane should be mathematically optimized for salt rejection and permeate flux.

2. Investigations should be carried out into the use of commercially available 1,3-benzenedisulphonyl chloride as crosslinking agent for PVAM.

3. Further investigations should be carried out into the incorporation of piperazine and related compounds into the PVAM precursor solution and the effect thereof on final membrane performance : a precursor of PVAM and piperazine should be crosslinked with Cl2S and tested, a precursor of PVAM and e.g. 2,5-dimethyl piperazine should be crosslinked with SCl and with Cl2S. A PVAM + piperazine/SCl membrane should be re-tested for its chlorine stability.

4. Attempts should be made to obtain a more complete extraction of ethylenediamine impurity from PVAM-FD, to yield a "cleaner" PVAM-CFD product than has been obtained to date, and PVAM-CFD/SCl membranes should be made with this precursor, then tested for rejection and permeate flux.

5. Membranes should be prepared from a PVAM-CFD precursor filled with piperazine, crosslinked with SCl and tested for RO performance at low pressure.

6. A copolymer of polyacrylonitrile and polyvinylalcohol should be synthesized and reacted with ethylenediamine to yield a PVAM copolymer containing PVOH repeat units. The use and effectiveness of this as precursor in PVAM UTF membrane fabrication should be investigated.

7. In the event of facilities ever becoming available, ESCA analyses of chemically damaged membrane surfaces should be carried out. Such studies could be of great value in providing a better understanding of chemical composition of and changes which take place in a UTF desalting barrier.

8. Upon the availability of the facility of solid-state ^{13}C nmr spectroscopy, an investigation should be carried out to ascertain the effectiveness of using this technique for analysis of this crosslinked desalting barrier and changes which take place, under various conditions.

9. Methods should be found by which the integrity of the tubular PVAM/SCI membranes could be improved by more effective crosslinking throughout the membrane.

<<<>>>

APPENDIX 1

TABLE 1: PVA UTF-MEMBRANES (FLAT-SHEET)

1(a) RESULTS OF TESTS ON MEMBRANES: PVA/IPC

Membrane Fabrication Conditions:

Polysulphone support cast from DMF solution (12%)

Concentration PVA precursor	[mass %]	3
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration IPC	[mass %]	5
Crosslink reagent contact	[min]	5
Post-crosslink drain time	[min]	5
Oven temperature	[°C]	115
Oven residence time	[min]	10

Membrane Test Conditions:

Applied pressure	[MPa]	4
Feed solution : NaCl	[ppm]	5 000
Temperature	[°C]	25

Membrane Performance:

Test Time [h]	Salt Rejection [%] 1	2	3	Permeate Flux [lmd] 1	2	3
4	92,4	96,3	92,6	578	503	498
20	92,5	94,5	93,6	528	528	498
78	92,4	94,5	93,6	528	523	498
92	92,7	93,9	94,1	513	498	462
Average (after 92 h)		93,6 ± 0,7			491 ± 26	

(b) RESULTS OF TESTS ON MEMBRANES: PVA/SCI

Membrane Fabrication Conditions:

Polysulphone support cast from DMF solution (12%)		
Concentration PVA precursor	[mass %]	3
Precursor contact time	[min]	60
Precursor drainage time	[min]	5
Concentration SCl	[mass %]	5
Crosslink reagent contact	[min]	5
Post-crosslink drain time	[min]	5
Oven temperature	[°C]	110
Oven residence time	[min]	5

Membrane Test Conditions:

Applied pressure	[MPa]	4
Feed Solution : NaCl	[ppm]	5 000
Temperature	[°C]	25

Membrane Performance:

Test Time	**Salt Rejection [%]**			**Permeate Flux [lmd]**		
[h]	**1**	**2**	**3**	**1**	**2**	**3**
22	97,3	97,0	95,8	727	747	682
48	97,6	97,0	96,3	911	896	896
70	98,0	97,5	96,8	787	792	797
95	98,1	97,6	-	767	807	-
117	98,1	97,6	-	759	787	-
166	98,2	97,8	-	737	737	-
Average (after 70 h)		97,4 ± 0,6			792 ± 5	

TABLE 2: PVAM-OD UTF-MEMBRANES (FLAT-SHEET)

2(a) RESULTS OF TESTS ON MEMBRANES: PVAM-OD/IPC

Membrane Fabrication Conditions:

Polysulphone support cast from DMF solution (13%)

Concentration PVAM-OD precursor	[mass %]	3
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration IPC	[mass %]	1
Crosslink reagent contact	[min]	5
Post-crosslink drain time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane Test Conditions:

Applied pressure	[MPa]	4
Feed Solution : NaCl	[ppm]	5000
Temperature	[°C]	25

Membrane Performance:

PAN reagent for PVAM-OD mol mass	Test Time [h]	Salt Rejection [%]			Permeate Flux [lmd]		
		1	2	3	1	2	3
14 500	3	60,5	70,3	71,0	2739	2739	2888
	22	67,4	69,6	71,0	2191	2291	2241
	44	67,3	69,5	59,4	1793	1942	1942
	70	72,4	72,5	73,2	1793	1793	1693
	Average (after 70 h)		72,7 ± 0,4			1760 ± 58	
86 000	3	68,0	66,6	46,1	3187	2988	3685
	22	63,3	65,5	54,5	2440	2689	2888
	44	67,3	69,5	60,2	2042	2171	2291
	70	68,2	70,7	62,0	1992	2092	2440
	Average (after 70 h)		67,0 ± 4,4			2174 ± 235	

2(b) RESULTS OF TESTS ON MEMBRANES: PVAM-OD/SCI

Membrane Fabrication Conditions:

Polysulphone support cast from DMF solution (13%)		
Concentration PVAM-OD precursor	[mass %]	3
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration SCI	[mass %]	2
Crosslink reagent contact	[min]	5
Post-crosslink drain time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane Test Conditions:

Applied pressure	[MPa]	4
Feed Solution : NaCl	[ppm]	5000
Temperature	[°C]	25

Membrane Performance:

PAN reagent for PVAM-OD	**Test Time**		**Salt Rejection [%]**			**Permeate Flux [lmd]**	
mol mass	**[h]**	**1**	**2**	**3**	**1**	**2**	**3**
14 500	3	74,8	78,6	75,5	1145	1195	1494
	25	82,0	81,5	184,5	847	896	1096
	69	83,8	83,7	87,0	657	647	747
	Average		84,6 ± 1,7			680 ± 58	
86 000	3	83,4	84,7	77,7	1295	1444	1295
	25	85,3	84,9	83,2	1046	1195	1096
	69	86,0	89,1	83,1	847	946	847
	Average		86,1 ± 3,0			881 ± 65	

2(c) RESULTS OF TEST ON MEMBRANES: PVAM-OD/Cl2S

Membrane Fabrication Conditions:

Polysulphone support cast from DMF solution (13%)		
Concentration PVAM-OD precursor	[mass %]	3
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration Cl2S (prior filtering)	[mass %]	2
Crosslink reagent contact	[min]	5
Post-crosslink drain time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane Test Conditions:

Applied pressure	[MPa]	4
Feed Solution : NaCl	[ppm]	5000
Temperature	[°C]	25

Membrane Performance:

PAN-reagent for PVAM-OD mol mass	Test Time [h]	Salt Rejection [%] 1	2	3	Permeate Flux [lmd] 1	2	3
14 500	3	90,1	91,1	94,1	996	1245	996
	21	94,2	93,2	96,1	797	1096	847
	117	96,1	96,0	97,0	747	896	747
	Average		96,4 ± 0,6			797 ± 86	
86 000	3	90,6	94,6	87,4	1892	1892	2042
	21	92,9	93,9	90,2	1643	1703	1693
	117	94,7	95,2	91,9	1394	1345	1444
	Average		93,9 ± 1,8			1394 ± 50	

APPENDIX 2

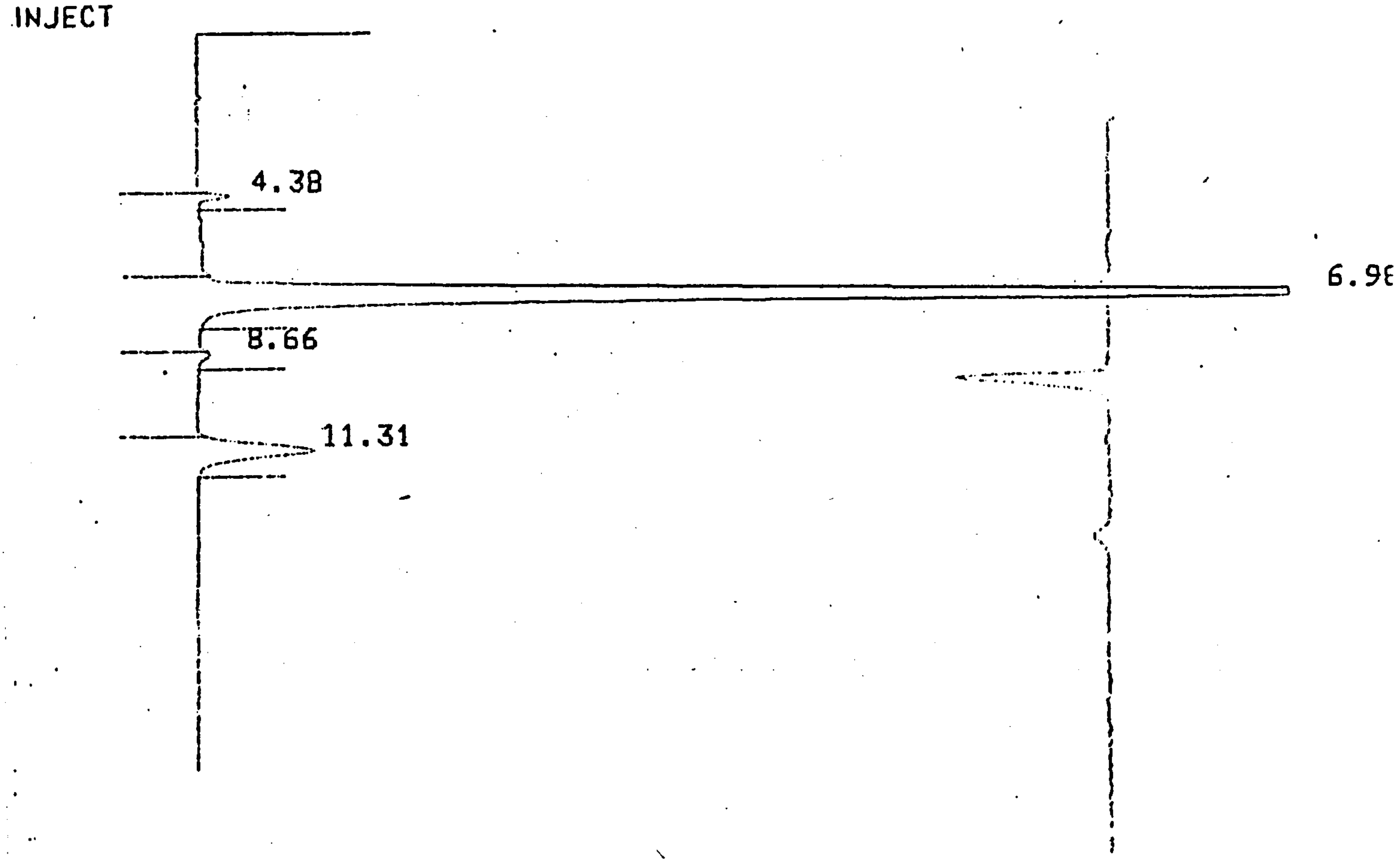
TABLE 1: MOLECULAR MASSES OF VARIOUS BATCHES OF PAN SYNTHESIZED AND CORRESPONDING PVAM BATCH NUMBERS

PAN		PVAM-FD
Batch no.	Mol.mass[a]	Batch no.
F7	15 600	2
-	-	3[b]
8	19 335	4
9	17 744	5
10	23 316	6
11	13 455	-
12	11 548	7
13	11 772	-
14	13 905	-
-	-	8[c]
15	13 905	9
16	26 631	10
17	19 900	
GO	13 201	11
1	7 426	12
2	23 458	13
3	12 465	14
4	14 997	15
5	15 904	16
6	8 056	17
7	8 445	18
8	8 513	19
9	11 273	20
10	8 865	21
11	10 092	22
12	12 314	23
13	18 266	24
14	14 655	25
15	13 227	26
16	13 649	27
17	13 015	28
E1	12 798	E1
2	27 476	2
4	9 945	4
5	13 435	5
6	14 863	6
7	11 143	7
8	11 499	-
9	10 879	-

Legend:

a - as determined by dilute solution viscometry
b - prepared from PAN Batches 7 and 8 (1 : 4)
c - prepared from PAN Batches 13 and 14 (3 : 7)

APPENDIX 3



```
SEP. 30, 1985   13:21:50      CHART  0.50 CM/MIN     FLOW       1.00 ML/MIN
PRESSURE   2700.0             DETECTOR   254/200          401/008
                              RUN #30                     CALC #0
COLUMN    C 18                SOLVENT     55MeOH/45H2O OPR ID:       5

EXTERNAL STANDARD QUANTITATION
SAM AMT     10.00000


 PEAK#           AMOUNT       RT          %
             266.24100       4.38        0.89
           26698.30000       6.98       89.78
             143.53800       8.66        0.48
            2628.46000      11.31        8.83
TOTAL      29736.50000                 100.00
```

FIGURE 1: TYPICAL HPLC ANALYSIS OF CRUDE PRODUCT OF 1-BENZOYL-2-ETHYLIMIDAZOLINE (MC 1)

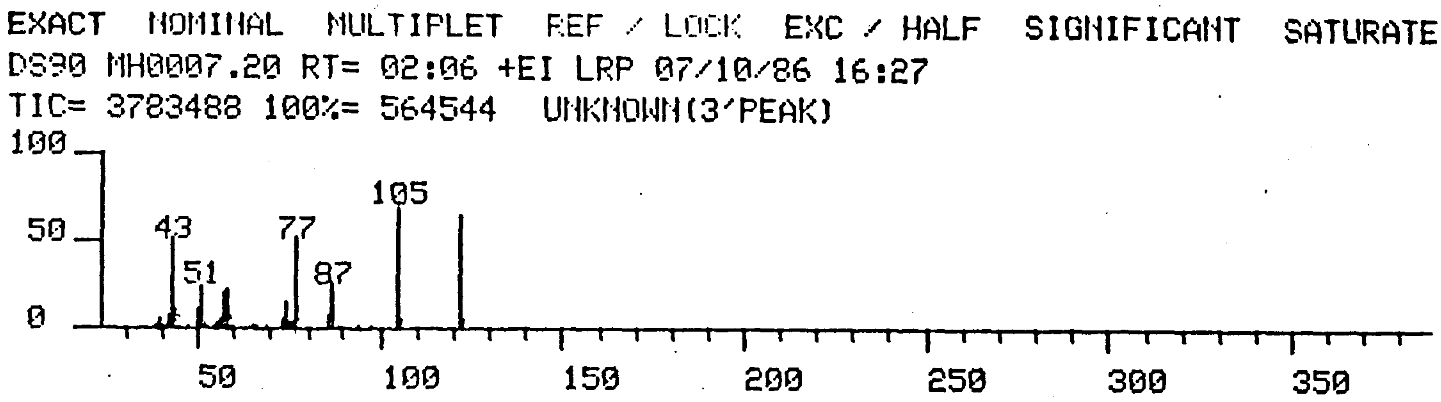


FIGURE 2: SIMPLIFIED MASS SPECTRUM OF PRODUCT OF BASE-CATALYZED HYDROLYSIS OF MC 1 WITH HPLC RETENTION TIME OF 3 MINUTES

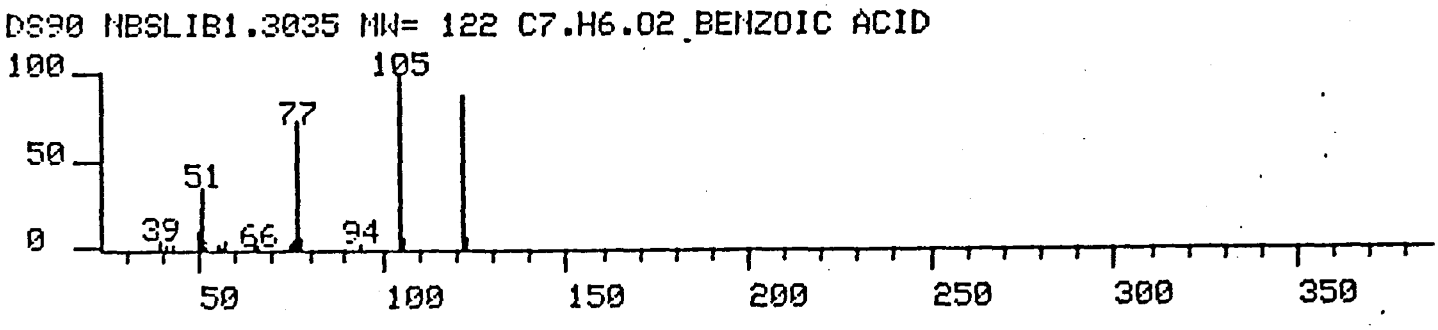


FIGURE 3: MASS SPECTRUM OF BENZOIC ACID

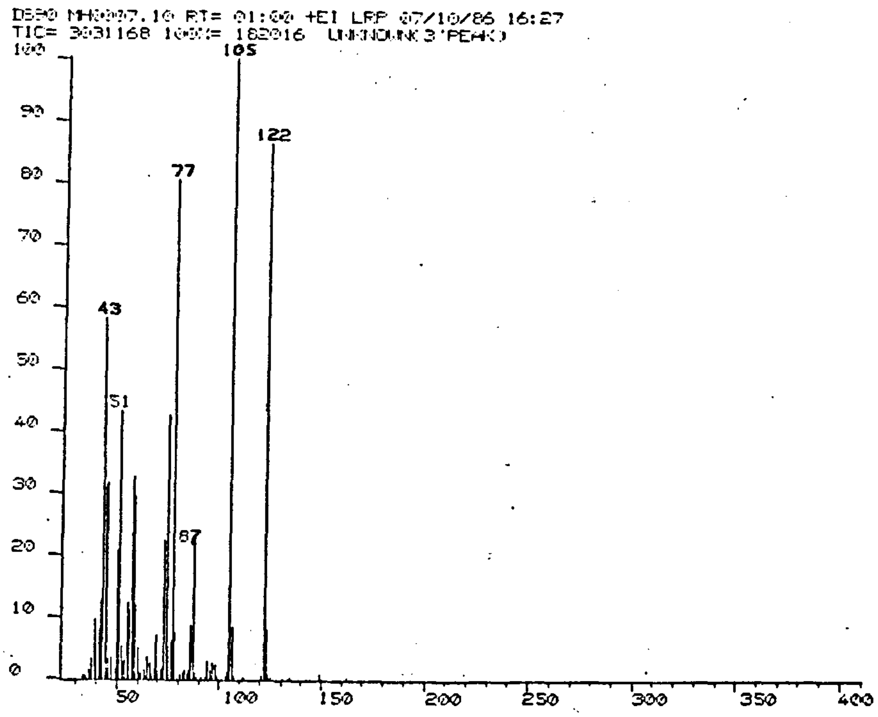


FIGURE 4: MASS SPECTRUM OF PRODUCT OF BASE-CATALYZED HYDROLYSIS OF MC 1 WITH HPLC RETENTION TIME OF 3 MINUTES
(Source temperature : < 100°C)

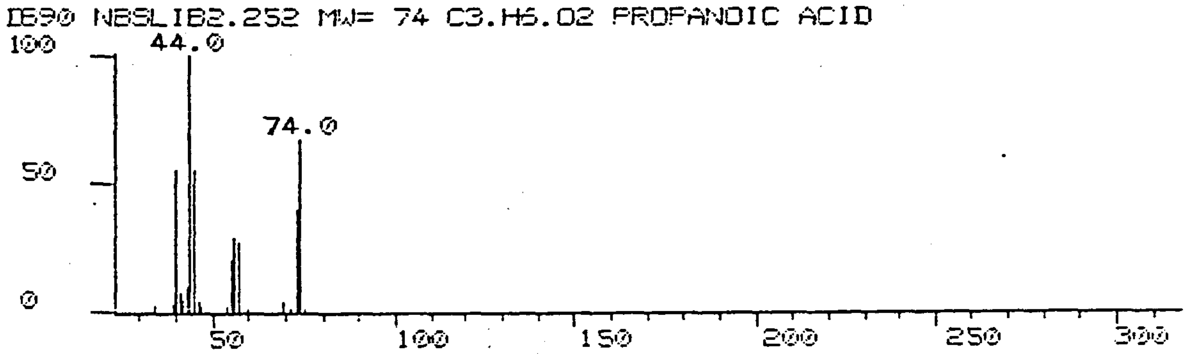
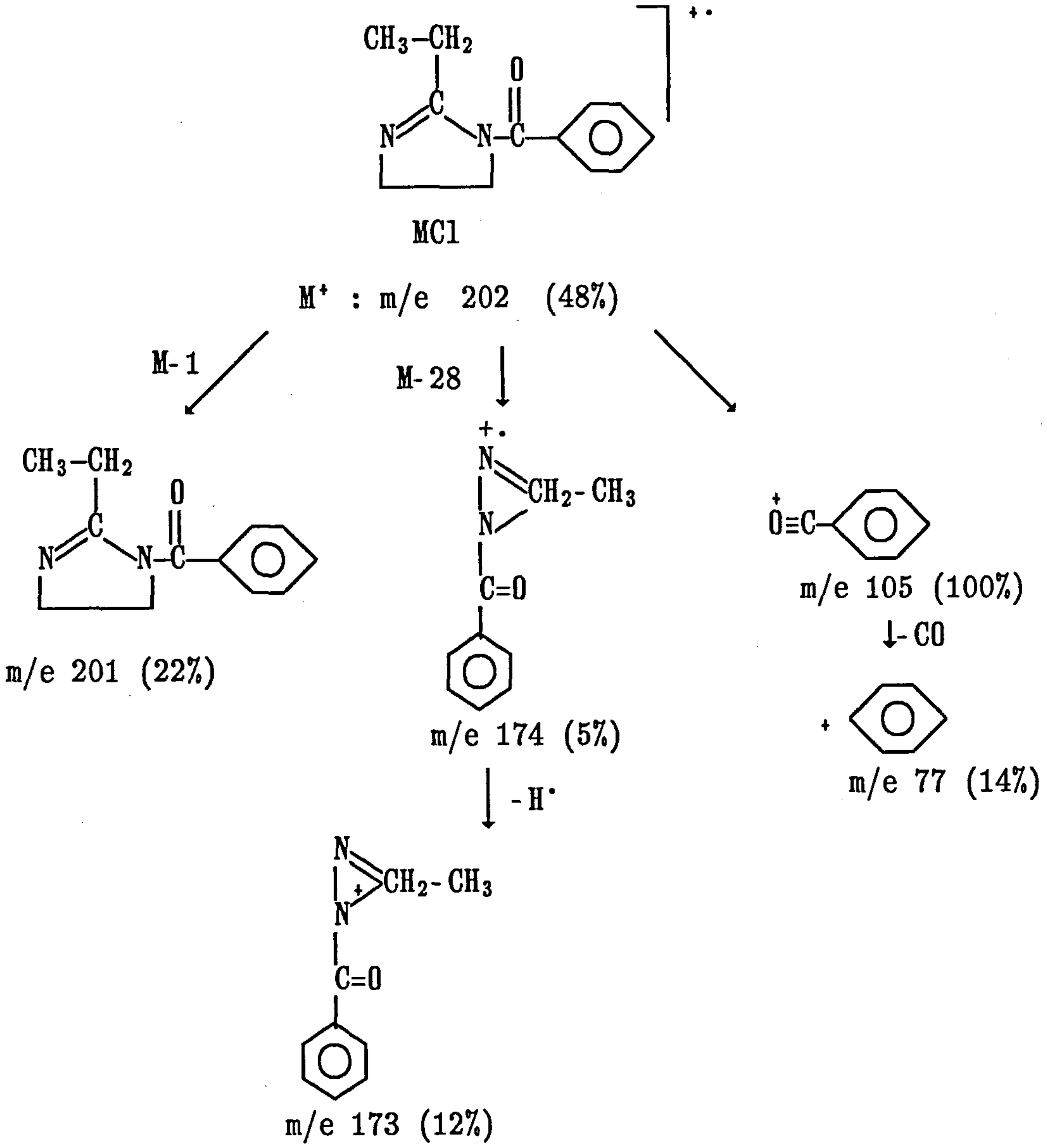


FIGURE 5: MASS SPECTRUM OF PROPIONIC ACID



Ref. Ohashi, M., Ohno, N., Kakisawa, H., The mass spectra of some alkyl and aryl imidazolines, Org. Mass Spectroscopy, 1 (1968) 703-712.

FIGURE 6: MASS SPECTRAL FRAGMENTATION PATTERN OF 1-BENZOYL-2-ETHYLIMIDAZOLINE (MC 1)

```
                              *********
                              NUMBER 5A
                              *********

TIME      CONC %    -ln[]     y=mx+c    ***********************************
(hrs)     (REAG.)                              Regression Output:
                                        Constant                  0.264324
    0      78.7     0.240      0.264    Std Err of Y Est          0.023588
 1.23      76.1     0.273      0.275    R Squared                 0.991162
 1.39      75.3     0.284      0.276    No. of Observations              8
 5.14      71.8     0.331      0.307    Degrees of Freedom               6
 7.17      71.1     0.341      0.324
25.44      63.2     0.459      0.475    X Coefficient(s)  0.008275
51.52      51.7     0.660      0.691    Std Err of Coef.  0.000318
74.46      40.5     0.904      0.880
                                        ***********************************
                                             k = 2.30E-06 (1/sec)
                              *********
```

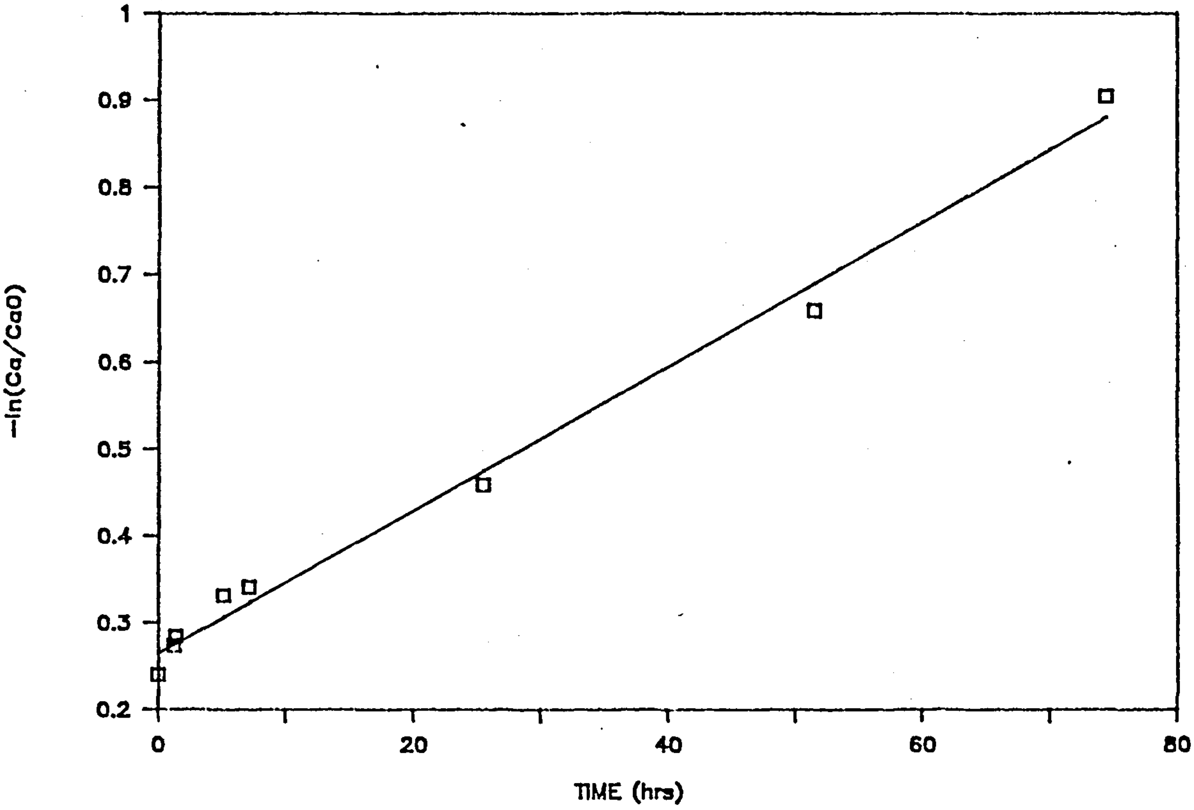


FIGURE 7: FIRST-ORDER APPROXIMATION OF THE RATE CONSTANT FOR THE HYDROLYSIS REACTION OF 1-BENZENESULPHONYL-2-ETHYLIMIDAZOLINE (MC 2)

APPENDIX 4

TABLE 1: RO PERFORMANCE OF PVAM-OD/Cl2S FLAT-SHEET MEMBRANES AFTER EXPOSURE TO CHLORINE (20 ppm; 24 h; pH 6,3; 22°C) UNDER STATIC CONDITIONS

	RO Performance			
	Baseline		After chlorine exposure	
Total Test Time [h]	Rejection [%]	Flux [lmd]	Rejection [%]	Flux [lmd]
96	99,2	238		
	98,5	387		
	99,1	297		
	98,9 ± 0,4	307 ± 75		
99			95,9	218
			97,4	323
			98,8	252
114			97,3	231
			98,4	323
			99,0	302
261			99,1	252
			98,2	323
			99,1	302
			98,8 ± 0,5	292 ± 37

Membrane fabrication conditions:

Similar to those described in Table 4.14, Section 4.4.2.2.

Membrane test conditions:

Applied Pressure	[MPa]	2
Feed solution: NaCl	[ppm]	2 000
pH		6,3
Temperature	[°C]	25

TABLE 2: THE EFFECT OF CHLORINE (10-20 ppm; pH 6,3; 22°C) ON THE RO PERFORMANCE OF PVAM-OD/Cl2S FLAT-SHEET MEMBRANES UNDER DYNAMIC CONDITIONS

Total Test Time [h]	Chlorine [Σ ppmh]	RO Performance Salt Rejection [%]	 Permeate Flux [lmd]
120	0	96,3 ± 1,0	305 ± 79
136	120	97,7 ± 1,5	454 ± 278
138	138	89,1 ± 1,1	273 ± 132
140,5	160	96,4 ± 1,9	268 ± 133
190	160	95,2 ± 2,2	812 ± 272

Membrane fabrication conditions:

As described for PVAM-OD/Cl2S membranes reported in Table 1, Appendix 4.

Membrane test conditions:

As described for PVAM-OD/Cl2S membranes evaluated under static conditions, as reported in Table 1, Appendix 4, with sodium hypochlorite added to the feed solution (10-20 ppm free chlorine).

TABLE 3: THE EFFECT OF CHLORINE (APPROXIMATELY 20 ppm; pH 6,4; 22°C) ON THE RO PERFORMANCE OF PVAM-OD/SCI FLAT-SHEET MEMBRANES UNDER DYNAMIC CONDITIONS

Total Test Time [h]	Chlorine [Σ ppmh]	RO Performance Salt Rejection [%]	 Permeate Flux [lmd]
96	0	92,8 ± 0,7	272 ± 67
103	80	94,2 ± 0,6	251 ± 60
114	80	80,3 ± 1,2	272 ± 76
115	95	93,7 ± 1,0	272 ± 6
128	97	88,5 ± 0,3	326 ± 0

Membrane fabrication conditions:

Concentration PVAM-OD	[mass %]	1
Precursor contact time	[min]	60
Precursor drainage time	[min]	2
Concentration SCI	[mass %]	1
Crosslinking reagent contact	[min]	5
Post-crosslink drainage time	[min]	2
Oven temperature	[°C]	100
Oven residence time	[min]	10

Membrane test conditions:

Applied Pressure	[MPa]	2
Feed solution: NaCl	[ppm]	2 000
Temperature	[°C]	25
Test time (prior chlorination)	[h]	96

TABLE 4: THE EFFECT OF CHLORINE (APPROXIMATELY 10 ppm; pH 6,3; 22°C) ON THE RO PERFORMANCE OF PVAM-OD & PIPERAZINE/SCI FLAT-SHEET MEMBRANES, EVALUATED UNDER DYNAMIC CONDITIONS

Total Test Time [h]	Chlorine [Σ ppmh]	RO Performance Salt Rejection [%]	 Permeate Flux [lmd]
146	0	90,4 ± 4,2	347 ± 99
147	8	95,9 ± 1,9	276 ± 94
162	8	88,9 ± 0,9	309 ± 114
163	15,5	96,4 ± 1,5	244 ± 81
165	15,9	94,5 ± 0,4	273 ± 97
183	15,9	90,3 ± 0,4	374 ± 120

Membrane fabrication and test conditions:

As described in Table 4.17, Section 4.4.2.3(b)

TABLE 5: THE EFFECT OF CHLORINE (APPROXIMATELY 5 ppm; pH 3,6; 20°C) ON THE RO PERFORMANCES OF TWO SETS OF PVAM-OD/SCI TUBULAR MEMBRANES, EVALUATED UNDER DYNAMIC CONDITIONS

Test Time [h]	Chlorine [Σ ppmh]	RO Performance Salt Rejection [%]	 Permeate Flux [lmd]	A^2/B x10^{-5}
Experiment 1:				
0	0	98,9 ± 0,1	897 ± 61	37,0
3,9	17,4	97,5 ± 0,3	783 ± 53	13,7
8,4	34,1	98,6 ± 0,1	755 ± 46	23,4
24,7	77,6	89,3 ± 0,2	770 ± 54	19,1
27,4	88,2	98,8 ± 0,1	687 ± 44	24,5
32,5	118,4	98,8 ± 0,1	672 ± 45	23,7
48,4	176,3	99,0 ± 0,1	633 ± 43	25,1
51,5	193,7	99,1 ± 0,1	588 ± 45	26,4
146	193,7	97,5 ± 0,3	743 ± 42	12,3
168,2	193,7	97,6 ± 0,3	767 ± 45	13,1
172,7	204,4	99,1 ± 0,1	634 ± 36	28,1
193	253	99,0 ± 0,2	590 ± 37	24,2
195,5	266	99,0 ± 0,2	590 ± 38	24,7
217,4	359	99,0 ± 0,2	637 ± 40	25,4
240,9	433	98,8 ± 0,2	632 ± 39	22,9
312,3	433	97,5 ± 0,4	892 ± 44	15,5
390,6	433	95,6 ± 0,6	953 ± 269	9,6
Experiment 2:				
0	0	99,3 ± 0,1	265 ± 27	14,1
3,9	17,4	99,2 ± 0,04	233 ± 23	11,9
8,5	34,1	99,3 ± 0,04	225 ± 27	12,8
24,9	77,6	99,2 ± 0,1	245 ± 32	11,2
28,7	88,2	99,3 ± 0,04	225 ± 27	12,2
33,8	118,4	99,2 ± 0,1	223 ± 29	10,0
48,3	176,3	99,2 ± 0,05	216 ± 31	10,2
52,7	193,7	99,3 ± 0,05	205 ± 30	10,5
146,5	193,7	98,8 ± 0,2	280 ± 35	8,6
168,2	193,7	98,2 ± 0,3	322 ± 35	6,5
171,7	204,4	99,1 ± 0,3	271 ± 29	11,7
193,0	253	99,0 ± 0,2	267 ± 29	9,9
195,4	266,2	99,0 ± 0,2	267 ± 29	9,7
217,3	359,1	98,7 ± 0,4	282 ± 31	8,3
240,7	432,9	98,8 ± 0,3	282 ± 38	9,1
312,2	432,9	97,3 ± 1,0	405 ± 41	5,9
390,7	432,9	91,7 ± 2,9	503 ± 38	

Membrane Fabrication Conditions:

Optimum formulation for PVAM-FD/SCl tubular membranes described in Section 4.4.4.2.

Membrane Test Conditions:

Applied Pressure	[MPa]	2
Feed Solution*: NaCl	[ppm]	2 000
pH		6,3 - 6,7
Temperature	[°C]	25
Test time (prior chlorination)	[h]	96

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*Feed solution frequently dosed with sodium hypochlorite solution to level of approximately 5 ppm free chlorine in feed solution.

TABLE 6(a): THE EFFECT OF CHLORINE, HOCl (5 ppm; pH 5,6; 20°C) ON THE RO PERFORMANCE OF PVAM-FD/SCI TUBULAR MEMBRANES

		RO Performance	
Test Time [h]	Chlorine [Σ ppmh]	Salt Rejection [%]	Permeate Flux [lmd]
0	0	90,6 ± 4,6	565 ± 137
2,22	8,58	95,0 ± 4,3	382 ± 101
18,61	8,88	94,9 ± 3,2	417 ± 104
25,14	53,38	94,8 ± 3,6	364 ± 89
90,0	53,38	91,5 ± 3,1	574 ± 102
95,68	66,78	90,5 ± 3,6	475 ± 84
98,14	79,08	90,3 ± 3,7	461 ± 78
116,20	79,08	89,4 ± 3,8	380 ± 19
121,85	105,18	89,0 ± 3,6	417 ± 66
139,18	105,18	89,1 ± 3,6	448 ± 71
145,0	133,78	88,3 ± 3,8	449 ± 70
163,16	133,78	88,7 ± 3,8	380 ± 57
169,01	162,08	86,4 ± 3,5	439 ± 65
282,0	162,08	74,5 ± 2,4	786 ± 91
306,2	162,08	66,1 ± 8,0	1648 ± 300
330,2	162,08	56,7 ± 9,5	2103 ± 373

TABLE 6(b): THE EFFECT OF CHLORINE, OCl^- (5 ppm; pH 8; 20°C) ON THE RO PERFORMANCE OF PVAM-FD/SCI TUBULAR MEMBRANES

		RO Performance	
Test Time [h]	Chlorine [Σ ppmh]	Salt Rejection [%]	Permeate Flux [lmd]
0	0	87,3 ± 7,7	498 ± 71
1,45	8,7	92,2 ± 7,6	662 ± 92
17,75	8,7	91,3 ± 6,4	759 ± 97
21,19	38,34	91,9 ± 7,4	750 ± 104
25,25	61,89	91,0 ± 8,0	804 ± 120
41,82	61,89	90,3 ± 7,5	921 ± 126
45,51	80,29	90,1 ± 8,3	860 ± 124
47,77	91,14	90,2 ± 8,0	891 ± 125
49,00	96,94	90,3 ± 7,8	928 ± 136
65,25	96,94	89,7 ± 7,3	980 ± 130
68,39	110,3	89,9 ± 7,2	1004 ± 127
71,79	127,0	89,1 ± 7,9	1083 ± 137
137,95	127,0	81,3 ± 6,3	1284 ± 115
143,25	141,78	85,5 ± 6,3	1160 ± 97
145,36	152,12	84,8 ± 6,8	1111 ± 95
164,25	152,12	84,0 ± 6,5	1183 ± 107
185,36	180,42	84,4 ± 6,1	1316 ± 52
190,36	205,42	84,5 ± 5,8	1468 ± 118
192,85	217,92	83,8 ± 5,9	1494 ± 99
209,45	217,92	81,9 ± 6,0	1447 ± 102
234,35	217,92	79,8 ± 5,2	1567 ± 100

Membrane Fabrication Conditions:

See Section 4.4.4.3 for optimum formulation for PVAM-FD/SCI tubular membranes. Membranes post-treated with poly(vinylalcohol) (immersion in 3% solution for 10 minutes)(51).

Membrane Test Conditions:

Applied Pressure	[MPa]	2
Feed Solution*: NaCl	[ppm]	2 000
Temperature	[°C]	25
pH		6,3 - 6,7 (for 6a) 7,9 - 8,1 (for 6b)

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*Feed solution frequently dosed with sodium hypochlorite solution to level of approximately 5 ppm free chlorine in feed solution.

pH adjusted with HCl or NaOH.