RESEARCH ON THE DEVELOPMENT OF POLYMERS FOR THE FORMATION OF DYNAMIC MEMBRANES

by

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PART 2:
THE SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF ZIRCONIUM-CHELATING POLYMERS FOR DYNAMIC MEMBRANE APPLICATIONS

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PART 1:
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PART 2:
THE SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF ZIRCONIUM-CHELATING POLYMERS FOR DYNAMIC MEMBRANE APPLICATIONS

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REPORT ON THE RESEARCH ON THE DEVELOPMENT OF POLYMERS FOR THE FORMATION OF DYNAMIC MEMBRANES.

PART 2. THE SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF ZIRCONIUM-CHELATING POLYMERS FOR DYNAMIC MEMBRANE APPLICATIONS.

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EXECUTIVE SUMMARY

1. *INTRODUCTION*

Insight was required in terms of the complex behaviour of polyelectrolytes with zirconium in order to understand dynamic membrane formation. This study, although initial, is providing trends between chemical structure and membrane performance.

2. *POLYMERS*

The following was accomplished:

a) Techniques for the polymerization of acidic monomers of different pKa values in homo- and copolymer form, even though no techniques were known in some of the cases. Totally novel systems imcludes poly(methacrylic acid-co-2-chloro acrylic acid) and poly(acrylic acid-co-2-chloro acrylic acid-co-methacrylic acid). The method for polymerizing acrylic acid with 2-chloro acrylic acid was substantially modified.

b) Techniques for characterization of these polymers were developed.

c) Polymers of varying molecular mass, conversion and copolymer composition were synthesized.

3. *MEMBRANE FORMATION*

The following polymers form dynamic hydrous zirconium (IV) oxide-polyelctrolyte membranes:

a) Poly(acrylic acid)

b) Poly(methacrylic acid)

c) Poly(2-chloro acrylic acid)

d) Poly(itaconic acid)

e) Poly(acrylic acid-co-methacrylic acid)

f) Poly(acrylic acid-co-2-chloro acrylic acid)

g) Poly(acrylic acid-co-itaconic acid)

h) Poly(methacrylic acid-co-2-chloro acrylic acid)

i) Poly(acrylic acid-co-vinyl acetate)

j) Poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid).

The majority of these polymers have never been used to form dynamic membranes.

3.1 Flux During Formation

Membrane flux depends on the charge density, or degree of ionisation of the polymer. The flux behaviour for membranes of homopolymers of unsaturated, monocarboxylic acid is governed by two mechanisms: first, the increase in charge density as the polymer ionises and, second, the decrease in flux due to pore size decrease due to polymer swelling due to like-charge repulsion.

These two factors remain more or less in balance until such time as the degree of ioisation of the polymer exceeds 50%, and at pH = pKa + 1 the swelling factor becomes dominant and there is a marked decrease in flux.

Although not clear-cut, the theory could be expanded to include homopolymers of dicarboxilic acids and copolymers. In these cases, the presence of two or more different carboxylic groups make the quantitative evaluation of flux behaviour virtually impossible.

3.2. Rejection Behaviour

The rejection behaviour of the non-chloro-containing polymer membrane is linked directly to the degree of ionisation of the polymer. This was established from figures relating to the membranes having as their polyelectrolyte component a homopolymer of a unsaturated vinyl monomer containing only one ionisable group.

For the chloro-containing polymer membranes, the rejection behaviour is influenced by the crosslinking reaction involving the labile chlorine atom. This causes ionisable groups to disappear, leading to the formation of ester groups (intermolecular). At pH values above 6,0 these ester bonds are apparently broken (saponified), leading to an increase in rejection with increasing pH.

4. MEMBRANE PERFORMANCE

4.1 Membrane Stability

Evaluation of membrane stability in terms of the average change in A^2/B values for the first 18 hours after completion of membrane formation reveals the following:

The folowing three membranes are stable over the test period:

a) Hydrous zirconium (IV) oxide-poly(acrylic acid)

b) Hydrous zirconium (IV) oxide-poly(itaconic acid)

c) Hydrous zirconium (IV) oxide-poly(acrylic acid-co-itaconic acid)

All other membranes evaluated show a decrease in performance figures ranging from 10 to 23% over a period of 18 hours.

4.2 Membrane Peak Performance

Comparisons between hydrous zirconium (IV) oxide-poly(acrylic acid) membranes and other hydrous zirconium (IV) oxide-polyelectrolyte membranes were done in terms of the average figures of merit after 18 hours of operation. The following membranes performed better than the Zr-PAA membranes:

a) Zr-PAA/VAC-1

b) Zr-PAA/ClAA-2

c) Zr-PMAA-4

d) Zr-PAA/MAA-1

e) Zr-TERP-1

f) Zr-PAA/IA-3

Of these hydrous zirconium (IV) oxide-poly(acrylic acid-co-vinyl acetate) membranes were outstanding.

4.3 pH Dependence

Rejection behaviour evaluated at given pH values confirm that:

> Because of shielding by charged sites the polylectrolytes in composite mebranes are not fully ionised at pH = 7.
>
> The effect of shielding is greater for the homopolymers of dicarboxylic acid momomers than for the homopolymers of monocarboxylic monomers.

The flux behaviour is consistent with the theory mentioned under heading 3.1

5. CHARGE DENSITY

Two trends were observed in the charge density measurements. The higher the charge density, the higher the salt retention by these membranes, and the lower the figure of merit for these membranes.

ABSTRACT

A series of homo- and copolymers based on the monomers : 2-propenoic acid, 2-methyl-2-propenoic acid, 2-chloro-2-propenoic acid, methylene butanedioic acid, ethenyl acetate and ethylene sulphonic acid have been synthesized and characterized. These polyelectrolytes were used with hydrous zirconium oxide to form novel dynamic membranes on Millipore filter substrates. These desalinating membranes were studied in terms of the chemical structure of the polyelectrolytes with regard to the effect of pH on their formation and performance characteristics. The effect of the charge density on the membranes was related to the membranes' figure of merit. Membrane studies were undertaken at pressures of 6 MPa and flow rates of 3,65 litres per minute.

INDEX

LIST OF FIGURES

Figure

LIST OF TABLES

LIST OF TABLES

Table

CHAPTER 1

INTRODUCTION

1.1 GENERAL

As the twenty-first century approaches, the rapidly expanding population of the world is putting the natural resources available to modern man under severe strain. The most readily available of these natural resources is water. Unfortunately, because of this ready availability water resources have been sadly abused, by industry and individual alike.

However, a new awareness of our environment is slowly changing the attitude of people towards all types of pollution and, therefore, to water pollution. Apart from the individual's daily needs, industry also needs water in its day-to-day operations. Water is needed for cleaning and for cooling purposes and as a medium for removing effluents of industrial processes. Water is often used in combinations of the above operations.

As Groves et al [1] state:

Industrial effluents may be:

(a) discharged to sewer with or without pretreatment;
(b) discharged to environment with extensive pretreatment;
(c) treated to reuse standard;
(d) treated at source by closed-loop recycle systems.

Because of increasingly strict legislation in many countries, (a) and (b) are becoming either extremely expensive or impossible, (c) and (d) are becoming environmentally and economically much more attractive. In this regard it is relevant to quote Minturn and Johnson [2]: "Increasing concern for the effect on environment of waste streams have (sic) caused more stringent requirements for treatment, and as a consequence, fees for discharge into municipal sewers are increasing."

The treatment of waste water by pressure-driven membranes has become more important over the past few decades. One of the latest developments in the treatment of high temperature effluents is the use of dynamically formed composite membranes. These membranes are formed on porous bodies by circulating past them, under pressure, solutions containing polyelectrolytes.

1.2 DYNAMICALLY FORMED MEMBRANES

Hyperfiltration or reverse osmosis can be defined as [3]: the process whereby salts are removed from saline waters by forcing the solution under pressure through appropriate membranes. Hyperfiltration has long been thought to be a solution to the purification of industrial wastewater.

As stated in section 1.1, economic aspects play an important role in the motivation for wastewater reuse. Other reasons [4] are the abatement of pollution and the value of industrial feedstocks which can be recovered. Among the industries in which reuse of wastewater could be economically viable is the textile industry [5] where the wastewater has a high temperature and reuse also can represent a saving of thermal energy.

Up to now the biggest disadvantage of "conventional" cast membranes is that they are unable to deal with highly polluted, strongly fouling or hot industrial effluents.

Within the ideal of providing practical solutions we can consider the discovery of dynamically formed membrane systems by Marcinkowsky [6] at the Oak Ridge National Laboratories in 1965. This, and the subsequent development, by Johnson *et al* [7], of the dual-layer or composite dynamically formed hydrous zirconium oxide-poly(acrylic acid) membrane are of great importance, as these membranes have the following advantages over "conventional" cast membranes:

- They have higher fluxes [8].
- They can operate at higher temperatures, so that they can be used to treat textile wastes at temperatures of up to 90°C [9].
- They can be regenerated in situ at low cost [8].

In terms of material usage they are also advantageous, as materials that are difficult to use in casting processes can be utilised [10]. These materials are not only good for the rejection of electrolytic substances, but can be used to filter non-electrolytic organic substances [11].

These membranes do, however, have some disadvantages as noted by Freilich and Tanny [12], namely, "they show a decrease in salt rejection with increasing feed salt concentration and there is a noted irreproducibility of membrane flux and salt rejection."

These membranes have, however, come into their own in areas such as the processing of pulp mill wastes [13], textile dyeing wastes [4, 14, 5], shower and laundry wastewater [8], coal gasification wastewater and wool-scouring plant wastes [1].

1.3 SCOPE AND OBJECTIVES

From the foregoing newer solutions are constantly being sought. The research described in this thesis is not aimed at solving any specific industrial type problem, nor is it intended to be a development exercise. It is intended rather to provide new insight into the capabilities of polymers used in the form of a dynamic membrane.

Since 1965 when Marcinkowsky [6] developed the dynamically formed hydrous zirconiun (iv) oxide membranes, and Johnson et al [7] developed the dual-layer or composite zirconium-polyacrylate membrane, there has been very little further development in the field of material choice as regards the polyelectrolyte constituent. Most work has been aimed at the optimization of membrane formation conditions, as well as at finding suitable applications for the dynamic membrane technology.

The purpose of this research is therefore to synthesize a number of polyelectrolytes, both homopolymers and copolymers, which will then be evaluated in terms of:

- their ability to form dynamic membranes;
- their formation characteristics; and
- their performance as dynamic membranes, both in terms of time and pH.

As a matter of course, the performance of the polyelectrolytes will be evaluated, by simple methods wherever possible, in terms of molecular mass and copolymer composition.

Forthcoming from the investigation should be a chemical structure/property interpolation. This will hopefully provide a start to forming a sound scientific basis for a better understanding and a prediction of the chemical structure needs of desired polyelectrolytes.

CHAPTER 2

HISTORY AND THEORETICAL BACKGROUND

2.1 REVERSE OSMOSIS

2.1.1 INTRODUCTION

Reverse osmosis is a membrane permeation process for separating relatively pure water (or other solvent) from a less pure solution. The solution is passed over the surface of an appropriate semipermeable membrane at a pressure greater than the osmotic pressure of the feed solution [15].

2.1.2 HISTORICAL LANDMARKS

Filtration is one of the oldest separation processes. According to Dickey, [16] straining through porous media was described by ancient Chinese writers and in ancient Hebrew scrolls. Aristotle mentions filtration through cloth. The use of pressure to speed up separation was introduced in the early 19th century. Initially only large solid particles were removed [17]. Since the day of the early mechanical separation methods many chemical and physiochemical methods for the purification of liquids have been developed, but the first researches into the application of the reverse osmosis process to water desalination were published in the mid 1950's by Prof. C.E. Reid et al and other groups at the University of California [18,19]. Reid discovered that neutral cellulose acetate membranes rejected 98% or more of salt from salt solutions of seawater concentration, however, permeation rates were low.

Advances in the development of the membranes were made by Loeb and Sourirajan who made cellulose acetate membranes of greatly enhanced flow by casting them from solutions containing perchlorate salts. The fluxes attained were high enough to encourage an interest in practical applications for these membranes [20].

At the same time, McKelvy et al studied the closely related ion-exchange membranes which were used for desalination [17]. The commercially available electrodialysis membranes they used gave lower fluxes and rejections than those of cellulose acetate, particularly at higher salt concentrations.

The development of reverse osmosis is well reviewed in books by Merton and Sourirajan [21, 22].

The theory and thermodynamic concepts of reverse osmosis are well reviewed by Dresner and Johnson [17]. Salt rejection by membranes in a reverse osmosis process is still regarded as a complicated process. In trying to explain the rejection phenomenon, two approaches have been followed:

- First, the "structural" approach by which attempts are made to correlate the physical micro structure of the membrane (pores etc.) or chemical properties of membrane components with salt rejection.

- Secondly, the "phenomenological" approach by which attempts are made to correlate the rejection behaviour of a given membrane with measurable macroscopic properties by using suitable mathematical models.

Models which have achieved prominence as explanations of rejection by neutral membranes are Callender's distillation mechanism, the sieve mechanism, the surface tension mechanism and the hydrogen-bonding mechanism. These models are reviewed by Dresner and Johnson [17]. Of particular interest in that review are the transport equations and phenomenological analysis that are applied to ion-exchange type membranes.

2.1.3 MEMBRANES

These can be divided into several broad categories.

2.1.3.1 Cellulose Acetate and other Carbohydrate-based Membranes

As these membranes are only of interest for comparison they are briefly summarized. In the class of cellulose acetate membranes the most important are the asymmetric membranes developed by Loeb and Sourirajan [20]. These can be varied in terms of the degree of acetylation, molecular mass and the use of different esters.

2.1.3.2 Other Neutral Membranes

Numerous polymers have been used for membranes. The more successful of these are also listed by Dresner and Johnson [17].

It is necessary to mention different methods of making neutral membranes (other than by casting a membrane film from a polymer solution). Early work discussed in the above review indicated that Johnson attempted, with mixed success, to make neutral membranes by forming them dynamically. Materials used were, for example, poly(acrylamide), poly(vinyl pyrrolidone), poly(vinyl methyl ether), and sucrose octaacetate.

Two other techniques that merit attention are the grafting of polymers onto films of different polymer compositions (used for some time for the preparation of electrodialysis membranes) [23] and plasma polymerization. By this latter method, membranes may be formed from many saturated organic monomers, which cannot be polymerized by conventional methods [24].

2.1.3.3 Ion-exchange Membranes

2.1.3.3.1 Permanent, detachable

Ion-exchange membranes are either organic films or inorganic materials. These include clay compacts [25] and Vycor (unfired) [26]. Typical of the organic membranes are poly(acrylic acid) grafted onto cellulose, [27] methacrylic acid grafted onto nylon-4 and polyethylene, [28, 29] or poly(styrene sulfonate), poly(vinyl pyridine) and acrylate grafted onto poly(ethylene), and poly(vinyl benzyl trimethylammonium chloride) grafted onto cellophane [30]. Chemically modified polymers have also been used. The best example of this is the sulphonated polyethylene membranes.

2.1.3.3.2 Dynamically Formed Membranes

These membranes are formed on porous bodies by circulating past these bodies solutions under pressure containing polyelectrolytes. Examples of the porous bodies can be:

- Microporous filter sheets
- Porous metals
- Carbon tubes
- Ceramic tubes
- Woven fabrics

For most applications the favourable pore size lies between 0,1 or 1,0 µm.

These membranes will be discussed in more detail in Section 2.2.

2.1.4 CONCENTRATION POLARIZATION

When water is pumped through a salt-rejecting membrane, the salt that is held back concentrates in a layer next to the membrane surface. This salt build-up is called concentration polarization. Problems associated are:

- Real membranes are not perfect and allow some of the salt present in the feed to pass through. The concentration of salt in the product will therefore increase as the salt concentration at the membrane surface increases.

- The salt build up at the interface increases the osmotic pressure of the solution at the interface, which in turn decreases the pressure effective in driving water through the membrane.

- Effective membrane surface may be diminished by precipitation of dissolved components, caused by excessive concentration polarization.

The relevant concentration polarization equations will be discussed in Section 2.5.

2.2 DYNAMIC MEMBRANES

2.2.1 A BRIEF HISTORICAL OVERVIEW

In June of 1965, A.E. Marcinkowsky, working at The Oak Ridge National Laboratories, observed that when a pressurized sodium chloride solution containing low concentrations of thorium tetrachloride ($\sim$ 0,001 Molal) was circulated past a porous silver frit of pore diameter 0,2µ, there was at first a rapid decrease in permeation rate, and that a substantial amount of the salt was filtered out [6]. After an initial sharp decrease in permeation flow, the rejection of the sodium chloride and the thorium tetrachloride continued to increase with time, while the permeation flux rate fell.

After a few days the thorium tetrachloride was completely rejected. Shortly afterwards, Kraus, Phillips, Marcinkowsky and Johnson [31] did work on forming membranes dynamically on bodies having a pore size diameter of upwards of 0,1 µ. This was done by exposing this body (a silver frit) to a pressurized feed solution containing small quantities of polyelectrolytes. The first polyelectrolyte to be evaluated was poly (vinylbenzyl trimethyl ammonium chloride), with a molecular mass of 120 000.

In 1967, Kraus, Shor and Johnson [3] reported that many materials are capable of forming dynamic membranes, (some species are present in natural feed waters). Among the materials listed by Kraus et al were the hydrous oxides of Al(iii), Fe(iii), Sn(iv), Zr(iv) and Th(iv), finely ground low density cross-linked ion exchange beads, clays (bentonite), humic acid and synthetic polyelectrolytes such as poly(styrene sulphonic acid), poly (methyl vinyl ether-co-maleic anhydride) and cellulose acetate hydrogen phtalate.

Then, in 1969, Johnson et al, [7] realised that in spite of the high fluxes shown by the hydrous oxide membranes a number of practical problems existed. These were:

- The salt rejections were too low.
- The pH range of some of the dynamically formed membranes did not match the ranges of pH of the waters to be treated.
- Frequently the presence of polyvalent counterions adversely affected the membrane performance to an unacceptable extent.

They then found, however, that one polyanion, namely, poly(acrylic acid), [32] formed membranes which though not immune to the effects of polyvalent cations gave higher rejections in the neutral pH range than most dynamic membranes did.

Subsequently they found that, when a dynamic membrane of hydrous zirconium oxide was exposed to an acidic solution containing poly(acrylic acid), a layer of the polyacid became attached to the zirconium oxide, thus forming a dual-layer membrane. This was probably the single most important achievement in the development of dynamic membranes.

Since that time ($\sim$ 1972) most research has centred on attempts to optimize the formation conditions of these dual-layer membranes; to explaining the kinetics governing the formation of dual-layer membranes, to finding applications for the technology of dynamically formed dual-layer or composite membranes and, to a much lesser extent, to investigate new materials. The first two of these directions will be discussed in more detail in Section 2.5, later in this chapter.

2.2.2 APPLICATIONS

In 1974, Minturn and Johnson [33] reported that dynamically formed hydrous zirconium (IV)-oxide-polyacrylate membranes (ZOPA) removed 98% of organic carbon from two commercial laundries' effluents. EI-Nasher [3] reported in 1976 that dynamically formed ZOPA membranes showed some promise for desalting brackish water and industrial wastewater.

Since then, the possibility of using dynamic membranes to recycle space craft wash-water [34] has been studied. Brandon, Porter and Gaddis [33] reported their studies on the recycling of hot textile effluents. They showed that dynamic membranes made it economically viable to recycle hot, high-strength wastewater. This was confirmed by Porter [36] in 1984.

Other applications studied were the treatment of wool-scouring and dye house effluents [1].

2.2.3 MEMBRANE FORMATION AND PERFORMANCE

Tanny and Freilich in 1977 [12] formulated a formation mechanism of dynamic hydrous zirconium(IV) oxide membranes on microporous supports. They reported that the flux decline that occurs during formation is consistent with a mathematical model involving two stages of membrane growth, i.e. a "pore-clogging" step and the growth of a conventional filter cake.

In a later study (1978), Tanny and Johnson [37] reported that dependence of the water flux on the concentration of poly(acrylic acid) in the feed during the formation of hydrous zirconium(IV) oxide-polyacrylate dynamic membrane indicated that the poly(acrylic acid) enters the pores of the hydrous zirconium(IV) oxide layer, rather than forming a second layer.

In the same year, Freilich and Tanny [38] contributed further to understanding of the formation mechanism from their studies on the effect of crossflow velocities and the pore size of the microporous support on dynamic membrane (ZOPA) performance.

2.2.4 NEW MATERIALS

Since the discovery of the composite membrane based on polyacrylic acid in 1972 by Johnson et al [7], very few new materials have been studied.

Exceptions are the work reported by Antoniou, Springer and Grohmann in 1980 [39] on the dynamic formation of poly (acrylamide) membranes on a Millipore filter and that of Wang Ying [40] reported on in 1983 on the formation of a dynamically formed poly(vinyl alcohol) membrane on porous ceramic supports. These two materials, however, were not dual-layer or composite membranes.

In 1984 Spencer, Todd and McLellan [41] reported the formation of dynamically formed polyblend membranes. These consisted of a ZOPA membrane onto which a primary poly(amine) or secondary or tertiary poly(amine) was deposited. None of the above materials showed any improvement on the existing zirconium-polyacrylate membranes. Beyond these studies, the literature is devoid of any sound polymer chemistry approach.

2.3 ZIRCONIUM CHEMISTRY : A BRIEF OVERVIEW

As the base layer of the dynamically formed membrane system is hydrous zirconium oxide, it is necessary to give a short review of the aqueous chemistry of zirconium. This will be necessary to explain effects such as low membrane stability referred to in later sections.

2.3.1 GENERAL ZIRCONIUM CHEMISTRY [42, 43, 44, 45]

Zirconium was discovered in 1789. Some of the fundamental properties of the zirconium aton are the following:

Zirconium, atomic number 40 and atomic weight 91,22 represents a mixture of 50.5% Zr^{90} and four heavier isotopes. It lies in Group IV A, Period 5 of the Periodic Table of elements. It is a member of the second transition series and has no stereochemical preferences.

It differs from transition elements in later groups (and, to a lesser degree, from hafnium and titanium in Group IV A) in its tendency to form four-valent compounds in preference to compounds of lower charge numbers. The ground state electron configuration in the outer shells of the atom is $4d^2 5s^2$:

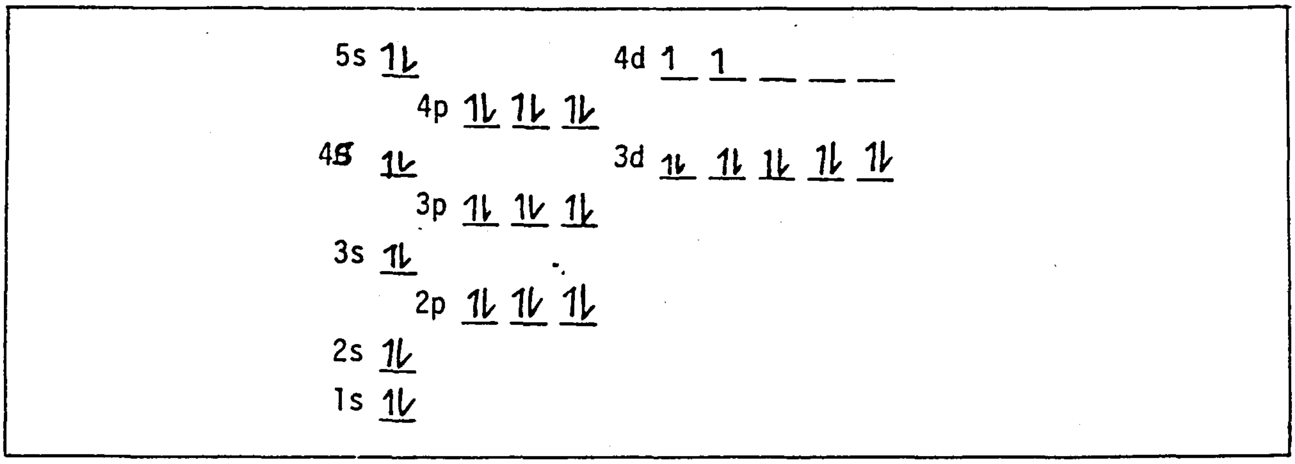


Fig. 2.1 Electron configuration of zirconium

The large stability of the Zr^{4+} state can be explained by the fact that the loss of four electrons (from the 4d and 5s orbitals) leaves the exceptionally inert rare gas configuration of krypton.

If one considers the ionization potentials for the loss of each successive electron, it is easy to see why zirconium loses four electrons so easily:

First ionization potential	6,95 eV
Second ionization potential	14,00 eV
Third ionization potential	24,10 eV
Fourth ionization potential	30,00 eV

2.3.2 THE AQUEOUS CHEMISTRY OF ZIRCONIUM

Because they have a high positive charge and a small ionic radius zirconium cations tend to hydrolyze strongly in aqueous solution with the corresponding liberation of hydrogen ions according to the equilibrium shown in figure (2.2) [42]:

$$Zr^{4+} + xH_2O \rightleftharpoons Zr(OH)_x{}^{(4-x)+} + xH^+$$

Figure 2.2 Hydrolysis of zirconium cation

Evidence [46, 47] suggests that these hydrolyzed zirconium ions, often referred to as oxo-zirconium ions are polymerized to a greater or lesser extent. Clearfield [43] stated that the zirconyl ion in zirconyl halides is a tetramer:

$[Z(OH)_2 \cdot 4H_2O]_4{}^{8+}$ and that this species also exists in aqueous solution.

The tetramer is formed by the formation of hydroxyl bridges between hydroloyzed zirconium ions. The first step is shown in Figure 2.3.

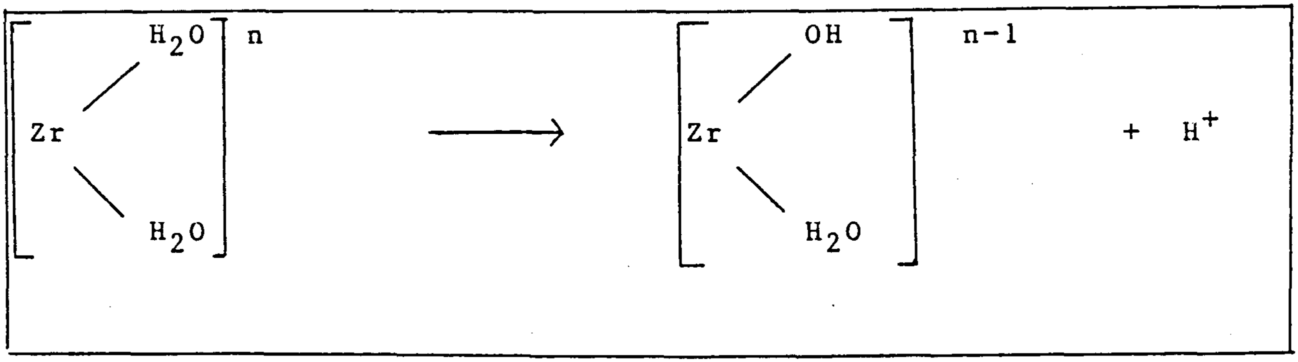


Figure 2.3: The first step in the formation of a zirconium tetramer.

The hydrolyzed species may now undergo condensation reactions to form hydroxyl bridges, as shown in Figure 2.4.

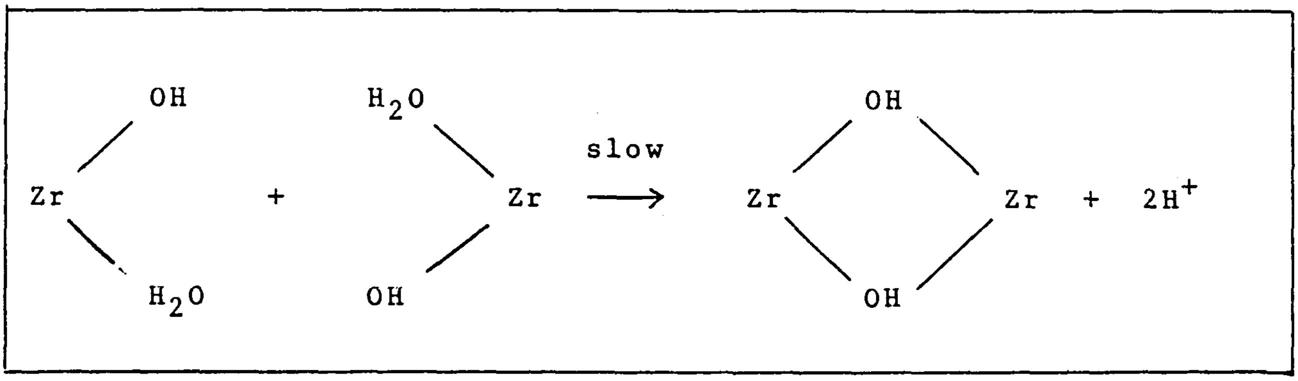


Figure 2.4: The formation of hydroxyl bridges.

This process leads to the formation of four double hydroxyl bridges and the formation of the tetramer that exists in aqueous solution [42].

Zaitsev [48] concluded that during ageing of zirconium oxide polymers, one oxygen bridge can be found from two hydroxyl bridges. This can be represented as follows (Figure 2.5).

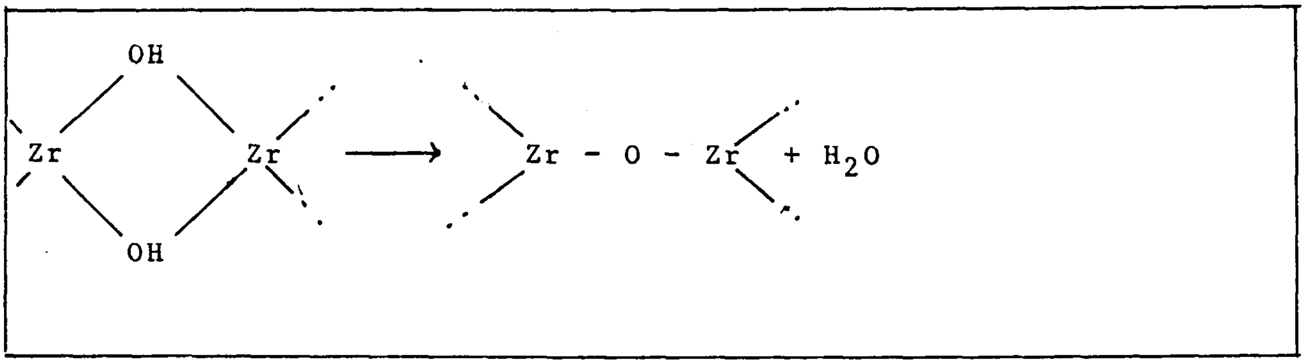


Fig. 2.5: The formation of a single oxygen bridge from two hydroxyl bridges

The process of double hydroxyl-bridging does not lead only to the formation of separate tetramers. Hydroxyl-bridging between zirconium atoms belonging to separate tetramers also take place. This results in the formation of large, three-dimensional polymers of linked tetramers. These polymers can be random (Figure 2.6) or ordered (Figure 2.7) [42].

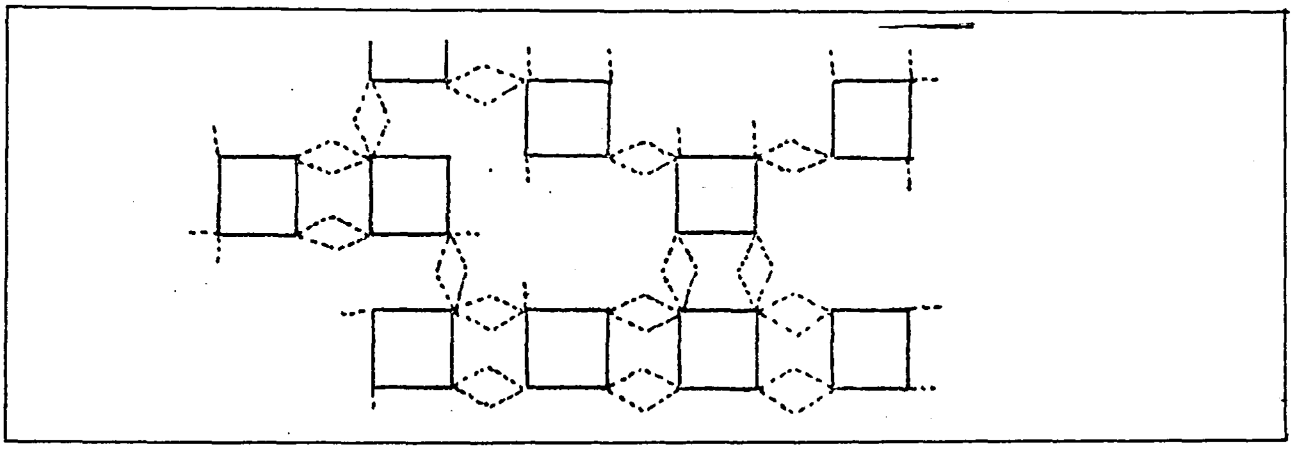


Fig. 2.6: Random hydrous zirconium polymer

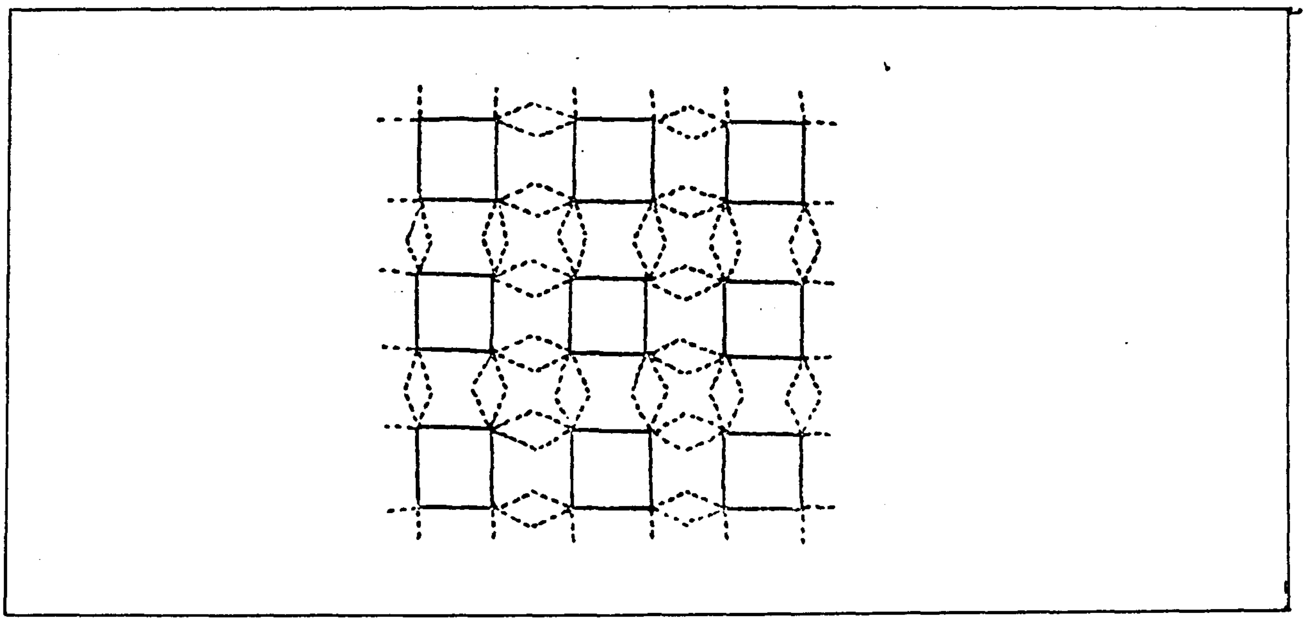


Fig. 2.7: Ordered hydrous zirconium polymer

The solid line squares in the above Figures represent the original tetrameric units, $Zr_4(OH)_8$. Each dashed line represents an ^-OH group formed by hydrolysis while each bent dotted line represents a hydroxyl bridge joining two tetramers.

Thus pure hydrous zirconium oxide can be described [42] as consisting of a three-dimensional aggregate of indefinite shape and size, comprising vast numbers of very loosely bound water molecules surrounding reactive hydroxyl groups and water coordinately bound to tetramers of zirconium atoms. The zirconium atoms of the tetramers are linked, both internally and to zirconium atoms of other tetramers, by less reactive bridging pairs of hydroxyl groups or by still less reactive oxygen atoms.

2.3.4 THE INTERACTION OF ZIRCONIUM WITH ORGANIC MOLECULES

On the bonding between hydrous zirconium oxide and other substances Hock [42] said:

Chelation of simple organic molecules containing hydroxyl, carbonyl or carboxyl groups must be assisted by the hydroxyl groups attached to the zirconium.

The available information on simple low molecular mass oxygen-containing organic compounds can be summarized as follows:

- Single hydroxyl groups will not chelate.
- Polyols exhibit some degree of chelation.
- Monocarboxylic and dicarboxyl acids will chelate with the same zirconium atom.
- Hydroxycarboxylic acids with OH and COOH groups on adjacent carbon atoms form very stable structures.
- There appears to be no chelation with ether groups even if the spacial geometry is correct.

From this it can be seen that the chemistry of coordination with the hydrous zirconium is a field deserving attention. The interaction of zirconium with polymeric compounds is even more important since small molecules do not perform the same as arrays of neighbouring chelating groups.

2.4 THE FORMATION OF DYNAMICALLY FORMED DUAL LAYER MEMBRANES

2.4.1 ZIRCONIUM

The basic aqueous chemistry of zirconium was discussed in some detail in Section 2.3.

2.4.1.1 Membrane Formation

Two models have been used to describe dynamic membrane formation on selective supports. The first, and possibly the most general model, involves the gel layers which form at the feed/membrane boundary during ultrafiltration of natural and synthetic polymers and polyelectrolytes.

The second involves the diffusion of polyelectrolyte molecules into the very fine pores of partially selective membranes. Examples of such supports are poly(acrylic acid), partially cured cellulose acetate [4] and even hydrous zirconium oxide itself.

Non-selective supports do not conform to either of these models, yet zirconium membranes are made, using colloidal suspensions, on such supports. Tanny [12], supported by Blatt [49], states that the formation of a dynamic hydrous zirconium oxide membrane on a non-selective support takes place in two stages:

These are:

(a) The pre-cake formation period during which a portion of the colloid particles are captured on the pore walls and the pore radius gradually narrowed. This process leads to lower fluid velocities and increase in particle capture over a shorter distance, eventually leading to pore closure.

(b) The building of a surface cake comprising agglomerated colloidal particles.

This model predicts correctly the effects of the feed concentration, the formation pressure on the zirconium content and the hydrodynamic resistance of the membrane.

(i) The Effect of Feed Concentration:

Tanny [50] reports that a longer time is required to form a dynamic membrane if the feed concentration is decreased.

(ii) The Effects of Porous Support Pore Size

Tanny [50] reports that the time needed to form a dynamic membrane, as well as the membrane characteristics vary only slightly if this primary pore size is in the range of 0,025 - 0,45 μ.

(iii) The Effect of pH on Membrane Formation

As the size of the hydrous zirconium particles are a function of the pH [50], pH will play a role in the time taken to form a dynamic membrane, as well as the amount of zirconium in the membrane.

Tanny [50] investigated the effect of pH, and came to the conclusion that, above pH 3.5 the formation of larger particles of hydrous zirconium in the feed would result in larger secondary pores formed in the membrane, increasing the flux. Below pH 3.5 the charge on the particles plays an increasingly important role. Due to this charge, particles rearrange themselves in such a way as to minimize repulsion and in doing so the number of voids increase giving a more porous zirconium structure.

Tanny [50] concluded that an optimum value for formation is between pH 3.2 and pH 3.8.

2.4.2 THE FORMATION OF THE POLYELECTROLYTE (POLY(ACRYLIC ACID)) LAYER

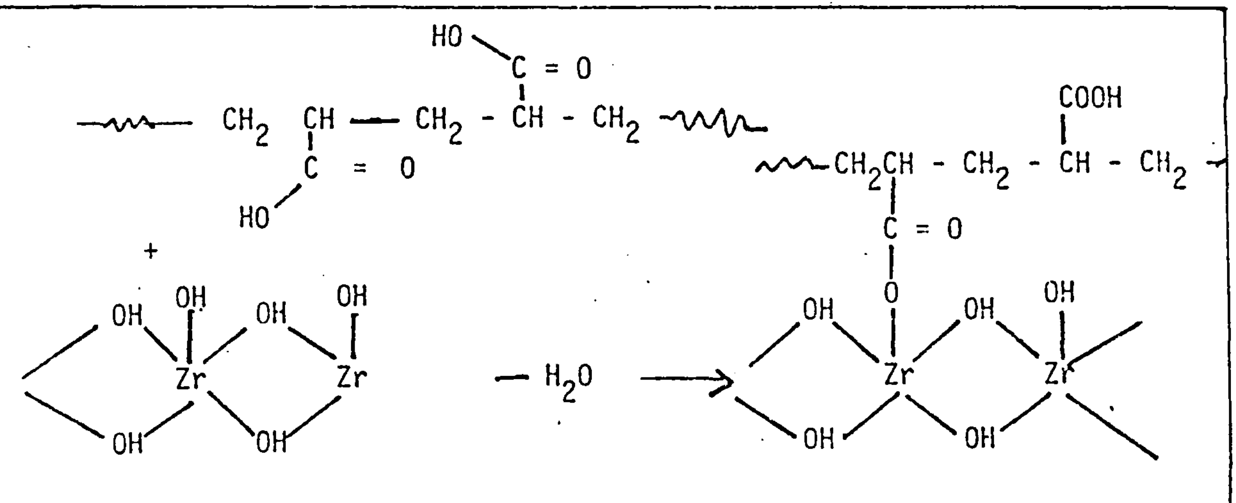
This can be subdivided into two sections.

(i) The physical mechanism of membrane formation:

Tanny and Johnson [37] suggest two mechanisms. First the poly(acrylic acid) layer is a gel deposit on top of the hydrous Zr(IV) oxide layer, or, second, the poly(acrylic acid) fills the pores of the formed hydrous oxide membrane. Studies have proved that molecular mass plays a role in membrane performance and these indicates that there is a necessity to match pore size and polymer size, so that the pore fill model is a viable one.

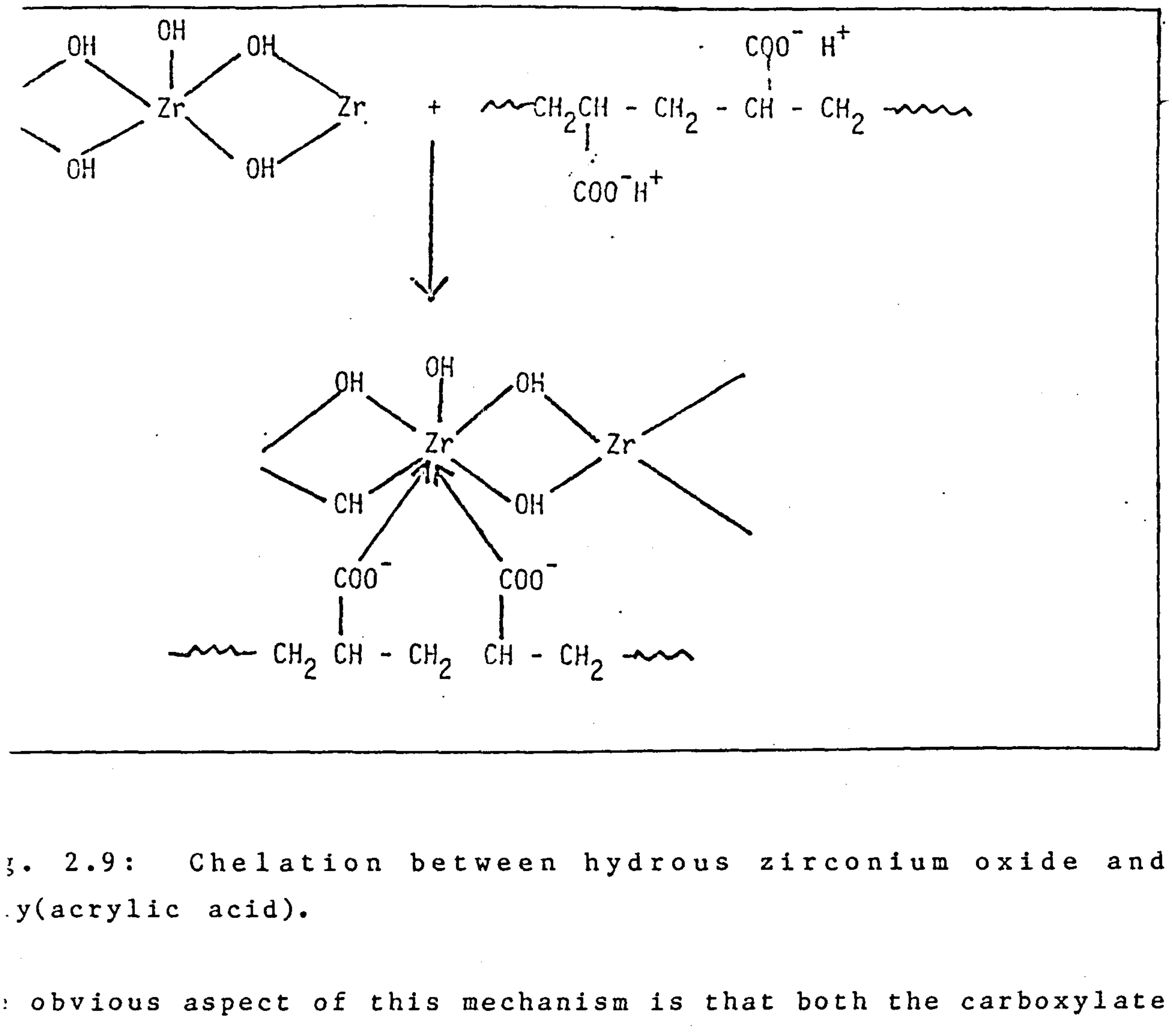
(ii) The interaction between zirconium oxide and poly(acrylic acid):

Hydrous zirconium oxide is an anion exchanger at acidic pH. Tanny and Johnson [37] suggested that as this is so there is a possibility that the poly(acrylic acid) carboxylate groups could attach themselves to positively charged sites on the zirconium sublayer. Another possibility is that a covalent bond between the polymer and the zirconium is formed (See Fig. 2.8) [9].



2.8: Covalent bonding between hydrous zirconium and (acrylic acid).

most likely method of interaction is one of chelation between carboxylic acid groups of the poly(acrylic acid) and the onium atom. The observations by Hock [42] on the chelation simple organic molecules with zirconium support this ibility (See Figure 2.9).



2.9: Chelation between hydrous zirconium oxide and y(acrylic acid).

obvious aspect of this mechanism is that both the carboxylate ups involved in chelation would have to be on the same side of polymer chain. The steric effects caused by this would ect the chelation process.

No conclusive proof on the type of interaction between zirconium and poly(acrylic acid) exists, but the one of chelation seems to be the most likely, and will be accepted as the mechanism for interaction. The following bears this out. When a ligand contains more than one donor atoms it may co-ordinate to more than one position on the cation to form a ring known as a chelate complex.

Multidentate ligands often form more stable complexes than monodentate ligands. A number of factors are involved in determining the stability of the chelate complex:

- Ligand repulsion occurs when 2 similar ligands, charged or neutral, are brought up to a single metal ion. With a multidentate ligand however some of this repulsion has already been built into the ligand.

- If distortion of bond angles in the ligand is to occur during complexing, chelation by the more rigid multidentate ligand is unfavourable unless its bite (distance between donor groups) is ideally suitable to the metal. Chelation tends to favour 5 and 6 membered rings with metals of the transition series since bond distortions are kept to a minimum in such rings.

- A restraint is that chelate ligands normally span cis-positions with regard to the metal ion. Hence geometrical restrictions are also of importance.

- Once one end of the chelating ligand is co-ordinated the chance of the second end co-ordinating is proportional to the effective local concentration around the metal ion.

- The longer and more flexible a chelate ligand the higher will be its internal entropy. Since one co-ordination this entropy will be lost, complex formation will not be favoured.

- The gain in translational energy on replacing two or more monodentate ligands (often solvent molecules) by 1 multidentate ligand contributes largely to the formation of chelates.

2.4.3 FACTORS AFFECTING MEMBRANE PERFORMANCE CHARACTERISTICS

2.4.3.1 Poly(acrylic acid) Molecular Mass

Johnson et al [7] determined the effect of poly(acrylic acid) molecular mass on the flux and rejection of composite Zr(IV)-PAA membranes. They found that rejection was a maximum in a molecular mass range of 50 000 to 150 000.

2.4.3.2 Circulation Velocity

The feed circulation velocity during membrane formation affects the flux more than the rejection, according to Johnson [7] and Minturn [51]. Thomas and Mixon [52] showed clearly that the final membrane flux increases markedly as the axial velocity during membrane formation is increased. The effect of the increase in velocity was not as marked on the extent of rejection as it was on the flux, but the combined effects of rejection and flux results in a better membrane formed at higher circulation velocities. Thomas and Mixon [52] quote optimum circulation velocities exceeding 6 $m.s^{-1}$.

2.4.3.3 pH at Poly(acrylic acid) Addition

Formation of the poly(acrylic acid) layer at pH 2,0 produces membranes which give the best membrane performance [7, 52]. (pH 3,2 - 3,8 is optimum for the formation of the Zr(IV) portion of the composite membrane (see section 2.5.1)).

2.4.3.4 System Pressure

(i) Formation pressure

Johnson *et al* [7], after forming membranes at pressures varying from 0,6 MPa to 6,0 MPa and then evaluating these membranes in terms of rejection and flux at a pressure of 6 MPa came to the conclusion that: As the formation pressure increases, the flux of the formed membrane decreases, while the rejection of the formed membrane increases, and *vice versa*.

(ii) Operating pressure

As with other R.O. membranes [22] flux and rejection increase with applied system pressure [7, 52].

2.4.3.5 Solution Concentration

The effect of solution concentration on neutral membranes is well documented [22]. The situation for dynamic membranes appears to be less clear-cut. These membranes have ion-exchange properties.

The ion exchange theory predicts that a plot of log (1-rejection) vs log concentration of solute, should lead to a slope of 1 for a univalent salt and approach a slope of 2 for a divalent salt. Johnson *et al* [7] showed that Zr(IV) - poly(acrylic acid) membranes have a slope of about 0,5 when the salt was univalent. Thus these membranes are not ideal ion-exchange membranes, even though they posess ion-exchange properties.

The observed rejection for dynamically formed membranes decrease with an increase in salt concentration in the feed.

2.4.3.6 Concentration Polarization

When flow rates past the membrane surface are low the rejected solute tends to build up a layer of higher-than-feed concentration at the interface, leading to observed rejections lower than those of which the membrane is capable.

Concentration polarization has been widely studied and reported, for example by Shor [53]. The relevant concentration polarization equations will be discussed in section 2.5.

2.5 MEMBRANE EVALUATION

2.5.1 GENERAL

Membranes have been evaluated in terms of A^2/B values, as proposed by Lonsdale [54], where A and B have the following meanings:

A = membrane constant for water permeation ($g/cm^2.s$)
B = membrane constant for salt permeation ($g/cm^2.s$)

This method, which was originally developed for cellulose acetate membranes (49) use the basic transport equations

Water flux F1 = $A(\Delta P - \Delta \pi)$ (1)

Where ΔP = pressure differences across the membrane
$\Delta \pi$ = osmotic pressure difference across the membrane

And:

Salt flux F2 = $B \Delta C$

Where ΔC = concentration difference across the membrane

2.5.2 CONCENTRATION POLARIZATION

As water is desalinated by passage through a membrane [17] there is an increase in solute concentration at the membrane and solution interface. This phenomenon is known as concentration polarization (C_p). The extent of C_p is defined by the ratio of the membrane wall solute concentration, Cw, to the bulk solute concentration, Cb.

A higher concentration polarization term would obviously lead to a lower permeate flux due to an increase in the $\Delta\pi$ term in equation (1) and an increase in salt flux due to greater Δ C term in equation (2). Thus it is obvious that a high Cp term has a negative effect on membrane performance.

Loeb [55] derived the following equation for Cp in the turbulent region of flow in TUBULAR MEMBRANES.

$$Cp = Cw/Cb = 1/Dr + (1 - 1/Dr) \exp (Fl\ Nsc^{0.67}/Ubjd) \quad (3)$$

Where Dr = Ratio of bulk solution concentration to product concentration
Fl = Product flux
Nsc = Schmidt number for salt diffusion
Ub = Bulk solution velocity
jd = Chilton-Corburn mass transfer factor

And Nsc = v/D
Dr = 1/(1-R)

Where v = kinematic viscosity
D = diffusion coefficient
R = membrane rejection

Further, the Chilton-Coburn mass transfer factor is

$$vd = 0{,}023\ Nre^{0.17} \quad (4)$$

Where Nre = Reynolds number
d = inside tube diameter

As the experimental work described in Section 4 was done in flat cells and not tubular membranes, the above could not hold true. However, as no concentration polarization equations for flat cells (other than stirred batch cells) could be found, it was decided to regard these flat cells as tubular membranes. This could be done as the feed solution in the flat cells follows a channel ("tube") over the surface of the membrane face (see Fig. 2.10). This channel in the face of the Perspex disk in the cell is primarily there to increase turbulence and thus decrease concentration polarization.

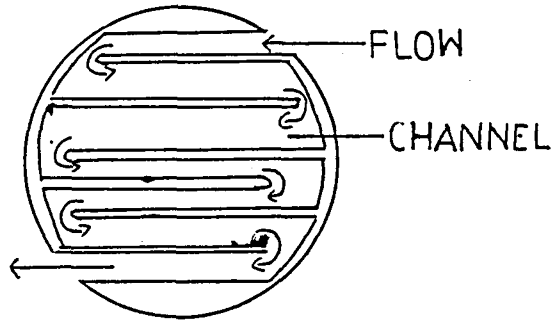


Fig. 2.10: Perspex turbulence promoter: upper view

In this study, therefore, the cross-sectional area of this channel in the Perspex disc was calculated, and from this it was possible to calculate the theoretical inside diameter of a tube of the same cross-sectional area. The above equations could then be used, albeit with a built-in error. This was acceptable as the equations were to be used to calculate membrane performance for all the membranes tested, and the relative values obtained would allow comparisons to be made between these membranes.

Further: $Nre = Ubd/v$

Now, by incorporating the Cp into the transport equations (1) and (2) we can, by simplifying the Cp equation, arrive at the following relationships:

$$Fl = A[\Delta P - \pi b(Cw/Cb) + (\pi b/Dr)] \qquad (5)$$

$$F2 = BCb\,[(Cw/Cb) - (1/Dr)] \quad (6)$$

$$Cw/Cb = 1/Dr + [1-(1/Dr)]\exp[F1v^{0,5}d^{0,17}/0,023Ub^{0,83}] \quad (7)$$

Calculating Cw/Cb (= Cp) and substituting this value into equations (5) and (6) enables the membrane constants B and A, and thus A^2/B, to be calculated.

A computer program was use in order to speed up these calculations. A listing of the computer program is given in appendix C.

2.6 MEMBRANE CHARGE DENSITY

This section deals in brief with the theory and concept of using membrane potentials to ascertain the membrane charge density of a fixed-charge membrane.

2.6.1 MEMBRANE POTENTIAL

A steady electromotive force (emf) arises between two different concentrations of an electrolyte, at a constant temperature and pressure, when they are separated by a membrane that contains fixed ionizable groups [56]. This emf is usually called the membrane potential.

Kobatake et al, [56] attempted to derive an equation for the electric potential P which arises between two solutions of a uni-univalent electrolyte of different concentrations C1 and C2 (C1 > C2) that is separated by a negatively ionizable membrane.

Kobatake also did work [57] on determining the effective charge density of fixed-charge membranes. He proposed an equation whereby the hydrodynamically effective charge density could be calculated by determining the Donnan equilibrium potential alone.

Then, in 1977, Siddiqi and Beg [58] summarized the work done by Kobatake and derived an equation for determining the thermodynamically effective charge density.

Siddiqi and Beg stated that, taking into account the Teorell-Meyer-Sievers theory (TMS theory) and the work done by Kobatake _et al_ [56, 57]:

For a negatively charged membrane separating two solutions of a 1:1 electrolyte (univalent) of concentrations C_1 and C_2, with $C_1 \quad C_2$, the electrical potential Em:

Where $Em = -RT/F\ [1/B\ \ln(C_2/C_1)]-(1 + 2\alpha - 2\gamma)\ \ln\ (C_2 + BX/C_1 + \alpha BX)$ (1a)

and $= u/(u + v)$

$B = 1 + KFX/u$

And F = Faraday constant

X = Charge density

u and v = Mobilities of anions and cations, respectively.

K = Constant dependent on the viscosity of the solution and structural details of the polymer network of which the membrane is composed.

To evaluate the membrane parameters, α and B , two limiting forms of eq. (1a) were derived:

When the external salt solution was low:

$$/Em^{\sigma}/ = 1/B\ \ln\ - (\gamma - D/\alpha\ B\gamma)(1 - 1/B - 2\alpha)(C_2/Xd) \quad (1)$$

Where $/Em\ / = FEm/RT$

and $\gamma = C_2/C_1$

With T = temperature in Kelvin; and R = gas constant

When the salt concentration is high:

$$1/t\_ = 1/(1-\alpha) + [(1 + B) - 2\alpha B)(\gamma - 1)/2(1 - \gamma)^2 \ln \ ](Xc/C_2) + \ldots \quad (2)$$

Where $t\_$ = apparent transference number of co-ions in a negatively charged membrane defined by:

$$/Em/ = (1 - 2t\_) \ln\gamma \quad (3)$$

(Xd = charge density in a dilute system;
Xc = charge density in a concentrated system)

If the above equations were to hold true, then Xc would have to equal Xd. This was found, experimentally, to be so [56].

Kobatake and Kamo [56] derived another equation (9) by using a different set of assumptions, namely, that the contribuion by mass movement is negligible and that small ions do not behave ideally in a charged membrane:

$$Em = RT/F\ [\ln C_2/C_1 + (2\alpha - 1) \ln (((4C_2{}^2 + \phi^2X^2)^{0.5} + (2\alpha - 1)\phi X)/((4C_1{}^2 + \phi^2X^2)^{0,5} + (2\alpha - 1)\phi X)) - \ln (((4C_2{}^2 + \phi^2X^2)^{0,5} + \phi X)/((4C_1{}^2 + \phi^2X^2)^{0,5} + \phi X)) \quad (4)$$

where ϕ is a characteristic factor of the membrane-electrolyte pair and represents a fraction of counterions not tightly bound to the membrane selection. The product ϕX is termed the thermodynamically effective charge density [58].

Kobatake et al [59] have proposed a simple method of using the following approximate equation for the diffusive contribution to the emf of a cell with transport.

$$Em = -RT/F(1 - 2\ Tapp)\ \ln C_2/C_1 \quad (5)$$

Where Tapp is the transference number of coions in the membrane phase. Comparison of equations (4) and (5) gives:

$$Tapp = (1 - 2\alpha)/2[\ln((4E_2{}^2 + 1)^{0.5} + 2\alpha - 1)/((4E_1{}^2 + 1)^{0.5} + 2 - 1)]/\ln + [\ln((4E_2{}^2 + 1)^{0.5} = 1)/((4E_1{}^2 + 1)^{0.5} + 1)]/2\ln\gamma \quad (6)$$

Where $E = C/\phi X$

When $C/\phi X = E \gg 1$; i.e. when the external salt concentration is high compared with ϕ, eq. (6) expands to

$$1/Tapp = 1/(1-\alpha) + ((\gamma-1)/\gamma \ln\gamma)(\alpha/(1-\alpha))(\phi X/C_1) \quad (7)$$

This equation indicates that the plot of 1/Tapp versus 1/Cl should give a straight line, and that the value of and OX for the concentrated solution of a given 1:1 electrolyte can be determined by the intercept and slope of the line.

Further, Kobatake and Kamo [59] found the difference between values of Tapp and t_ obtained experimentally to be less than 2%, so that, for practical reasons:

$$Tapp = t_-$$

Thus, using

$$Em = -RT/F\ (1-2\ Tapp)\ln(C_2/C_1) \quad (8)$$

to determine Tapp for measured Em, ϕX can be determined from a series of Em measurements of various Cl and C2 values, if C2/Cl =

constant.

Using equations (8) and (7), a computer programme was written to evaluate ϕX from the values of Cl and Em. A listing of this programme appears in Appendix C. (An IBM PC microcomputer was used).

2.7 FREE-RADICAL POLYMERIZATION

2.7.1 GENERAL

The process of free-radical polymerization can be discussed under four headings. These are:

- Free-radical formation
- Initiation of polymerization
- Propagation
- Termination

Of those, only the formation of free radicals will be discussed here. The initiation of polymerization, propagation and termination will be discussed, together with the steady-state kinetics and copolymerization equations, in Appendix D.

2.7.2 FREE-RADICAL FORMATION

A free radical is often formed because many organic reactions lead to the formation of a species having an odd number of electrons, and therefore, an unpaired electron. Such species are known as free radicals.

These free radicals can be generated in many ways, of which only a few relevant to this study will be discussed.

Peroxides and Azo Compounds

The single most important reaction in this field is the thermal or photochemical decomposition of benzoyl peroxide, as depicted in Figure 2.11.

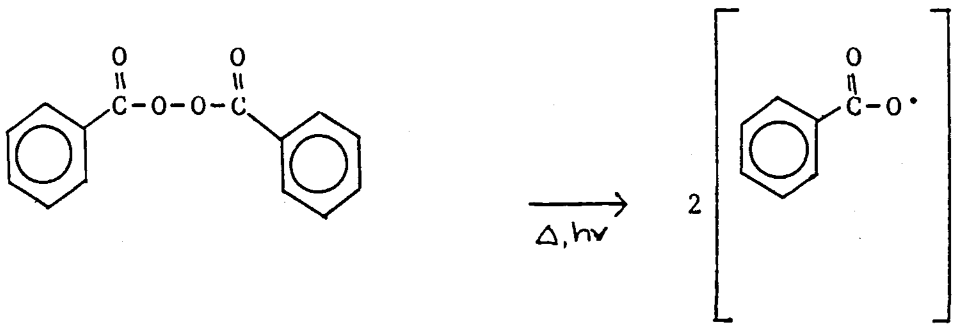
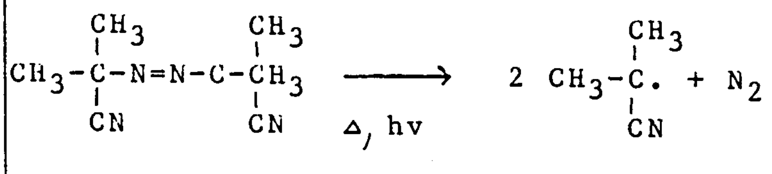


Fig. 2.11: The thermal decomposition of benzoyl peroxide.

The most popular initiator of the azo class is α, α-azobis(isobuyro-nitrile) or AIBN. See Fig. 2.12.



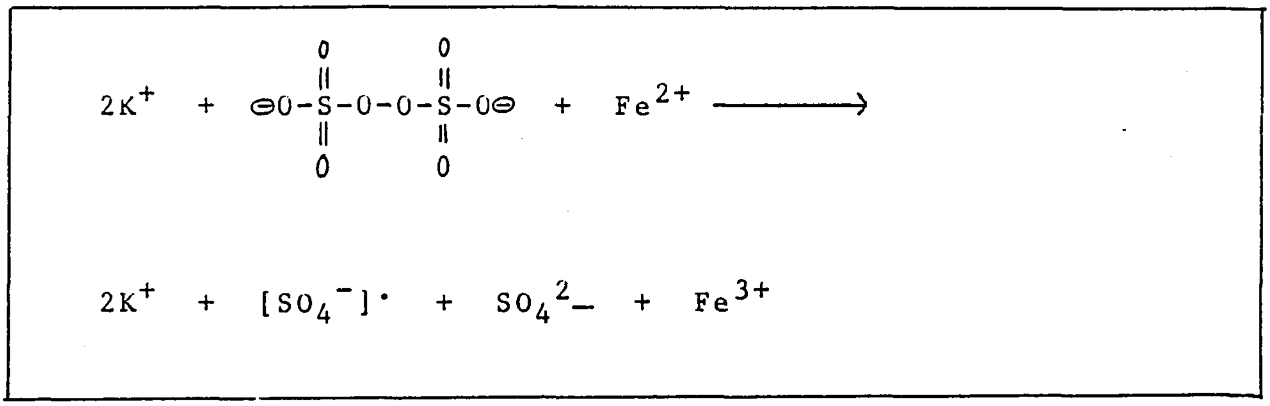
$$\mathrm{CH_3-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3} \xrightarrow[\Delta,\ h\nu]{} 2\ \mathrm{CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot} + \mathrm{N_2}$$

Fig. 2.12: The decomposition reaction of AIBN.

2.7.2.2 Decomposition of Persulphate Ions, or the Redox Initiation of Persulphate

This method of radical initiation by persulphate decomposition is commonly used in aqueous systems. The most commonly used persulphate is potassium persulphate, $K_2S_2O_8$.

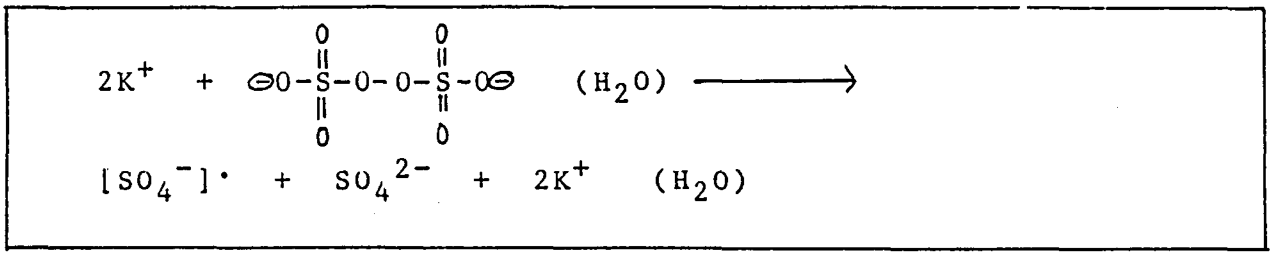
The reaction normally involves the transfer of a single electron, The reaction normally involves the transfer of a single electron, either at low temperature by a redox agent such as Fe^{2+} (see Fig. 2.13) or at elevated temperatures without the benefit of the reducing agent (Fig. 2.14):



$$2K^+ + {}^{\ominus}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{\ominus} + Fe^{2+} \longrightarrow$$

$$2K^+ + [SO_4^-]^{\cdot} + SO_4^{2-} + Fe^{3+}$$

Fig. 2.13: Reduction of persulphate by Fe^{2+}



$$2K^+ + {}^{\ominus}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{\ominus} \quad (H_2O) \longrightarrow$$

$$[SO_4^-]^{\cdot} + SO_4^{2-} + 2K^+ \quad (H_2O)$$

Fig. 2.14: Thermal decomposition of persulphate

There are numerous other examples of initiators [60, 61] but these will not be discussed here.

2.8 POLYMERIZATIONS : A BRIEF BACKGROUND

2.8.1 GENERAL

Details of initiators required, polymerization techniques, kinetics and so on are of extreme importance but are readily available in a number of publications [60, 61]. For the reader, therefore, only a brief discussion is given in Appendix A. As is discussed in Section 2.8.2, a number of polymers were synthesized. As some of the polymers synthesized were novel, no reference could be found to these polymers in the literature. Where, however, background literature could be traced references to this is included to offer an established working basis to the study undertaken.

2.8.2 HOMOPOLYMERS

2.8.2.1 Poly(2-propenoic acid) or Poly(acrylic acid)

The polymer is prepared by the free-radical mechanism. A number of different ways are documented. Among these are the method of polymerization in aqueous medium with hydrogen persulphate as initiator (Silberberg *et al*, [62]), in butanone medium with AIBN as intiator (Morawitz and Kanadian [63]), in aqueous medium with a persulphate as initiator [64] and in 1,4 dioxane as medium using benzoyl peroxide as initiator (Seymour [65]). The method chosen for polymerization in this study was one used by Habert, Huang and Burns [66]. The polymerization is done in an ethyl benzene/toluene mixture with AIBN as initiator, at 70°C.

2.8.2.2 Poly(2-methyl-2-propenoic acid) or Poly(methacrylic acid)

The polymer is generally made by free-radical mechanisms. This can be done in aqueous medium in the presence of a persulphate as initiator [64] at 50°C, or, as is done in this work, the polymerization can be carried out in dioxane as medium at 50°C with benzoyl peroxide as initiator, as described by Silberberg *et al* [62].

2.8.2.3 Poly(methylene butanedioic acid or Poly(itaconic acid)

As with all of the polymers in this study polymerization is done by free-radical mechanism. Polymerization can be done in aqueous medium at a temperature of 50°C with potassium persulphate as initiator (Nagai and Yoshida, [67]) or in dioxane and DMF at a temperature of 50°C to 60°C using benzoyl peroxide as initiator, as described by Gufarov *et al* [68].

The method used was one described by Marvel *et al* [69], polymerizing in a medium of 0.5 N HCl using persulphate initiation and a temperature of 50°C. This method was also used by Tate [70] at a reaction temperature of 60°C.

2.8.2.4 Poly(ethylene sulfonic acid) or Poly(vinyl sulphonic acid)

As with most of the polymers, various methods for their preparation occur in literature. Among these is a method of distilling the dry monomer under nitrogen at low pressure [71]. Breslow and Hulse [72] describe a method whereby ethylene sulphonic acid is polymerized in aqueous medium with potassium persulphate as initiator at a temperature of 55°C.

The method followed was one described by Breslow and Kutner [73], polymerizing in aqueous medium at temperatures ranging from 0°C to 10°C, using a persulphate-bisulphite redox intiator system.

2.8.2.5 Poly(2-chloro-2-propenoic acid) or Poly(2-chloro acrylic acid)

This polymer can be synthesized in aqueous medium with potassium persulphate as initiator, in the presence of sodium bisulphite [64, 74]. Reference is also made by Bryce [70] to the polymerization in 28% ammonium hydroxide with potassium persulphate as initiator.

The polymerization reaction was that described by Minsk and Kenyon [75]. This is done in dioxane at 199°C for 3 hours, using benzoyl peroxide as initiator.

2.8.3 COPOLYMERIZATION

In most cases copolymer ratios that were desired in this study did not match those mentioned in the literature. Nevertheless it was possible to compare the polymerization techniques.

2.8.3.1 Poly(2-propenoic acid-co-2-methyl-2-propenoic acid) or Poly(acrylic acid-co-methacrylic acid)

No direct reference was found to procedures for preparing this polymer.

2.8.3.2 Poly(2-pronenoic acid-co-methylene butanedioic acid) or Poly(acrylic acid-co-itaconic acid)

Marvel and Shepherd [69] describe the copolymerization as being done in aqueous medium at 26°C using potassium persulphate as initiator. This method was followed in essence, although the polymerization was carried out at 40°C instead.

2.8.3.3 Poly(2-propenoic acid-co-ethenyl acetate) or Poly (acrylic acid-co-vinyl acetate)

Reference was found to this copolymerization describing a reaction in aqueous medium [72], using benzoyl peroxide as initiator. The method followed was one of reaction in 1,4 dioxane using benzoyl peroxide as initiator.

2.8.3.4 Poly(2-propenoic acid-co-2-chloro-2-propenoic acid or Poly(acrylic acid-co-2-chloro acrylic acid)

A single reference in the parent literature, describes a method whereby monomers are mixed in a 1:1 ratio in mineral oil, treated with benzoyl peroxide at 80°C, to give a 50/50 copolymer [92].

In this study the method was modified (See Chapter 4).

2.8.3.5 Poly(2-methyl-2-propenoic acid-co-2-chloro-2-propenoic acid) or Poly(methacrylic acid-co-2-chloro acrylic acid)

Following the success obtained with the acrylic acid-2-chloro acrylic acid copolymerization, this copolymerization was attempted using the same modified method described in section

2.8.3.4.

2.8.4. TERPOLYMERS

2.8.4.1 Poly(2-propenoic acid-co-2-methyl-2-propenoic-acid-co 2-chloro-2-propenoic acid) or Poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid)

No literature reference was found.

2.9 MONOMER SYNTHESIS

2.9.1 2-Chloro-2-Propenoic Acid or 2-Chloro-Acrylic Acid

A number of publications have been found which describe methods for the synthesis of 2-chloro acrylic acid, or 2-chloro-2-propenoic acid. These methods include the addition of chlorine to acrylic acid, followed by dehydrochlorination at 300°C over Al_2O_3 [76], alkaline hydrolysis of methyl-2,3 dichloro propionate [77] or as described by Yasnitskii [78], treatment of $ClCH_2CH(OH)CN$ with aqueous H_2SO_4 in the presence of copper foil to give 2-chloro-2-propenoic acid. Owen and Babatunde Sumade [79] report that refluxing chloroacrylonitrile in 60% aqueous H_2SO_4 containing hydroquinone gives the required product in 60% yield.

The method followed was one reported by Marvel, Dec, Cooke and Cowan in 1940 [80]. This includes, in the final stages, the treatment of methyl-2,3-dichloropropionate with barium hydroxide to give the required product.

2.10 POLYMER CHARACTERIZATION

A brief background into the theory of the Universal Calibration Method is given below. As the method comprises the use of viscometry and gel-permeation chromatography (GPC) or size exclusion chromatography (SEC), brief theoretical discussions of these methods are given below.

2.10.1 DILUTE SOLUTION VISCOMETRY

This method is well reviewed by Billmeyer [81] and the theory will not be discussed here. The theory is reviewed briefly in Appendix B. It will be sufficient to say here that the method consists of comparing the rates of flow, through a capillary tube, of solutions containing various concentrations of polymers with the rate of flow through the tube of the solvent alone. The ratios of these rates will indicate the polymer size and therefore molecular mass, in solution.

2.10.2 AQUEOUS SIZE EXCLUSION CHROMATOGRAPHY

A brief theoretical discussion and background on aqueous size exclusion chormatography are given below.

Size exclusion chromatography (SEC) is an important technique for determining the molecular mass and molecular mass distribution of polymers in dilute solution [82].

For polymers soluble in organic solvents, SEC is a common analytical technique. However, SEC methods for water soluble polymers have not yet reached the same level of developments as the SEC technique has for polymers soluble in organic solvents.

The reasons for this, inter alia, are:

- A lack of readily available monodisperse, water-soluble polymer standards [82].

- Difficulties in obtaining chromatographic supports for aqueous systems that possess the necessary separation characteristics, and the presence of additional separation mechanisms, such as ion inclusion and ion exclusion [82].

Separation in aqueous SEC is principally differential migration of molecules between flowing solvents and the solvent within the porous matrix of an SEC column packing. Separation occurs because the total accessible volume of the column varies with the size of the polymer molecules in solution. Smaller macromolecules will usually "see" more pore volume and spend relatively longer times inside the porous matrix than larger macromolecules will. The larger macromolecules have a smaller pore volume available to them and elute from the column earlier than the smaller macromolecules.

As the size of macromolecules, particularly of water-soluble materials, is the governing factor regarding the separation of macromolecules by a SEC column, it is important to realize that in order to be able to interpret SEC data effectively, the relationship between the size of the macromolecule in solution and the molecular mass must be known. Flory [83] proposes:

$$[\eta] = \phi o (r_1^2)^{3/2}/M = \phi o \; ^3(r_0^2)^{3/2}/M$$

M = Molecular Mass

$[\eta]$ = intrinsic viscosity

$r_1 2$ = mean-square end-to-end distance

$(r_0 2)$ = unperturbed mean square end-to-end distance

α = expansion factor

ϕ_o = constant ($- 3{,}6 \times 10^{21}$)

The size of an uncharged, isolated macromolecule in solution as specified by the mean-square end-to-end distance depends on the molecular mass, the interaction between the polymer and the solvent and intramolecular polymer-polymer interactions [81]. Although the conformational statistics for polymers in non-polar solvents are well understood [84], this is not so for polyions in polar solvents [85]. For polyelectrolytes, the molecular conformation depends on the amount and type of charged species, ionic strength of the solvents, and molecular mass [82]. For polyelectrolytes in solution, electrostatic repulsion between the charged species, ionic strength of the solvent, and molecular mass [81]. For polyelectrolytes in solution, electrostatic repulsion between the charged species on the polymer backbone will cause an expansion of the macromolecule and increase the local chain stiffness [85]. This chain expansion can be regarded as being equivalent to an increase in excluded volume.

In addition to molecular size, separation by size exclusion is also strongly dependent on the molecular shape. The more extended the conformation of a macromolecule, the more it will be excluded from the pores of SEC packing [82]. For a given molecular mass, a rod-shaped molecule will elute earlier than random coil polymer of the same molecular mass will.

In addition to the effect of molecular size on the separation mechanisms, other factors can influence the separation process [82]. These are important for polyelectrolytes, where interactions between the polymer, solvent and support can be significant.

Adsorption of the polymer on the chromatographic resin may affect the extent of separation. In systems where the polymer and the support have opposite charges, electrostatic interaction may cause the polymer to elute later. Whatever the cause of the adsorption phenomena, they can cause not only larger elution volumes, but also cause the elution profile to exhibit multiple peaks [86]. There may also be cases where the polymer may be irreversibly adsorbed to the the support surface [86].

Where the polymers and chromatographic supports do not interact electrostatically, penetration of polymer into the pores of the support depend on molecular size only. However, if charged groups are present on the surface of the resin, electrostatic repulsion may cause polyelectrolytes not to diffuse into the pores of the support [87] (Polyelectrolytes of like charges), thus diminishing the effective pore volume and causing the polymer to elute earlier than a neutral polymer of the same size would. This is called ion exclusion.

During chromatography, when two or more ionic solutes are present, the size of the pore-opening can prohibit free passage of the polyion. Simple electrolytes however, are able to penetrate, and because of the presence of larger ions external to the pore, smaller ions will penetrate to minimize electrostatic repulsion. This is called ion inclusion.

As stated before, SEC can be used to determine molecular masses of polymers, if the relationship between polymer molecular mass and retention volume can be established. As was also said above, well-characterized standards of water soluble polymers are not available.

A secondary calibration scheme that has been developed and which is fairly widely used is the universal calibration procedure proposed by Grubuisic et al [88].

2.10.3 THE UNIVERSAL CALIBRATION METHOD

This method of calibration [88] is based on the predictions afforded by the following equations:

$$[\eta] = \phi_0 \ (r^2)^{3/2}/M$$

or

$$M[\eta] = \phi_0 \ (r^2)^{3/2}$$

Thus the product $M[\eta]$ is proportional to the hydrodynamic volume. It follows [88] that a plot of log $M[\eta]$ vs the SEC elution volume should yield a common curve for a given chromatographic support, irrespective of the chemical structure of the polymer. A calibration curve can therefore be constructed by using a set of polymer standards of known molecular mass. The intrinsic viscosity data for the set of standards is obtained and so are the retention volumes (in the same solvents used for viscometry). This then permits the construction of a calibration curve.

Although this technique has been investigated and its validity demonstrated for non-polar solvents [89, 90], little work has been done for polar solvents. However, Spatorico and Beyer showed [91] that the technique could be used for sodium polystyrene sulphonates and dextrans in Na_2SO_4 solutions at molarities varying from 0,2 to 0,8.

2.11 pH TITRATIONS

The background is briefly discussed in Appendix B.

CHAPTER 3

EXPERIMENTAL OBJECTIVES AND EQUIPMENT

3.1 GENERAL

Two factors largely influence membrane desirability. These are membrane performance (taking both flux and salt rejection into consideration) and membrane stability.

As discussed in Chapter 2, the present state-of-the art dynamic membrane is the hydrous zirconium (IV) oxide-poly (acrylic acid) dual layer or composite membrane.

It was the object of this study to synthesize organic polyelectrolytes, to characterize them and to evaluate them as polyelectrolyte component in hydrous Zirconium (IV)-oxide-polyelectrolyte composite membranes. This evaluation has been done in terms of membrane performance, membrane stability, formation characteristics and effect of pH on membrane performance. These evaluations will have poly(acrylic acid) as comparative standard, but as the formation conditions may or may not be optimum for all the polymers concerned, and as molecular mass plays a role in membrane performance, these evaluations of membrane performance will be only comparative in nature, and not conclusive of desirability as dynamic membrane components.

3.2 SYNTHESIS OBJECTIVES

3.2.1 HOMOPOLYMERS

The following homopolymers synthesized:

3.2.1.1 Poly(2-propenoic acid)
3.2.1.2 Poly(2-methyl-2-propenoic acid)
3.2.1.3 Poly(methylene butanedioic acid)

3.2.1.4 Poly(ethylene sulphonic acid)

3.2.1.5 Poly(2-chloro-2-propenoic acid)

3.2.2 COPOLYMERS

3.2.2.1 Poly(2-propenoic acid-co-2-methyl-2-propenoic acid)

3.2.2.2 Poly(2-propenoic acid-co-2-chloro-2-propenoic acid)

3.2.2.3 Poly(2-propenoic acid-co-methylene butanedioic acid)

3.2.2.4 Poly(2-propenoic acid-co-ethenyl acetate)

3.2.2.5 Poly(2-methyl-2-propenoic acid-co-2-chloro-2-propenoic acid)

3.2.2.6 Poly(2-propenoic acid-co-ethylene acetate)

3.2.3 TERPOLYMERS

3.2.3.1 Poly(2-propenoic acid-co-2-methyl-2-propenoic acid-co-2-chloro-2-propenoic acid)

3.2.4 MONOMERS

3.2.4.1 2-Chloro-2-propenoic acid

The methods followed to synthesize these are formulated in Chapter 4.

3.3. CHARACTERIZATION OBJECTIVES

The polymers have been characterized in terms of intrinsic viscosity and molecular mass. They have also been characterized, as far as the co- and terpolymers are concerned, in terms of composition. The methods are discussed in Chapter 4.

3.4 EVALUATION OBJECTIVES

The polymers have been evaluated as dynamic membrane components. This evaluation took place in terms of

- membrane performance, and the effect of the pH thereon
- membrane stability
- membrane formation

These membranes, once they were formed, were evaluated in terms of the charge density on the membrane. An attempt was made to correlate the charge density with the membrane performance.

3.5 EQUIPMENT

3.5.1 SYNTHESIS EQUIPMENT

3.5.1.1 Vacuum line and reaction vessels

A vacuum line (Fig. 3.1) was constructed as a copy of a line used previously by postgraduate students at this institute. This system utilises 2-way taps to facilitate the alternate use of high vacuum to degas reaction mixtures, and inert gas (argon) to flush out the system.

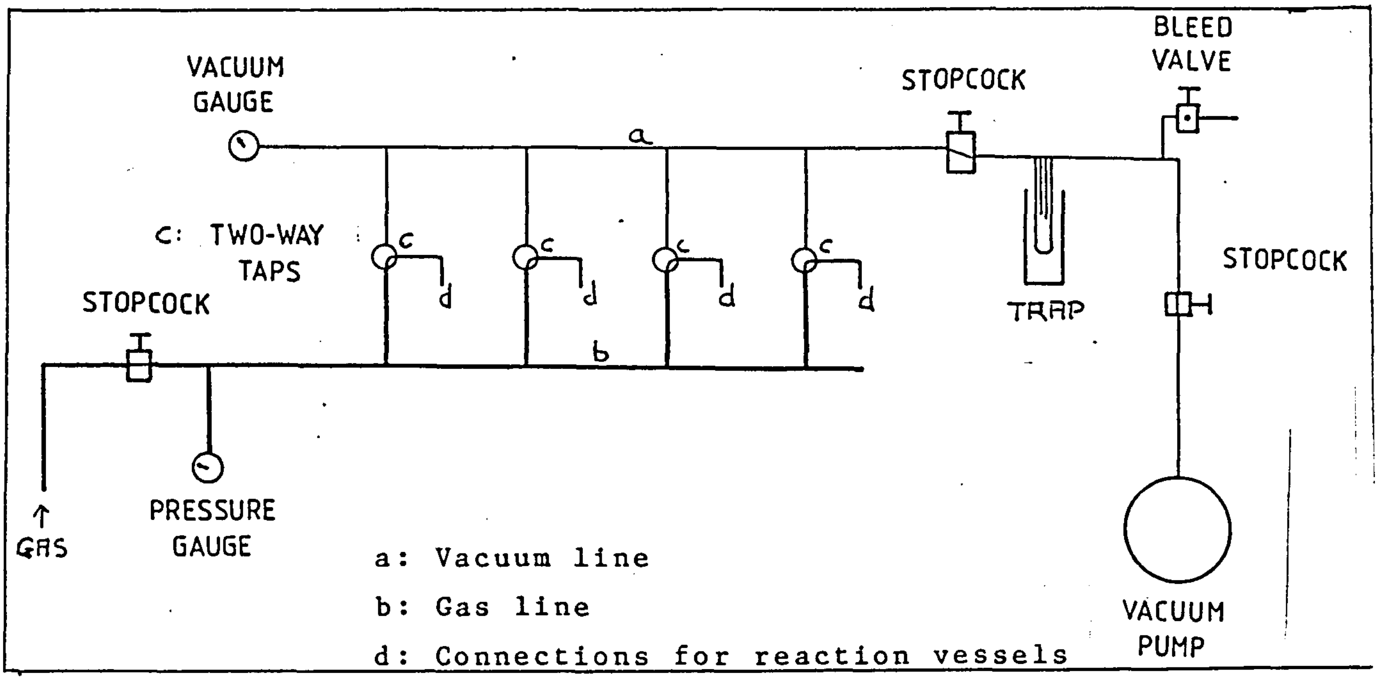
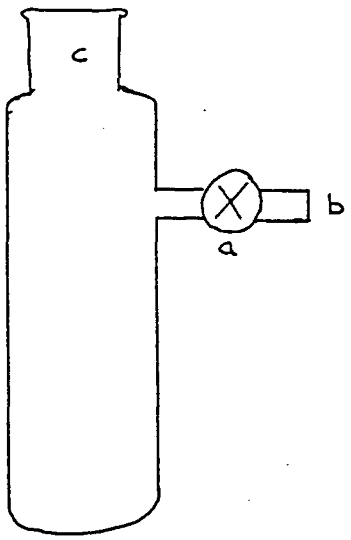


Fig. 3.1: Schematic representation of the vacuum line.



a : Stopcock
b : Connecting point to the vacuum line
c : Ground glass joint

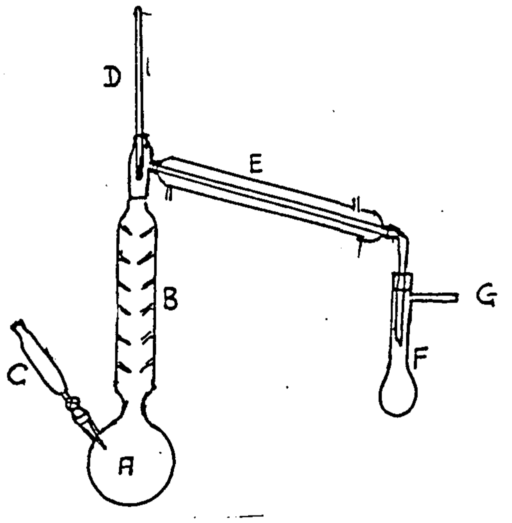
Fig. 3.2: Glass reaction vessel

3.5.1.2 Vacuum Pump

A SPEEDIVAC model was used to provide the vacuum for degassing the reaction mixtures.

3.5.1.3 Distillation Equipment

The distillation equipment (fig. 3.3) was connected to the vacuum line in order to facilitate the purification of liquid monomers at relatively low temperatures. The equipment consisted of a 2-necked 50 ml round bottomed flask, a 6-inch vigraux-column, adaptor, thermometer, jacketed distillation head and a monomer trap.



A : Round-bottomed flask
B : Vigreaux column
C : Dropping funnel
D : Thermometer
E : Condenser
F : Monomer trap
G : Connecting point to vacuum line

Fig. 3.3: Distillation equipment

3.5.2 EVALUATION AND CHARACTERIZATION EQUIPMENT

3.5.2.1 Gel-permeation Chromatograph

Gel-permeation chromatography (GPC) was done using a Waters 150°C instrument connected to a Waters Data Module.

The column used for the GPC work, which was aqueous in nature, was one Millipore E-500 column.

3.5.2.2 Viscometer

Dilute-solution viscometry was done using a Ubbelohde viscometer. All viscometry was done in a water-bath at 313°K. Temperature control was achieved by using a circulator.

3.5.2.3 pH Titrations

These were done using a Metrohm automatic titrator.

3.5.2.4 Electrolytical Cell

This cell, used to determine the charge density of fixed charge membranes, was built with the assistance of Mr. N Dowler, also of this institute, following work done by Kobatake et al [56, 57, 59]. The cell was built along similar lines as the one used by

Kobatake [56, 59]. (Fig. 3.4). The cell has openings to facilitate the immersion of salt bridges and stirring shafts and tubes for easy draining. The cell was seated in a water bath at 298°K, temperature control being effected by means of a circulator.

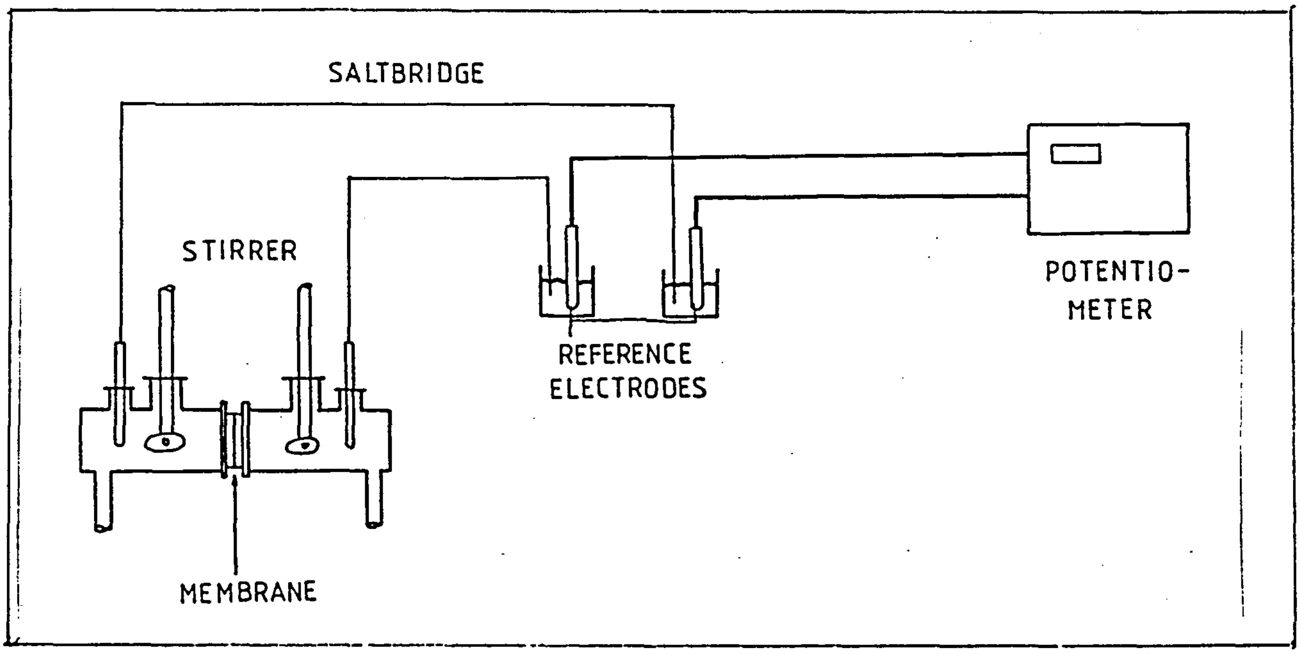


Fig. 3.4: Schematic representation of electrolytical cell.

3.3.2.5 Membrane Coating- and-Evaluation Equipment

A schematic representation of this equipment is given in Figure 3.5. Water, containing a low concentration of a salt, is pumped at a set rate past three flat-sheet membranes, (the formation of these membranes is discussed in Section 4.4.2) at high pressure (6 MPa). Permeate passes through the fixed-charge membranes, through a cell where the conductivity is measured and back to the feed tank where it is mixed with the water that bypassed the membranes. In this way the feed concentration remains constant.

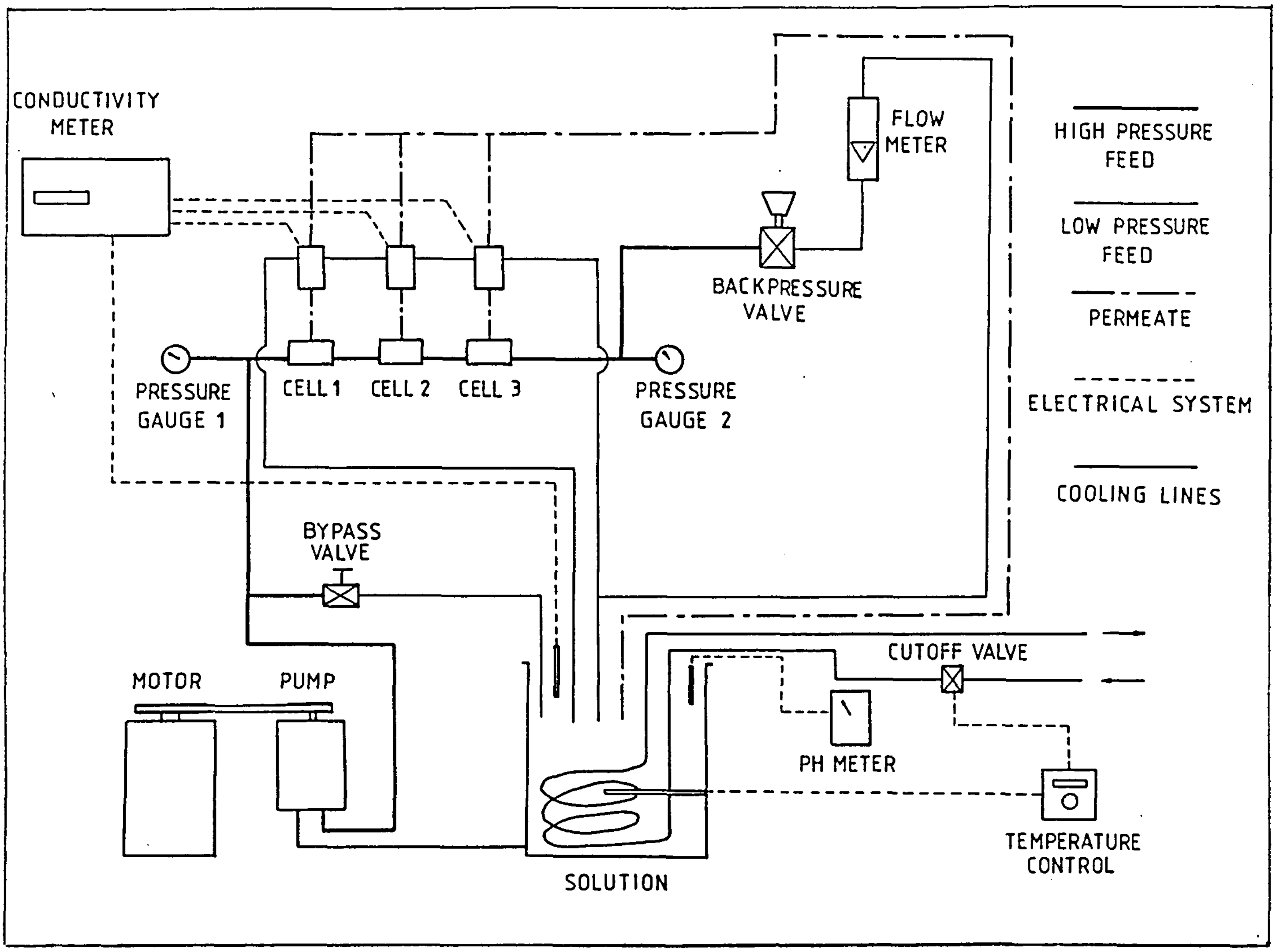


Fig. 3.5: Schematic representation of the membrane coating and evaluation equipment.

CHAPTER 4

EXPERIMENTAL METHODS

4.1 MONOMERS

The monomers used were :

(i) 2-Propenoic acid, AR grade from FLUKA, distilled immediately before use.

(ii) 2-Methyl-2-propenoic acid, AR grade from FLUKA, distilled immediately before use

(iii) Methylene butanedioic acid, AR grade from FLUKA, used as received.

(iv) Ethylene sulfonic acid, AR grade from FLUKA, used as received

(v) Etheyl acetate, AR grade from FLUKA, distilled immediately before use

(vi) 2-Chloro-2-propenoic acid, prepared and purified according to the method described in Section 4.1.1

4.1.1 2-CHLORO-2-PROPENOIC ACID : PREPARATION

This was the only monomer not available, and had to be synthesised. The method of Marvel et al [45], including the alkaline hydrolysis of methyl-2,3-dichloro propionate was used for the synthesis.

Methyl-2,3-dichloropropionate (20,0 g, 1,24 x 10^{-1} moles) was added dropwise to a mixture of distilled, deionized water (150,0 ml) and barium hydroxide octahydrate (70,0 g, 2,22 x 10^{-1} moles).

The reaction mixture was stirred at room temperature for 2 hours, then acidified with conc H_2SO_4 (10,0 g, 1,02 x 10^{-1} moles) in water (20,0 ml).

The resulting product was extracted five times with diethyl ether, (50 ml per extraction), and the extract dried overnight over anhydrous magnesium sulphate. The solution was then decanted and evaporated to dryness at room temperature under reduced pressure. The 2-chloro-2-propenoic acid was purified by several recrystallisations from petroleum ether (30° - 60°C b.p.) and then dried at room temperature under reduced pressure.

The yield was 5,17 g, or 38,50%.

The formation of the 2-chloro-2-propenoic acid was confirmed by a melting point analysis and carbon 13 and proton - NMR Spectra. These are shown in Appendix D.

4.2 POLYMERIZATIONS

4.2.1 PRE-REACTION SEQUENCE

All reactions were carried out in reaction vessels of the type described in Section 3.5.1.1 (See Fig. 3.2).

The vessel was covered with stainless steel gauze to safeguard against pressure build-up. After the ingredients had been added the stopcock on the vessel was closed and the vessel immersed in a freezing mixture of ice and water. The degassing and flushing procedures were carried out for all reaction mixtures in order to remove all traces of oxygen from the system. The vessel was attached to the vacuum line via the side arm. The vessels were stoppered with ground glass stoppers.

The stopcock on the reaction vessel was then opened. The two-way tap on the operating vacuum line was then switched to the vacuum side, subjecting the reaction mixture to vacuum. This caused the dissolved gases, including oxygen to be evacuated and the two-way tap was left in this position until bubbling of the reaction mixture stopped. The two-way tap on the vacuum line was then switched to the position which allowed the argon gas, supplied to the gas side of the vacuum line, (see Fig. 3.1), to fill the reaction vessels. The two-way tap was then switched to the vacuum side again in order to remove all the argon and other gas remaining in the reaction mixture. This was done five times.

4.2.2 HOMOPOLYMERIZATIONS

4.2.2.1 <u>2-Propenoic Acid (Acrylic acid)</u>

(i) Monomer structure

$CH_2 = CH - COOH$

(ii) Method

Two mixtures containing:

(1) Freshly distilled 2-propenoic acid(16,4 g, 2,78 x 10^{-1} moles), toluene (35,0 ml) ethyl benzene (65,0 ml) and AIBN (2,70 x 10^{-1} g, 1,60 x 10^{-3} moles)

(2) Freshly distilled 2-propenoic acid (16,4 g, 2,78 x 10^{-1} moles), toluene (35,0 ml), ethyl benzene (65,0 ml) and AIBN (8,20 x 10^{-1} g, 4,90 x 10^{-3} moles)

The reaction mixtures was degassed as described in Section 4.2.1.

The stirred reaction mixtures were heated to, and maintained at 343°K for 1,5 hours. Therafter the reactions were terminated by cooling the mixtures. During the reactions the polymers formed precipitated out.

The polymers were washed five times with benzene and then dried at 313°K to constant mass under reduced pressure.

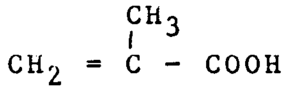
(iii) Yields:

(1) 14,85 g or 88,48 % of powdery white polymer : PAA-1
(2) 15,22 g or 90.68 % of powdery white polymer : PAA-2

The Universal Calibration method, using 0,5 M Na_2SO_4 as solvent was used to determine the molecular masses. Results are given in Chapter 5.

4.2.2.2 2-Methyl-2-Propenoic Acid (Methacrylic Acid)

(i) Monomer structure



$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - COOH$$

(ii) Method (A)

Three mixtures containing:

(1) Freshly distilled 2-methyl-2-propenoic acid (10,0 g, 2,30 x 10^{-1} moles), 1,4 dioxane (25,0 ml) and benzoyl peroxide (9,00 x 10^{-2} g, 3,70 x 10^{-4} moles);

(2) Freshly distilled 2-methyl-2-propenoic acid (10,0 g, 2,30 x 10^{-1} moles), 1,4 dioxane (25,0 ml) and benzoyl peroxide (1,80 x 10^{-1} g, 7,40 x 10^{-4} moles); and

(3) Freshly distilled 2-methyl-2-propenoic acid (10,0 g, 2,30 x 10^{-1} moles), 1,4 dioxane (25,0 ml) and benzoyl peroxide (2,70 x 10^{-1} g, 11,1 x 10^{-4} moles)

were prepared.

These reaction mistures were degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to, and maintained at, 333°K for 0,75 h. After reaction white viscous solutions formed. The three reaction mixtures were dissolved in excess methanol and the polymers then precipitated with diethyl ether. They were purified by being redissolved in methanol and reprecipitated with diethyl ether. This was done three times.

The polymers were then dried to constant mass under reduced pressure at ambient temperature.

(iii) Yields:

(1): 9,42 g, or 94,2% of glassy polymer : PMAA-1
(2): 9,97 g, or 99,7% of glassy polymer : PMAA-2
(3): 9,98 g, or 99,8% of glassy polymer : PMAA-3

The universal calibration method, using 0,5 M Na_2SO_4 as solvent was used to calculate molecular masses. As these molecular masses proved to be too high (see Chapter 5) the polymerization, was repeated using a higher concentration of initiator and stopping the reaction before conversion was complete. This proved satisfactory.

(iv) Method (B)

To freshly distilled 2-methyl-2-propenoic acid (10,0 g, 1,2 x 10^{-1} moles) in 1,4-dioxane (25,0 ml), benzoyl peroxide (9,00 x 10^{-1} g, 3,70 x 10^{-3} moles) was added as initiator.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to and maintained at 333° K for 0,5 h. The reaction was stopped short of full conversion by rapid cooling and the addition of hydroquinone as radical scavenger.

The polymer was isolated, purified and dried in the same way as described in method A.

(v) Yield:

3,80 g or 38,0 % of glassy polymer : PMAA-4

The universal calibration method, with 0,5 M Na_2SO_4 as solvent was used to determine the molecular mass. Results are given in Chapter 5.

4.2.2.3 Ethylene Sulfonic Acid (Sodium Salt) (Vinyl Sulfonic Acid (Sodium Salt)

(i) Monomer structure

$$CH_2 = CH - SO_3H$$

(ii) Method (A)

Three mixtures containing:

(1) a 40% solution of sodium ethylene sulphonate (12,0 g, 9,20 x 10^{-2} moles), $K_2S_2O_8$ (8,70 x 10^{-2} g, 3,21 x 10^{-4} moles) and $NaHSO_3$ (3,5 x 10^{-2} g, 3,36 x 10^{-4} moles);

(2) a 40% solution of sodium ethylene sulphonate (12,0 g, 9,2 x 10^{-2} moles), $K_2S_2O_8$ (1,30 x 10^{-1} g, 4,81 x 10^{-4} moles) and $NaHSO_3$ (5,30 x 10^{-2} g, 5,09 x 10^{-4} moles); and

(3) a 40% solution of sodium ethylene sulphonate (12,0 g, 9,2 x 10^{-2} moles), $K_2S_2O_8$ (1,74 x 10^{-1} g, 6,44 x 10^{-4} moles) and $NaHSO_3$ (7,00 x 10^{-2} g, 6,73 x 10^{-4} moles)

were prepared.

These reaction mixtures were simultaneously degassed as described in Section 4.2.1.

The reaction mixtures were maintained at 277° K for 270 hours and shaken occasionally.

The formed polymers were precipitated with methanol and purified by redissolving them in water and then reprecipitating them with methanol. This was done three times. The polymers were finally dried to constant mass under reduced pressure at ambient temperature.

(iii) Yield:

(1): 7,66 g or 63,8% of strawcoloured polymer : PVSA-1
(2): 9,60 g or 80,0% of strawcoloured polymer : PVSA-2
(3): 11,20 g or 96,6% of strawcoloured polymer : PVSA-3

The Universal Calibration method using 0,5 M Na_2SO_4 as solvent was used to determine molecular mass.Results are reported in Chapter 5.

(iv) Method (B)

To a 40% solution of ethylene sulphonic acid (sodium salt), (12,1 g, 9,20 x 10^{-2} moles), $K_2S_2O_8$ (4,00 x 10^{-2} g, 1,48 x 10^{-4} moles) and $NaHSO_3$ (1,60 x 10^{-2} g, 1,53 x 10^{-4} moles) were added.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was maintained at 277° K for 200 hours, with occasional shaking.

The polymer was isolated, purified and dried as described in method (A).

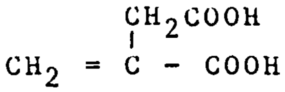
(v) Yield

10,10 g or 83,5% of straw-coloured polymer : PVSA-4

The Universal Calibration method using 0,5 M Na_2SO_4 as solvent, was used to determine molecular mass. Results are reported in Chapter 5.

4.2.2.4 Methylene Butanedioic Acid (Itaconic Acid)

(i) Monomer structure



$$CH_2 = \overset{\overset{CH_2COOH}{|}}{C} - COOH$$

(ii) Method

Three mixtures containing:

(1) Methylene butanedioic acid (10,0 g, 7,70 x 10^{-2} moles), distilled, deionized water (40,0 ml) concentrated HCl (1,5 ml) and $K_2S_2O_8$ (5,00 x 10^{-2} g, 2,10 x 10^{-3} moles);

(2) Methylene butanedioic acid (10,0 g, 7,70 x 10^{-2} moles), distilled, deionized water (40,0 ml), concentrated HCl (1,5 ml) and $K_2S_2O_8$ (1,00 x 10^{-1} g, 4,20 x 10^{-3} moles); and

(3) Methylene butanedioic acid (10,0 g, 7,70 x 10^{-2} moles), distilled, deionized water (40,0 ml), concentrated HCl (1,5 ml) and $K_2S_2O_8$ (1,50 x 10^{-1} g, 6,30 x 10^{-3} moles)

were prepared.

These reaction mixtures were degassed simultaneously as described in Section 4.2.1.

The stirred reaction mixtures were then heated to, and maintained at, 323° K for 67 hours. The reaction mixtures were poured into an excess of cold acetone. This caused the polymers to precipitate. The polymers were purified by dissolving them in water and reprecipitating in acetone. This was repeated three times. The polymers were dried to constant mass under reduced pressure at 323° K.

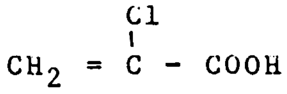
(iii) Yield:

(1): 3,56 g or 35,6% of polymer: PIA 1
(2): 5,12 g or 51,2% of polymer: PIA 2
(3): 4,95 g or 49,5% of polymer: PIA 3

The Universal Calibration method, using 0,5 M Na_2SO_4 as solvent was used to determine molecular mass. These results are given in Chapter 5.

4.2.2.5 2-Chloro-2-Propenoic Acid (2-Chloro Acrylic Acid)

(i) Monomer structure



$CH_2 = \overset{\overset{Cl}{|}}{C} - COOH$

(ii) Method A

To a mixture of 2-chloro-2-propenoic acid (3,10 g, 2,90 x 10^{-2} moles) and 1,4 dioxane (7,0 ml), benzoyl peroxide (7,50 x 10^{-3} g, 3,10 x 10^{-5} moles) was added as initiator.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to, and maintained at, 353° K for 2,5 hours. The resulting viscous mixture was diluted with 1,4 dioxane and precipitated with diethylether. The polymer was purified by dissolving it in 1,4 dioxane and precipitating it with diethylether. This was done three times. The polymer was dried to constant mass at ambient temperature under reduced pressure.

(iii) Yield:

3,01 g or 97,1% of polymer : PCIAA-1

(iv) Method B

To a mixture of 2-chloro-2-propenoic acid (2,65 g, 2,50 x 10^{-2} moles) in 1,4 dioxane (10,0 ml), benzoyl peroxide (1,00 x 10^{-2} g; 4, 10 x 10^{-5} moles) was added as initiator.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to and maintained at 363° K for 2,5 hours. The product was isolated, purified and dried as described in method (A).

(v) Yield:

2,60 g or 98,1% of polymer : PCIAA-2

(vi) Method (C)

To a mixture of 2-chloro-2-propenoic acid (2,20 g, 2,03 x 10^{-2} moles) in 1,4 dioxane (6,0 ml), benzoyl peroxide (5,00 x 10^{-3} g, 2,10 x 10^{-5} moles) was added.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to and maintained at 363°K for 2 hours. The product was isolated, purified and dried as described in method (A):

(vii) Yield:

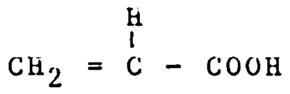
2,10 g or 95,5% of polymer : PCIAA-3

The molecular masses of these polymers were determined by means of the Universal Calibration method, using 0,5 M Na_2SO_4 as solvent. The results are reported in Chapter 5.

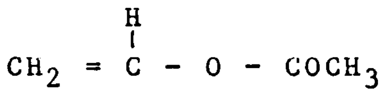
4.2.3 COPOLYMERIZATIONS

4.2.3.1 2-Propenoic Acid and Ethenyl Acetate (Acrylic Acid and vinyl Acetate)

(i) Monomer structures



$CH_2 = \overset{H}{\overset{|}{C}} - COOH$



$CH_2 = \overset{H}{\overset{|}{C}} - O - COCH_3$

(ii) Method

To a mixture of freshly distilled 2-propenoic acid (3,24 g, 4,50 x 10^{-2} moles) and freshly distilled ethenyl acetate (1,95 g, 2,27 x 10^{-2} moles) in 1,4 Dioxane (20,0 ml), benzoyl peroxide (5,5 x 10^{-3} g, 2,27 x 10^{-5} moles) was added.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to, and maintained at, 353°K for 5,5 hours. The polymer was isolated by diluting the reaction mixture with 1,4 dioxane and precipitating the polymer with methanol. The polymer was purified by redissolving it in 1,4 dioxane and reprecipitating it with methanol. This was done three times. The polymer was dried to constant mass under reduced pressure at 323°K.

(iii) Yield

The stirred reaction mixtures were heated to, and maintained at, 313° K for 24 hours. The three polymers formed were isolated by slowly pouring the reaction mixtures into excess acetone, causing the polymers to precipitate. The polymers were purified by dissolving them in water and precipitating them in acetone. This was done three times. The polymers were dried to constant mass under reduced pressure at 313° K.

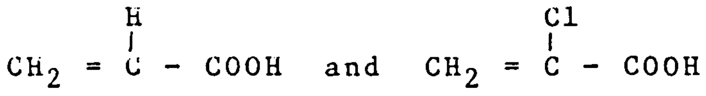
(iii) Yield:

(1): 5,40 g or 52,7% of polymer : PAA/IA-1
(2): 5,75 g or 56,1% of polymer : PAA/IA-2
(3): 8,97 g or 87,6% or polymer : PAA/IA-3

The Universal Calibration method, using 0.5 M Na_2SO_4 as solvent was used to determine molecular mass. Results are reported in Chapter 5.

4.2.3.3 2-Propenoic Acid and 2-Chloro-2-Propenoic Acid (Acrylic Acid and 2-Chloro Acrylic acid)

(i) Monomer structures



$CH_2 = \overset{H}{\overset{|}{C}} - COOH$ and $CH_2 = \overset{Cl}{\overset{|}{C}} - COOH$

(ii) Method (A)

To a mixture of freshly distilled 2-propenoic acid (2,15 g, 3,00 x 10^{-2} moles) and 2-chloro-2-propenoic acid (2,10 g, 2,00 x 10^{-2} moles) in 1,4 dioxane (15,0 ml), benzoyl peroxide (2,00 x 10^{-2}, 8,26 x 10^{-4} moles) was added.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to and maintained at 353° K for 5,5 hours. The formed polymer was isolated by precipitation with ether and purified by dissolving in 1,4 dioxane and precipitating it with ether. This was done three times.

The polymer was dried to constant mass under reduced pressure at ambient temperature.

(iii) Yield:

4,20 g or 98,8% of polymer : PAA/ClAA-1

(iv) Method (B)

To a mixture of freshly distilled 2-propenoic acid (2,15 g, 3,00 x 10^{-2} moles) and 2-chloro-2-propenoic acid (2,00 g, 1,80 x 10^{-2} moles) in 1,4 dioxane (10,0 ml), benzoyl peroxide (5,40 x 10^{-3} g, 2,23 x 10^{-5} moles) was added.

The reaction mixture was degassed as described in Section 4.2.1.

The reaction was then carried out according to method (A).

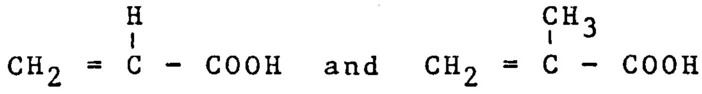
(v) Yield:

4,10 or 98,6% of polymer PAA/ClAA-2

The Universal Calibration method,using 0.5 M Na_2SO_4 as solvent was used to determine molecular masses for both polymers. Results are reported in Chapter 5.

4.2.3.4 2-Propenoic Acid and 2-Methyl-2-Propenoic Acid (Acrylic Acid and Methacrylic Acid)

(i) Monomer structures


$CH_2 = \overset{H}{C} - COOH$ and $CH_2 = \overset{CH_3}{C} - COOH$

(ii) Method

To a mixture of freshly distilled 2-propenoic acid (2,50 g, 3,47 x 10^{-2} moles) and freshly distilled 2-methyl-2-propenoic acid (2,98 g, 3,47 x 10^{-2} moles) in 1,4 dioxane (150 ml), benzoyl peroxide (1,00 x 10^{-2} g, 4,13 x 10^{-5} moles) was added.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to, and maintained at, 333° K for 1 hour. The formed copolymer was isolated by dissolving the reaction mixture in methanol and precipitating the polymer with ether. It was then purified by dissolving it in methanol and precipitating it with diethyl ether. This was done three times. The polymer was dried to constant mass under reduced pressure at a temperature of 313° K.

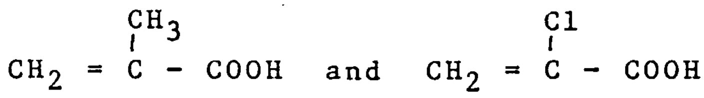
(iii) Yield:

5,21 g or 95,1% of copolymer : PAA/MAA-1

The Universal Calibration method using 0.5 M Na_2SO_4 as solvent was used to determine molecular mass. The results are reported in Chapter 5.

4.2.3.5 2-Methyl-2-Propenoic Acid and 2-Chloro-2-Propenoic Acid (Methacrylic acid and 2-chloro Acrylic acid)

(i) Monomer structures


$CH_2 = \overset{CH_3}{C} - COOH$ and $CH_2 = \overset{Cl}{C} - COOH$

(ii) Method

To a mixture of freshly distilled 2-methyl-2-propenoic acid (2,06 g, 2,4 x 10^{-2} moles) and 2-chloro-2-propenoic acid (1,96 g, 1,80 x 10^{-2} moles) in 1,4 dioxane (10,0 ml), benzoyl peroxide (3,84 x 10^{-2} g, 1,58 x 10^{-4} moles) was added.

The reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to, and maintained at, 353°K for 5 hours. The formed copolymer was isolated by precipitating it with diethylether after diluting the reaction mixture with dry 1,4 dioxane. It was then purified by dissolving it with 1,4 dioxane and precipitating with diethyl ether. The polymer was dried to constant mass under reduced pressure at ambient temperature.

(iii) Yield :

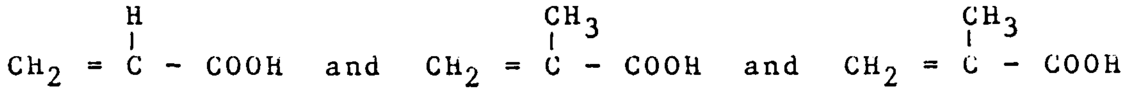
4.01 g or 99,0% of brittle white copolymer : PMAA/ClAA-1

The Universal Calibration method, using 0,5 M Na_2SO_4 as solvent was used to determine molecular mass. The results are reported in Chapter 5.

4.2.4 TERPOLYMERS

4.2.4.1 2-Propenoic Acid and 2-Methyl-2-Propenoic Acid and 2-Chloro-2-Propenoic Acid (Acrylic Acid and Methacrylic Acid and 2-Chloro-acrylic acid)

(i) Monomer structures



$$CH_2 = \overset{\overset{\displaystyle H}{|}}{C} - COOH \quad \text{and} \quad CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - COOH \quad \text{and} \quad CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - COOH$$

(ii) Method

To a mixture of freshly distilled 2-propenoic acid (1,57 g, 2,10 x 10^{-3} moles), freshly distilled 2-methyl-2-propenoic acid (1,54 g, 1,80 x 10^{-2} moles) and 2-chloro-2-propenoic acid (1,50 g, 1,40 x 10^{-2} moles), in 1,4 dioxane (15,0 ml) benzoyl peroxide (3,55 x 10^{-2} g, 1,47 x 10^{-4} moles was added.

This reaction mixture was degassed as described in Section 4.2.1.

The stirred reaction mixture was heated to, and maintain at, 353°K for 5 hours. The formed terpolymer was isolated by diluting the reaction mixture with dry 1,4 dioxane and precipitating it with diethyl ether. It was purified by dissolving the terpolymer in 1,4 dioxane and precipitating it with of diethyl ether. This was done twice.

(iii) Yield :

4,56 g or 98,9% of terpolymer : TERP-1

The Universal Calibration Method, using 0,5 M Na_2SO_4 as solvent was used to determine molecular mass. The results are reported in Chapter 5.

4.3 POLYMER CHARACTERIZATION

4.3.1 DILUTE SOLUTION VISCOMETRY

As the Mark-Houwinck constants for all the copolymers synthesized in this work do not exist, molecular mass determination by dilute solution viscometry alone was not possible. It was therefore thought advisable to try to adapt the Universal Calibration Method (see Section 2.10) in order to determine molecular mass.

All viscometry was done in 0,5 M sodium sulphate as solvent. The 0,5 M sodium sulphate in deionized, distilled water was filtered twice through a Millipore HA (0,45 µ) filter, before the polymer was added.

All the polymer solutions were made up in 25 ml volumetric flasks. The concentration aimed at was 1,0% (M/V) i.e. about 0,25 g of polymer in 25 ml of Na_2SO_4. The mixtures were either agitated by means of a flask shaker, or placed in a sonic bath for 10 minutes to dissolve the polymer.

After solution was complete, 20 ml of the polymer solution was accurately pipetted into the viscometer.

The viscometer is suspended in a water bath, temperature-controlled at 308°K. The flow rates of solvent and four concentrations of the polymer solution were measured until agreement to 0,05 s was obtained in three consecutive readings.

4.3.2 GEL PERMEATION CHROMATOGRAPHY

A brief overview on the technique and theory of GPC is given in Section 2.9.2. In this Section only the method followed is given.

A Waters 150C gel permeation chromatograph was used, using one Millipore E-500 column. The mobile phase was 0,5 M Na_2SO_4.

The polymer solutions used were drawn from the volumetric flasks used to make up the solutions for viscometry. These were then diluted to 0.5% (M/V) into 4 ml vials used to hold samples in the instrument. The solutions were filtered into the vials through an aqueous membrane filter (Millipore HA), under pressure.

These vials, (up to 16 at a time) were placed on a carousel and placed in the instrument. The required run time, flow rate, injection volume and detector sensitivity were programmed into the instrument and all the necessary measurements were done by the instrument. The data were displayed as a graphic plot and print-out via a Waters data module.

The elution time for each polymer was noted and the procedure was repeated two more times to ensure that the elution time remained constant.

4.3.3 UNIVERSAL CALIBRATION METHOD

The theory of this method was given in Section 2.10. To set up a calibration curve, a series of dextrans were used as primary standards. These dextrans had molecular masses of 12 500; 17 500; 40 000; 70 300 and 151 000. Two poly(acrylic acid) samples were used as secondary standards, after their molecular mass had been obtained through viscometry. These secondary standards had molecular masses of 75 300 and 148 000 respectively. A solution of each standard was made up in 0,5 M Na_2SO_4.

The intrinsic viscosity of each of the standards were determined. Thereafter the retention times of these same solutions were determined by GPC.

The product of the molecular mass (M) and the intrinsic viscosity ($[\eta]$) was calculated and then log $M[\eta]$ was plotted against the retention time for each standard. The staight-line plot achieved in this way was used as the calibration curve. The curve is given in Chapter 5 (See Fig. 5.2).

All the synthesized polyelectrolytes were evaluated in terms of intrinsic viscosity and GPC retention times. Their molecular mass can thus be determined by means of the calibration curve. Results are given in Chapter 5.

4.4 MEMBRANE FORMATION AND EVALUATION

4.4.1 INTRODUCTION

Many authors [7, 37, 54] have shown that formation conditions affect the performance of dynamically formed membranes. For comparative purposes, therefore, formation conditions for all membranes studied were standardized. The figures of merit, (A^2/B) which depend on both flux and rejection was chosen as a reasonable basis for comparison.

As poly(acrylic acid) is the present state-of-the-art polyelectrolyte in dynamically formed composite membranes, the formation conditions chosen were those recommended for hydrous zirconium oxide-poly(acrylic acid) composite membranes. Membranes made with all other polymers have been compared with that made with poly(acrylic acid) after :

(i) completion of formation (pH 7,00)
(ii) 18 hours of use (pH 7,00)
(iii) pH 8,00 is reached
(iv) pH 9,00 is reached.

4.4.2 FORMATION OF DYNAMICALLY FORMED COMPOSITE MEMBRANES

The procedure used was based on that specified by Johnson, Minturn and Wadia [7], with small modifications detailed in Sections 4.4.2.1; 4.4.2.2 and 4.4.2.3.

4.4.2.1 Cleaning Procedures

The formation of a membrane was always preceded by a thorough cleaning of the membrane coating and evaluation equipment. The procedure recommended was:

(i) Wash with aqueous NaOH (pH 11,00) for 1-3 hours at 308° K
(ii) Rinse with reverse osmosis permeate (hereafter called RO permeate)
(iii) Wash with aqueous HNO_3 (pH 1,00); wash for 1-3 hours at 323° K.
(iv) Rinse with RO permeate until the pH of the permeate equals the pH of the feed

(v) Repeat until a check for Fe++ present by using Prussian Blue as indicator is negative and all oil contaminants are removed. This is especially important after long shut-down periods.

4.4.2.2 Formation of the Zirconium Layer

The recommended procedure was:

Use Millipore filters, HA, rated at 0,5 u as backing material in the cells. Add RO permeate in the feed tank (Fig. 3.5) and circulate at 3,67 $l.min^{-1}$ through the system. Adjust the backpressure to 2 MPa. Bring the pH to 4,00 with HNO_3. Add $NaNO_3$ to 2g/1. Then add the zirconium salt ($Zr(NO_3)_4$) to $1,0 \times 10^{-4}$ M. With the addition of the Zirconium nitrate, the pH drops, and is readjusted to between 3,75 and 3,90 using 10% sodium hydroxide solution. The back pressure is then increased by 1 MPa every 5 minutes until it reaches 6 MPa.

The flux and rejection are monitored. The zirconium membrane is complete when values of 500 - 700 $lm^{-2}hr^{-1}$ for flux and 30-55% for rejection is attained.

The pH is then lowered to 2,00 with HNO_3 and the feed tank is drained. Fresh RO permeate is added and the pH adjusted to 2,00. The system is rinsed and the tank drained again in order to remove all membrane preparation chemicals.

4.4.2.3 Formation of the polyelectrolyte-zirconium membrane

The recommended procedure was:

Refill the tank with RO permeate and adjust the pH to 2,00. Add 2g/l $NaNO_3$ and recirculate at 3,67 l/min and 6 MPa. Add 50 ppm polyelectrolyte. Now increase the pH by 0,5 pH units every 30 minutes with 10% sodium hydroxide solution, until the pH reaches

7,00. Flux and rejection measurements are monitored throughout the period of membrane formation and repeated 18 hours later, when the membrane has stabilized. At this point the pH must be adjusted to 8,00 and the membrane allowed to equilibrate for 45 minutes before the flux and rejection are measured again. The pH is then adjusted to 9,00 and equilibration and measurements repeated.

The membrane can then be removed from the cell and stored in distilled water in the refrigerator for use in charge density evaluations.

The data obtained are fed into the computer program (Appendix C) written to evaluate the A^2/B values at all four points of measurement.

4.5 CHARGE DENSITY DETERMINATION

4.5.1 METHOD

These charge density determinations were carried out in the electrolytic cell which had been designed and built. (See Section 3.5.2.4 and Fig. 3.4). Due to an insufficiency of information [56, 58, 59] on to the experimental technique used to determine the charge density of formed membranes, a empirical method had to be developed. This was done by testing a few membranes to determine how long it took the membrane to equilibrate, and the effects of stirring speed and other factors.

A large amount of experimentation was necessary to determine the equilibration time required and to attain optimum stirring rates. Suggestions by Kobatake [59] as regards cell design helped to solve problems such as the effect of the stirrers on membrane potential values, and enabled a standard technique to be established. Important requirements in the measurement of the charge density were:

- The membrane should always be placed in the cell in the same position, tested with until the membrane face always in the same direction.

- Four different sets of two solutions each of aqueous $NaNO_3$ were required; in each set and the concentrations differed by a factor of 10.

- The less concentrated of the two solutions required to be placed on the side of the membrane face.

- Both solutions required to be stirred by a pair of Teflon fans. Normally periods of 8-12 hours were required for the readings to stabilize.

- After 12 hours the solutions could be drained and replaced with fresh solutions of the same concentration. These solutions also required to be stirred for 12 hours. The potential difference accros the membrane could then be read by switching off the stirrers and allowing the reading on the potentiometer to settle.

- The solutions were then drained and a fresh set of solutions placed in the cell, and the procedure repeated.

The sets of solutions used were :

0,1 M/1,0 M
0,25 M/0,5 M
0,01 M/0,1 M
0,005 M/0,05 M

The values obtained from the potential difference measurements for the various membranes were entered into a computer program (see Appendix C) in order to calculate the thermodynamically effective charge density (see Section 2.6).

CHAPTER 5

RESULTS AND DISCUSSION

5.1 INTRODUCTION

The objectives of the study were to create polymers and to study their properties when complexed with Zirconium oxide in the form of dynamic membranes. Information on the synthesized copolymers with respect to reactivity ratio was not available, nor was information regarding the chemical proportions to be used and the variations in molecular mass of the polymers.

In the following sections an endeavour will be made to describe the properties of the dynamic membranes formed with these polymers as polyelectrolytes in terms of charge densities. The data obtained will be used to determine trends and to evolve ideas which can be used as a basis for future research.

5.2 POLYMER CHARACTERIZATION

Polymer preparation and purification are described in Section 4.2.

5.2.1 MOLECULAR MASS AND STRUCTURE

In order to determine molecular mass, it was necessary to determine the intrinsic viscosity of these polymers (See Section 4.3). The intrinsic viscosities of certain standards were used to set up a GPC calibration, using the Universal Calibration Method (See Section 4.3). Viscosity measurements give real values in terms of the intrinsic viscosity, [n], but cannot be related directly to molecular mass, as the Mark-Houwink values do not exist. The determination of these values for polymers will be a study in it's own right.

Dextran standards were used to set up a calibration curve (see Section 4.3). The calibration curve is given in Fig. 5.1.1. The molecular mass of the synthesized homo- and copolymers was determined using this calibration curve (See Table 5.2.1).

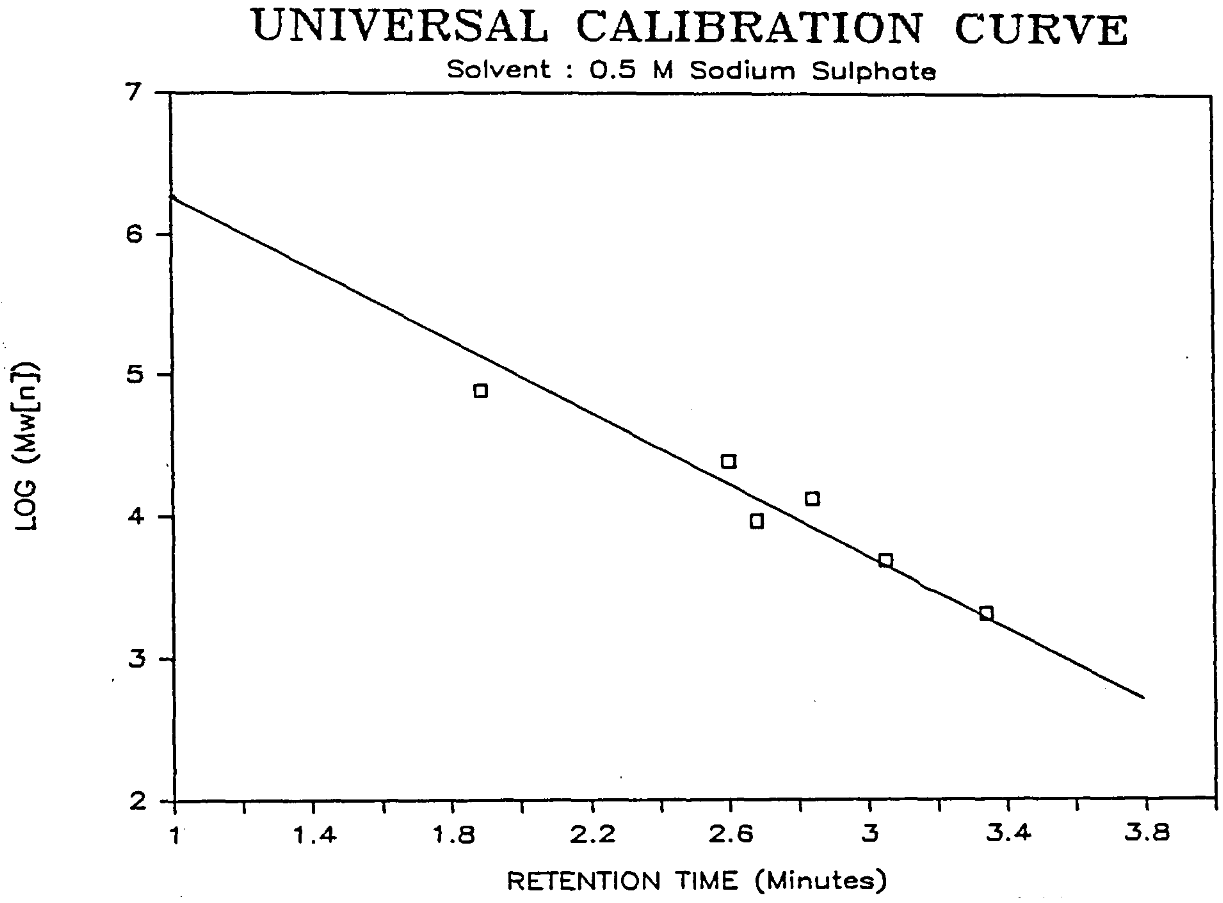


Fig. 5.1.1

Polymer	$[\eta]$	Retention Time (m)	log (Mw$[\eta]$)	Molecular Mass
PAA-1	0.152	2.74	3.88	50 000
PAA-2	0.124	2.67	3.97	75 000
PIA-1	0.265	2.34	4.21	61 200
PIA-2	0.275	2.38	4.19	56 300
PIA-3	0.285	2.50	4.09	43 200
PCIAA-1	0.375	1.95	4.57	99 000
PCIAA-2	0.100	2.95	3.70	19 000
PCIAA-3	0.174	1.95	4.57	214 000
PMAA-1	0.137	1.89	4.62	304 000
PMAA-2	0.135	1.93	4.58	281 600
PMAA-3	0.133	1.91	4.60	299 300
PMAA-4	0.240	2.01	4.52	138 000
PAA/MAA-1	1.360	1.90	4.61	30 000
PAA/1A-1	0.586	1.99	4.53	60 000
PAA/IA-2	0.678	2.00	4.52	49 000
PAA/IA-3	0.646	2.10	4.43	41 000
PAA/VAC	0.088	2.60	4.00	113 600
PAA/CIAA-1	0.310	2.06	4.47	95 200
PAA/CIAA-2	0.183	2.75	3.87	40 510
PVSA-1	0.0846	3.24	3.45	33 310
PVSA-2	0.811	3.25	3.44	33 960
PVSA-3	0.686	3.29	3.40	36 620
PVSA-4	0.0636	3.50	3.22	26 000
TERP-1	0.431	2.10	4.43	63 500
PMAA/ CIAA-1	0.564	2.09	4.45	50 000

Table 5.2.1

5.2.2 COPOLYMER COMPOSITION

Once the molecular mass had been determined, the copolymers were analyzed, using titration techniques, for composition. See Chapter 4 for experimental method and calculations. The results are given in Table 5.2.2.

No attempt was made to determine the composition of polymer obtained in a 100% yield as this would be the composition of th monomers used in the reaction.

For other copolymers, a pH titration was done to the first en point (the full ionisation of the stronger acid) and th copolymer composition was calculated.

For the poly(acrylic acid-co-vinyl acetate) copolymer a p titration to the end point was used to calculate the percentag of acrylic acid in the polymer.

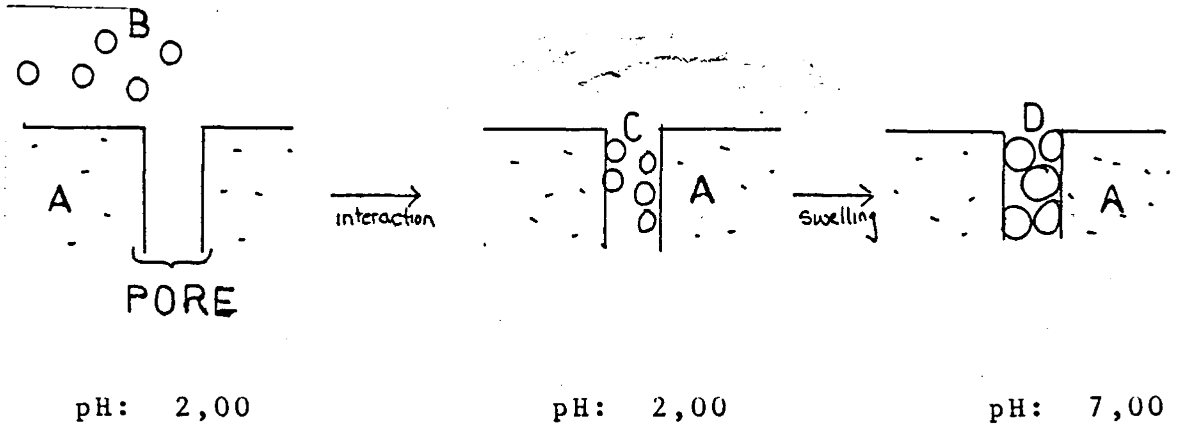
Polymer	Feed Ratios A	B	C	Mol. Mass	Conversion	Composition A	B	C
PAA/MAA-1	0,50	0,50	-	30 000	0,98	0,50	0,50	
PAA/IA-2	0,65	0,35	-	49 000	0,56	0,65	0,35	
PAA/IA-3	0,65	0,35	-	41 000	0,87	0,65	0,35	
PAA/VAC-1	0,50	0,50	-	113 000	0,58	0,60	0,40	
PAA/CIAA-1	0,60	0,40	-	95 200	0,99	0,60	0,40	
PAA/CIAA-2	0,63	0,37	-	40 500	0,99	0,63	0,37	
PMAA/CIAA-1				50 000	0,98			
TERP1	0,40	0,35	0,25	63 500	0,99	0,40	0,35	0,2

Table 5.2.2: Feed ratios, molecular mass, conversion ar composition of copolymers.

5.3 POLYMER EVALUATION

5.3.1 DYNAMIC MEMBRANE FORMATION

place. When the pH is increased (pH 2,00 at the start of formation, see Section 4.4.2) the polymer swells due to ionisation and the pores of the zirconium membrane fill. Schematically it can be represented as follows: (Fig. 5.3.2).



A: Hydrous zirconium oxide
B: Polymer molecules in solution (low charge density)
C: Polymer molecules that have interacted with zirconium (low charge density)
D: Swollen polymer molecules (high charge density)

Fig. 5.3.2: A schematic representation of composite membrane formation

It can be said, therefore, that during composite membrane performance the following happens.

- Polymer molecules interact with the hydrous zirconium oxide
- As the pH is raised the polymer ionizes and the resulting higher charge density causes the polymer to swell.
- Due to the swelling of the polymer molecules the membrane pore size decreases.
- Due to the increase in charge density these ion-exchange membranes will exhibit a higher rejection at pH 7,00 than at pH 2,00.

Thus if the flux decreases, and the rejection increases after the initial membrane is formed, a composite membrane can be said to have been formed.

In order to evaluate the ability of the various polyelectrolytes to form dynamic membranes, measurements of flux and rejection were made after 30 minutes of formation (pH 2,50) and after 24 hours after the start of formation (pH 7,00).

The results are given in Table 5.3.1.

(i) Poly(acrylic acid)

Polymer	pH	Time(h)	Rejection(%)	Flux ($l.m^{-2}.d^{-1}$)
PAA-1	2,5	0,5	32,4	5 440
	7,0	24,0	82,8	1 540
PAA-1	2,5	0,5	39,1	4 440
	7,0	24,0	86,3	1 360
PAA-2	2,5	0,5	32,3	3 900
	7,0	24,0	89,2	2 100
PAA-2	2,5	0,5	13,7	12 320
	7,0	24,0	73,1	2 800

Table 5.3.1: Membrane flux and rejection values for Zr-poly (acrylic acid) membranes

(ii) Poly(methacrylic acid)

Polymer	pH	Time (h)	Rejection%	Flux (lm.$^{-2}$d^{-1})
PMAA 3	2,5	0,5	32,6	5 500
	7,0	24,0	50,5	4 800
PMAA 3	2,5	0,5	34,9	5 980
	7,0	24,0	52,3	5 070
PMAA 1	2,5	0,5	21,1	7 340
	7,0	24,0	59,7	7 060
PMAA 1	2,5	0,5	22,7	8 430
	7,0	24,0	58,6	7 790
PMAA 4	2,5	0,5	34,2	10 150
	7,0	24,0	71,6	9 060
PMAA 4	2,5	0,5	32,3	12 140
	7,0	24,0	71,6	9 780

Table 5.3.2: Membrane flux and rejection values for Zr-poly (methacrylic acid) membranes

As with the poly(acrylic acid), there is definite evidence of the formation of dynamic membranes. There is, for the most part, not as marked an increase in rejection as with poly(acrylic acid), yet the rejection does increase while the flux decreases, albeit much less so than with poly (acrylic acid).

(iii) Poly(itaconic acid)

Polymer Nr	pH	Time(h)	Rejection (%)	Flux($lm^{-2}.d^{-1}$)
PIA 2	2,5	0,5	33,3	10 050
	7,0	24,0	58,3	8 520
PIA 2	2,5	0,5	39,8	9 878
	7,0	24,0	56,1	10 500
PIA 2	2,5	0,5	47,4	9 510
	7,0	24,0	55,7	9 330
PIA 3	2,5	0,5	33,5	11 780
	7,0	24,0	54,7	10 510

Table 5.3.3: Membrane flux and rejection values for Zr-poly(itaconic acid) membranes

As in the previous two cases, we can see a definite increase in rejection, coupled with a decrease in flux, except with one membrane. These polymers do, therefore, form composite membranes with hydrous zirconium(iv) oxide.

The small decline in flux can be ascribed to the fact that this polymer would have, theoretically, a much higher charge density at neutral pH than poly(acrylic acid), since it has two ionizable groups per monomer. This higher charge density would result in a higher degree of hydrophilicity, and thus an increased water flux. This high hydrophilicity would be offset by swelling of the polymer due to charge repulsion and the resultant decrease in pore size.

(iv) Poly(vinyl sulfonic acid)

Polymer	pH	Time(h)	Rejection (%)	Flux($1.m^{-2}.d^{-1}$)
PVSA 1	2,5	0,5	29,7	15 950
	7,0	24,0	48,2	7 790
PVSA 1	2,5	0,5	15,5	36 240
	7,0	24,0	47,0	8 520
PVSA 1	2,5	0,5	26,5	17 580
	7,0	24,0	46,6	8 335
PVSA 4	2,5	0,5	31,7	18 480
	7,0	24,0	38,4	11 415
PVSA 4	2,5	0,5	26,9	24 640
	7,0	24,0	40,1	13 050
PVSA 4	2,5	0,5	24,5	21 380
	7,0	24,0	40,4	12 230

Table 5.3.4: Membrane flux and rejection values for Zr-poly(vinyl sulfonic acid) membranes

Although the rejection did not reach a high final value for any of these membranes, there was an increase in rejection ranging from about 10% to 32%, from 30 minutes after the start of formation and 24 hours after the start of formation. Simultaneously the flux decreased, in all cases, quite substantially.

This indicates the formation of a composite dynamically formed hydrous. Zirconium(iv)-poly(vinyl sulfonic acid) membrane. Johnson [17] reported that this polymer did form a dynamic membrane.

(v) Poly(2-chloro acrylic acid)

Polymer nr	pH	Time (h)	Rejection (%)	Flux(l.m^{-2}.d^{-1})
PCIAA 1	2,5	0,5	45,2	12 050
	7,0	24,0	61,7	9 060
PCIAA 1	2,5	0,5	45,4	13 230
	7,0	24,0	63,8	10 420
PCIAA 1	2,5	0,5	40,0	12 600
	7,0	24,0	63,8	9 240
PCIAA 2	2,5	0,5	38,9	7 610
	7,0	24,0	41,9	7 970
PCIAA 2	2,5	0,5	39,8	8 700
	7,0	24,0	41,5	8 880
PCIAA 3	2,5	0,5	45,8	9 970
	7,0	24,0	48,3	11 420
PCIAA 3	2,5	0,5	40,6	12 320
	7,0	24,0	47,9	11 960

Table 5.3.5: Membrane flux and rejection values for Zr-poly (2-chloro acrylic acid) membrane

The evidence of the rejection values indicates the formation of a composite membrane. The differing behaviour of the flux in the case of polymers PCIAA 2 and PCIAA 3 is puzzling, but these polymers were of much lower molecular mass than PCIAA 1 was. These polymers all behaved differently during formation, compared with all the other polymers evaluated. Possible reasons for this will be discussed later on.

(vi) Poly(acrylic acid-co-methacrylic acid)

Polymer	pH	Time (h)	Rejection (%)	Flux($1.m^{-2}.d^{-1}$)
PAA/MAA 1	2,5	0,5	45,3	7 520
	7,0	24,0	60,1	6 430
PAA/MAA 1	2,5	0,5	40,8	8 880
	7,0	24,0	53,4	7 970
PAA/MAA 1	2,5	0,5	50,0	10 150
	7,0	24,0	60,9	9 785
PAA/MAA 1	2,5	0,5	48,2	7 610
	7,0	24,0	66,6	8 515
PAA/MAA 1	2,5	0,5	49,2	8 790
	7,0	24,0	68,8	9 970
PAA/MAA 1	2,5	0,5	63,6	8 790
	7,0	24,0	68,1	9 970

Table 5.3.6: Membrane flux and rejection values for Zr-poly (acrylic acid-co-methacrylic acid)

Rejection values clearly indicate the formation of composite hydrous zirconium (iv) oxide-poly (acrylic acid-co-methacrylic acid) membranes. Half of the flux values indicate a slight decrease in flux, while the other half show an actual increase in flux over a period of 24 hours. However, if one looks at the figures for flux at the completion of formation (Appendix A), at pH 7,00, it can be seen that the figures for the flux are all lower than those at pH 2,5. The above table shows only results 18 hours after completion of formation and a flux increase. This flux increase then is due to some membrane debonding, as all the rejection values from pH 7,00 at completion of formation to pH

7,00 after 18 hours after formation (by an average of 10%).

Nevertheless, the formation of composite membranes by these polymers is clearly demonstrated.

(vii) Poly(acrylic acid-co-itaconic acid)

Polymer	pH	Time (h)	Rejection (%)	Flux($l.m^{-2}.d^{-1}$)
PAA/IA 3	0,5	0,5	34,3	8 150
	7,0	24,0	78,0	5 980
PAA/IA 3	0,5	0,5	4,8	25 000
	7,0	24,0	75,6	7 880
PAA/IA 2	0,5	0,5	14,2	6 250
	7,0	24,0	77,8	4 350
PAA/IA 2	0,5	0,5	14,1	6 885
	7,0	24,0	75,3	4 440
PAA/IA 2	0,5	0,5	16,1	4 900
	7,0	24,0	73,1	3 625

Table 5.3.7: Membrane flux and rejection values for Zr-poly (acrylic acid-co-itaconic acid) membranes

For both the polymers evaluated, quite sharp differences in rejection values, ranging from 44% to 71% over the pH range of 2,50 to 7,00 and the time range of 0,5 to 24,0 hours, and declining flux values over the same pH and time ranges clearly demonstrate the formation of dynamic hydrous zirconium (iv) oxide-poly (acrylic acid-co-itaconic acid) membranes.

(viii) Poly(acrylic acid-co-2-chloroacrylic acid)

Polymer	pH	Time (h)	Rejection (%)	Flux ($l.m^{-2}.d^{-1}$)
PAA/CIAA 1	2,5	0,5	46,4	5 800
	7,0	24,0	62,0	5 440
PAA/CIAA 1	2,5	0,5	48,1	6 430
	7,0	24,0	65,2	5 980
PAA/CIAA 1	2,5	0,5	44,5	6 250
	7,0	24,0	65,2	5 890
PAA/CIAA 2	2,5	0,5	55,9	9 060
	7,0	24,0	73,5	7 250
PAA/CIAA 2	2,5	0,5	47,9	12 685
	7,0	24,0	75,8	8 430

Table 5.3.8: Membrane flux and rejection values for Zr-poly (acrylic acid-co-2-chloro acrylic acid) membranes

Rejection values show an increase from the start of formation to 24 hours after the start of formation, ranging from 15% and 28%. A decrease in flux is evident throughout. Dynamic membranes are therefore formed.

(ix) Poly(methacrylic acid-co-2-chloro acrylic acid)

Polymer	pH	Time (h)	Rejection (%)	Flux($l.m^{-2}.d^{-1}$)
PMAA/CIAA 1	2,5	0,5	51,1	13 050
	7,0	24,0	58,1	12 500
PMAA/CIAA 1	2,5	0,5	54,8	14 500
	7,0	24,0	57,2	13 410
PMAA/CIAA 1	2,5	0,5	34,4	20 115
	7,0	24,0	53,9	13 230

Table 5.3.9: Membrane flux and rejection values for Zr-poly (methacrylic acid-co-2-chloro acrylic acid) membranes.

Although the final rejection values for these membranes are low, compared with poly(acrylic acid), rejection and flux figures indicate the formation of dynamic membranes. Of note is the very high initial rejection, at pH 2.5, in comparison with the final figure obtained. This is a characteristic of all the polymers containing 2-chloro acrylic acid.

(x) poly(acrylic acid-co-vinyl acetate)

Polymer	pH	Time (h)	Rejection (%)	Flux($l.m^{-2}.d^{-1}$)
PAA/VAC-1	2,5	0,5	55,9	3 990
	7,0	24,0	88,2	2 720
PAA/VAC-1	2,5	0,5	60,2	4 800
	7,0	24,0	92,8	3 800
PAA/VAC-1	2,5	0,5	56,6	4 890
	7,0	24,0	93,2	3 900

Table 5.3.10: membrane flux and rejection values for Zr-poly(acrylic acid-co-vinyl acetate) membrane.

The large increases in rejection, ranging from 32% to 37% over the measurement period, the high final rejection figures, and the flux decline clearly demonstrates the formation of dynamic membranes.

(xi) poly(acrylic-co-methacrylic-co-2-chloro acrylic acid)

Polymer	pH	Time (h)	Rejection (%)	Flux($l.m^{-2}.d^{-1}$)
TERP-1	2,5	0,5	49,8	12 870
	7,0	24,0	61,7	11 420
TERP-1	2,5	0,5	40,1	17 400
	7,0	24,0	64,0	12 140
TERP-1	2,5	0,5	40,1	14 130
	7,0	24,0	63,4	11 325

Table 5.3.11: Membrane flux and rejection values for Zr-poly(acrylic-co-methacrylic-co-2-chloro acrylic acid) membranes.

The average increase in rejection of about 20% in rejection over the measurement period, and the decrease in flux over the same period, show the formation of dynamic membranes.

5.3.1.1.2 Summary

All of the following polymers form dynamically formed composite membranes with hydrous zirconium (iv) oxide sublayers:

- Poly(acrylic acid)
- Poly(methacrylic acid)
- Poly(2-chloro acrylic acid)
- Poly(vinyl sulfonic acid)

- Poly(itaconic acid)
- Poly(acrylic acid-co-methacrylic acid)
- Poly(acrylic acid-co-2-chloro acryclic acid)
- Poly(acrylic acid-co-itaconic acid)
- Poly(acrylic acid-co-vinyl acetate)
- Poly(methacrylic acid-co-2-chloro acrylic acid)
- Poly(acrylic-co-methacrylic-co-2-chloro acrylic acid)

5.3.2 MEMBRANE FORMATION: THE EFFECT OF pH ON REJECTION AND FLUX

5.3.2.1 Introduction and Definitions

As the composite membranes formed are ion-exchange membranes (101) the effect of the charge density on the membrane is of great importance when membrane behaviour is to be explained. As the charge density depends on the degree of ionisation and thus on the strength of the unsaturated acid used to make the polymer.

There were no documented values for pKa for some of the monomers used to synthesize the polymers used in this study. The relative acid strengths for these monomers were determined titrimetrically using 0,1 N NaOH as a standard. (See Chapter 4.)

The values of pKa are tabled below:

Monomer	pKa1	pKa2	pKa3
Acrylic acid	4,25	-	-
Methacrylic acid	4,50	-	-
Itaconic acid	3,83	5,45	-
Vinyl sulfonic acid	3,00	-	-
2-chloro acrylic acid	2,76	-	-

Table 5.3.12: The pKa values for the monomeric acids used to synthesize the homo- and copolymers.

In order to be able to compare membrane rejection of various membranes, it was decided to define a value, R_f where:

$$\overline{R_f} = \Sigma R_f / n \qquad (1)$$

and $$R_f = R_{3,5}/R_m \qquad (2)$$

where $R_{3,5}$ = rejection of the membrane at pH=3,50

and R_m = maximum rejection of the membrane

Thus R_f = fraction of the maximum rejection attained at pH3.5

amd $\overline{R_f}$ = Average fraction of maximum membrane rejection, for n membranes

n = 1, 2, 3 .....

The pH value of 3,50 was adopted on as a comparative value as membranes sometimes take a little longer to form than is expected, and also as such some membranes form only at pH 2,5 or even 3,0. At pH 3,5 a membrane has been formed in all cases.

5.3.2.2 Non-Chlorine Containing Polymers

All the results are given in Appendix A. Data drawn from these tables were used to draw graphs of membrane flux and rejection behaviour during formation. During formation of the membrane, the flux and rejection were monitored prior to each pH adjustment (See Section 4 for experimental method).

There were seven polymers in the group of non-chlorine containing polymers. They were poly(acrylic acid), poly(methacrylic acid), poly(itaconic acid), poly(acrylic acid-co-methacrylic acid), poly(acrylic acid-co-vinyl acetate) and poly(acrylic acid-co-itaconic acid) and poly(vinyl sulfonic acid).

The results are discussed below. Solid lines in the graphs are intended to show the average trend through the points plotted. The legends on the following graphs are in the form: x.y. The figure before the period (x) denotes the polymer number, and the figure after the period (y) denotes the membrane number.

(i) Poly(acrylic acid)

The notable features in Figs. 5.3.4 and 5.3.5 are:

- A sharp rise in rejection at pH 2,0 to pH 3,5, unmatched by any other pH change of similar magnitude.
- A steady-state flux evidenced in the region of pH 3,5 to pH 4,5.
- A noted decline in flux in the pH range 5,0 - 6,0.

The sharp rise in rejection might be attributed to two factors:
(a) The formation of the membrane, and (b) the increase in charged species in the membrane.
(a) Would cause a decrease in pore size.
(b) Would increase the net fixed charge on the membrane.

With an increase in pH, there was an increase in net fixed charge on the polymer. This had two effects: First, like charges repel one another, leading to polymer swelling and thus pore size decreasing. This would decrease flux. Second, increase in charge would increase the hydrophilic character of the membrane. This would increase water flux. Schematically:

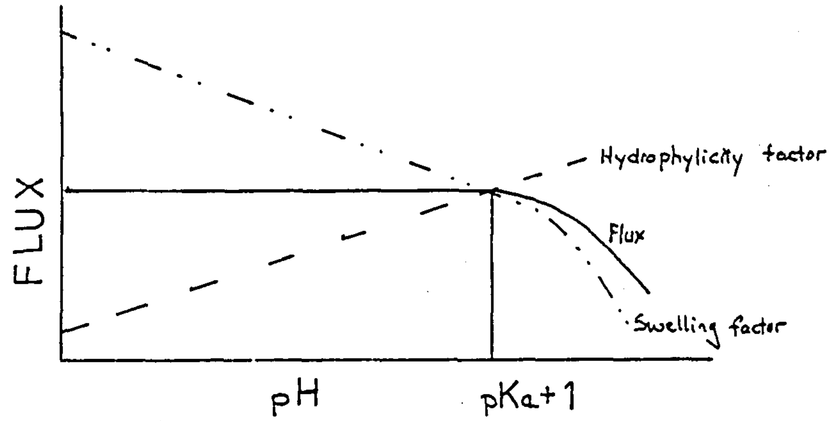


Fig. 5.3.3 Schematic representation of flux behaviour

These factors appear to have a balanced role in the flux behaviour until such time as the pH reaches the level of about pKa + 1. At this stage polymer swelling takes over as the dominant factor and there is a decrease in flux. This can be seen clearly in figure 5.3.5.

The rejection for the membrane increases steadily from pH 2,0 to pH 7,0, although the initial increase between pH 2.0 and 3.5 is the highest, as explained earlier in this section. The increase in rejection with the increase in pH is to be expected. These membranes are ion-exchange membranes, (101) and as such will exhibit increase in rejection with increase in net fixed charge.

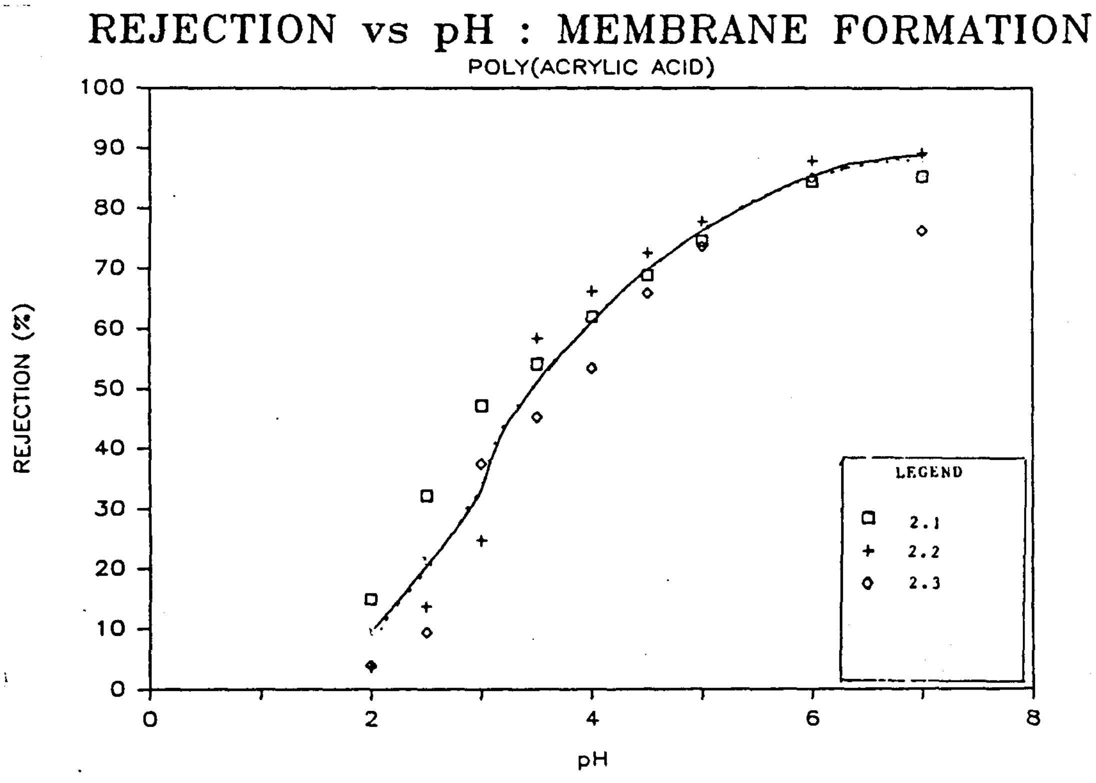


Fig. 5.3.4

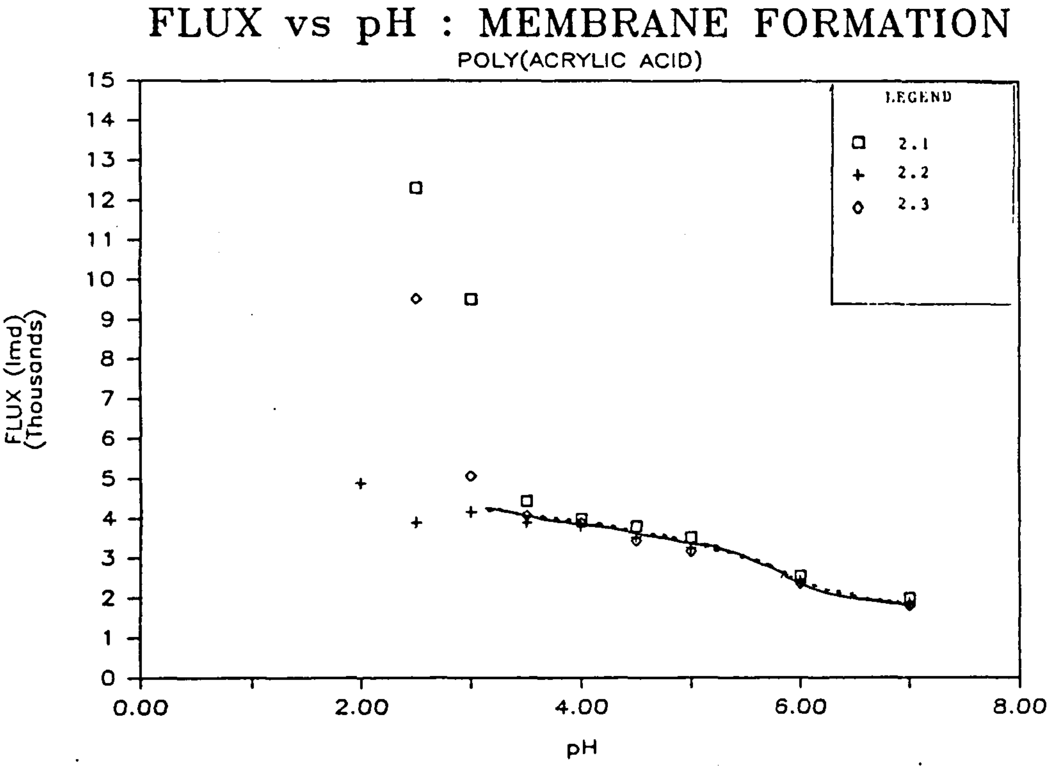


Fig. 5.3.5

The $\overline{R_f}$ value for these membranes is 0,62.

(ii) Poly(methacrylic acid)

The points of note that arise from Figs. 5.3.6 and 5.3.7, are:

- The initial rise in rejection in the range pH 2,0 to 3,5 is not as noticeable as with poly(acrylic acid).
- The flux exhibits a "steady state" between pH 3,5 and, in this case, pH 5,0. Only when the pH becomes greater than 5,0 is there a noticeable downward trend in the flux values.

The rejection behaviour in these membranes shows an $\overline{R_f}$ value of 0,50. This is lower than that of the zirconium-poly(acrylic acid) membranes. The pKa value of poly(methacrylic acid) is higher (4,50 to 4,25) than that of poly(acrylic acid), so that at pH = 3,50 the poly(methacrylic acid) would therefore be less ionised (percentage-wise) than the poly(acrylic acid); therefore the $\overline{R}_f$ value is lower.

The flux behaviour once again bears out the assumption that the flux is dependent on two factors. i.e. the swelling and the hydrophylicity of the polymer. (See Section 5.3.2.2(i)). At the pH value of pKa+1, i.e. at pH = 5,5 the rejection decreases more markedly than over the preceding range of pH values. (See Fig. 5.3.6 and also Table A.1 in Appendix A).

(iii) Poly(vinyl sulphonic acid)

These zirconium-poly(vinyl sulphonic acid) membranes show an $\overline{R}_f$ value of 0,86. As the pKa is lower than those of poly(acrylic acid) and poly(methacrylic acid) the polymer would be more ionised at pH 3.5 (percentage-wise) and a higher $\overline{R}_f$ value would, therefore, be expected.

The flux and rejection characteristics (see Figs. 5.3.8 and 5.3.9) of these membranes are puzzling. At the pH level of 4,0 the rejection starts decreasing, while the flux increases or

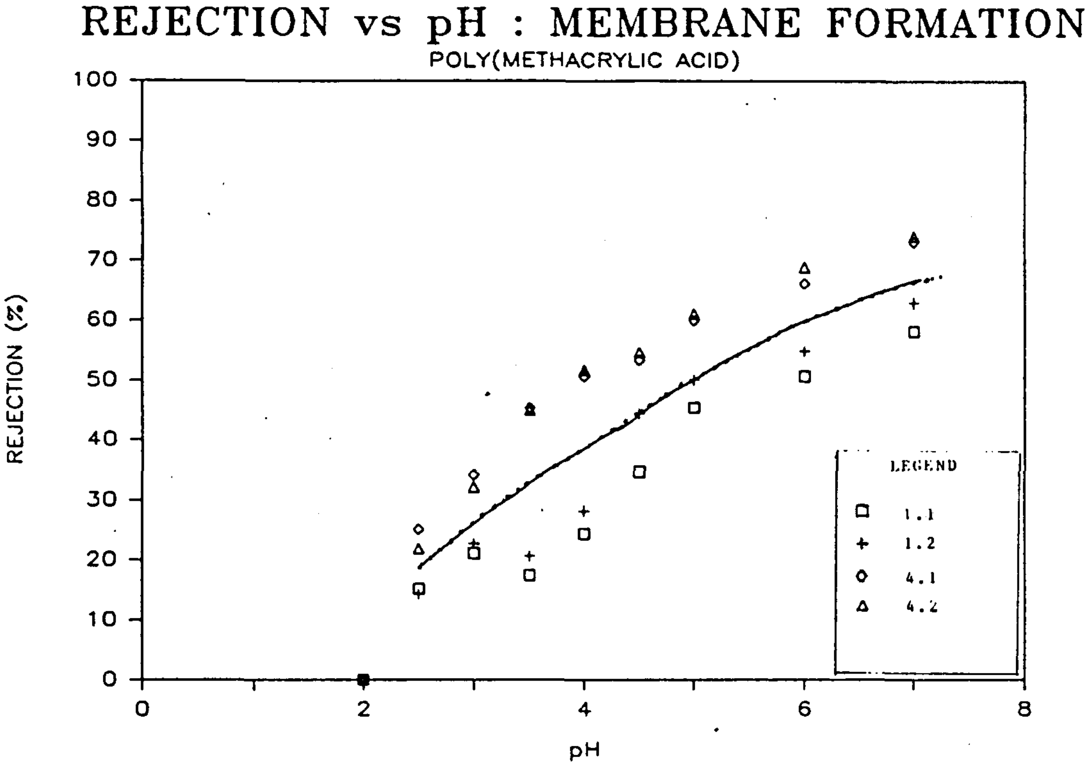


Fig. 5.3.6

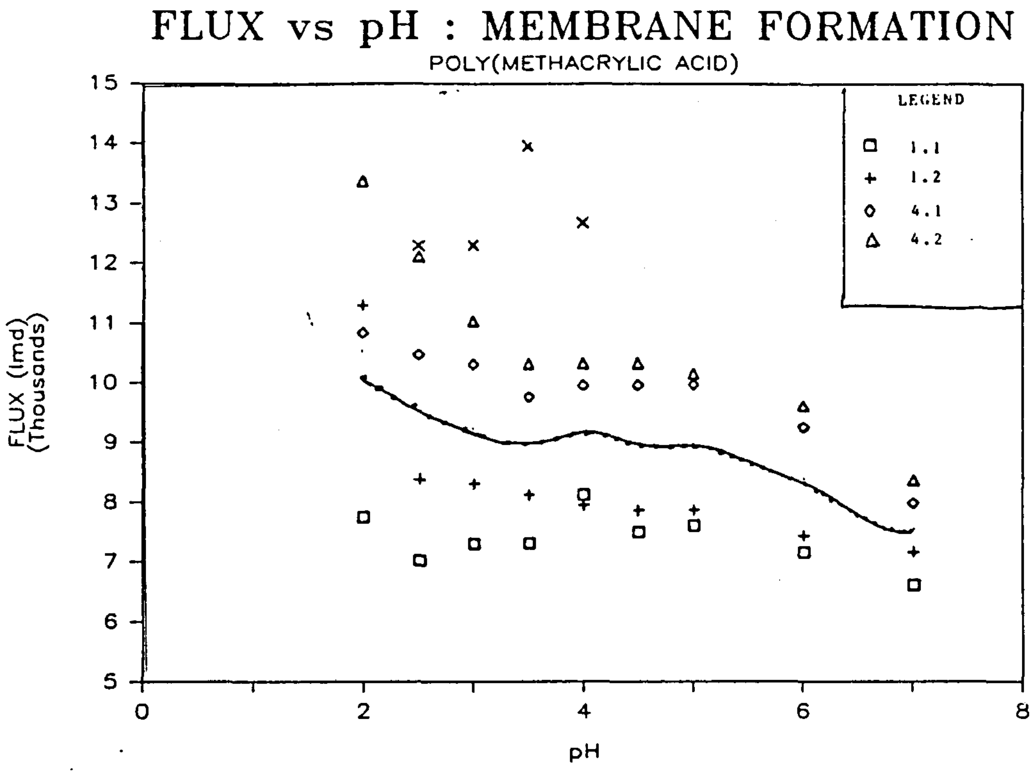


Fig. 5.3.7

remains steady. As the polymer affords no ready possibility for crosslinking, this could not be the explanation for the drop in rejection. The only possible explanation could be that, due to the low molecular mass of PVSA-4 (26 000), the membrane pores are so large that above 50% ionisation (pH 3,0 and above), the surface of these pores are electrically charged to such an extent that counterions are attracted to the pore surfaces, coions are repelled to the pore centres, and a double layer of the type familiar in colloid chemistry appears on the pore surfaces. In this double layer the ionic concentrations and the electric potential are highly non-uniform [17]. The effect of these non-uniformities is to enhance the salt invasion of a ion-exchange membrane. Thus the presence of "large" pores in the case of these membranes cause a drop in rejection when the ionisation of the polymer reaches a level of above 50%. The flux remains fairly steady, as the double layer will enhance flux, but at same time polymer swelling will decrease the flux.

(iv) Poly(itaconic acid)

This is a polymer with two carboxylic groups on a monomer. These groups have different pK values (3,83 and 5,45). The $\overline{R_f}$ value for the zirconium-poly(itaconic acid) membranes is 0.67, which puts it between poly(vinyl sulfonic acid) and poly(acrylic acid). This is so with the pKa_1 value as well. It would appear as if the second carboxylic group (pKa_2 = 5,45) is totally unionised at pH 3,5 and that the polymer behaves like a poly(monocarboxylic acid). The $\overline{R_f}$ value can therefore be explained in terms of the pKa_1 value of 3,83.

The eventual flux values for these polymers are quite high, ranging from 11 960 to 12 870 l.m^{-2}.d^{-1}. There is no sudden decline in flux over the formation range of pH. In this case the effect of ionizing of the second carboxylic group (pKa_2 = 5.45) increases the hydrophylicity to such an extent that it becomes the dominating factor in the flux behaviour. Swelling now plays a lesser role, and the flux remains constant. (See Figs. 5.3.10

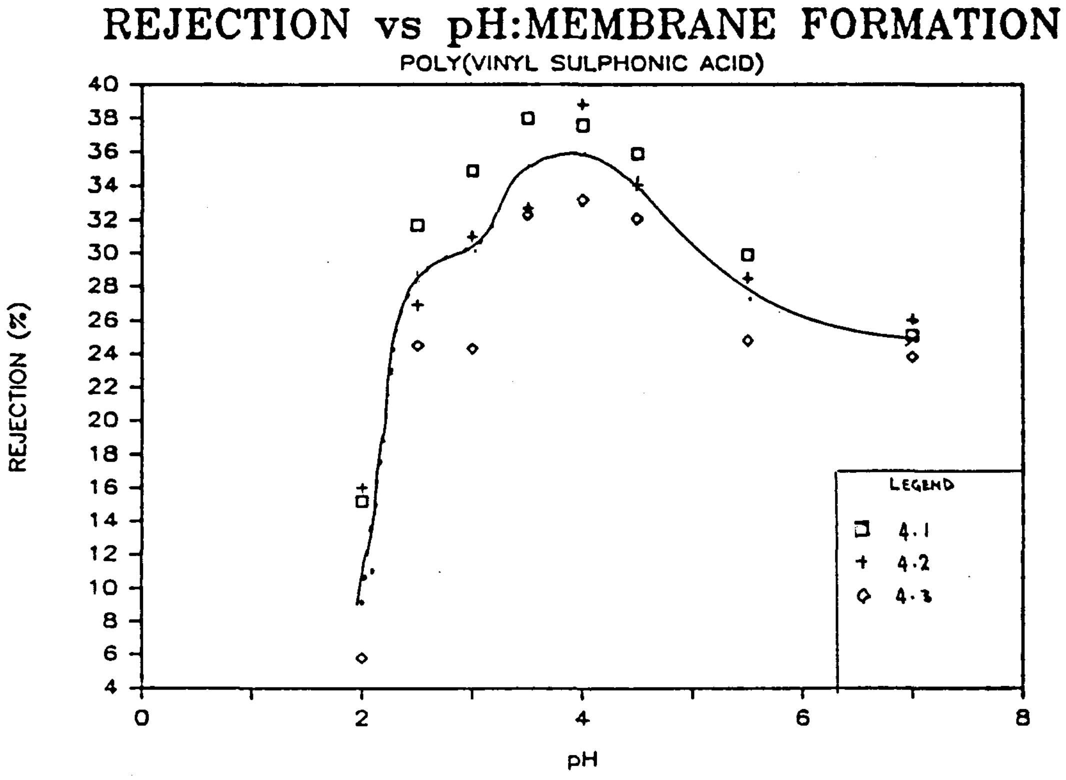


Fig. 5.3.8

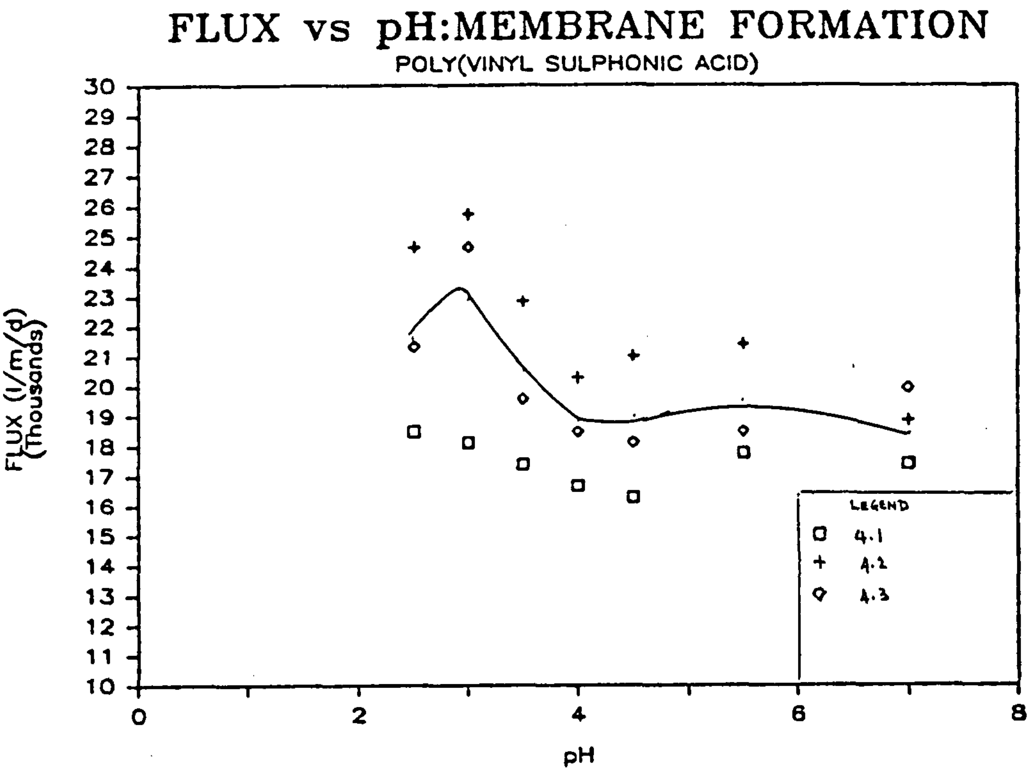


Fig. 5.3.9

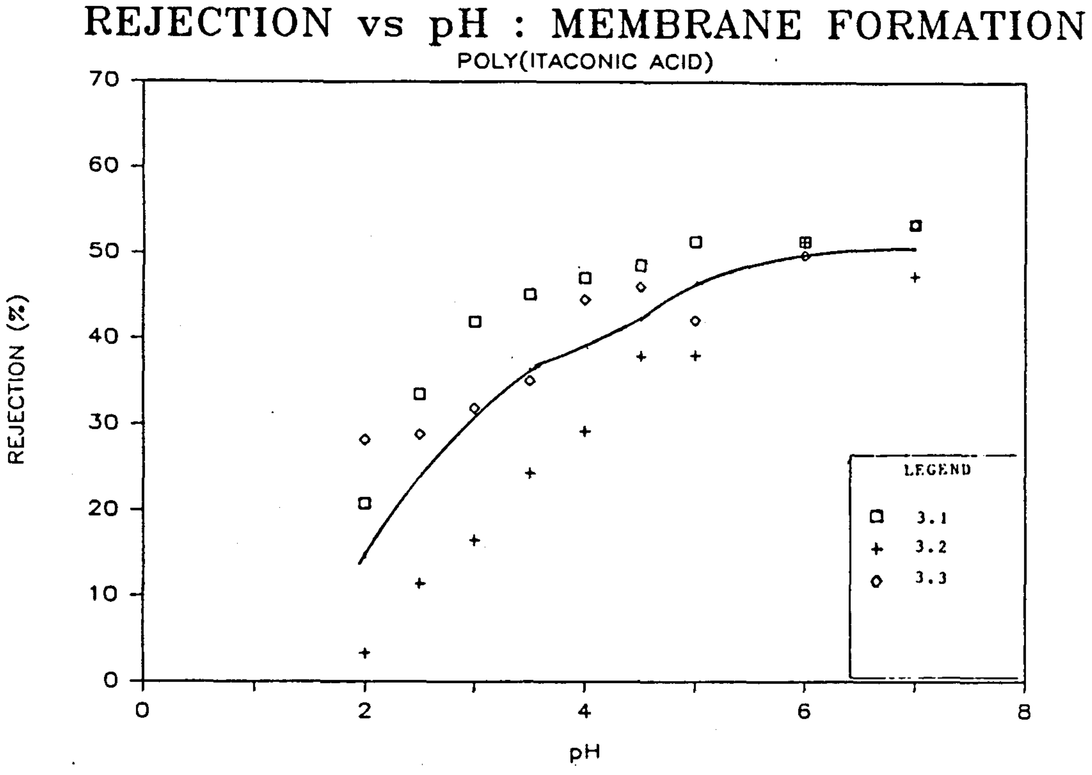


Fig. 5.3.10

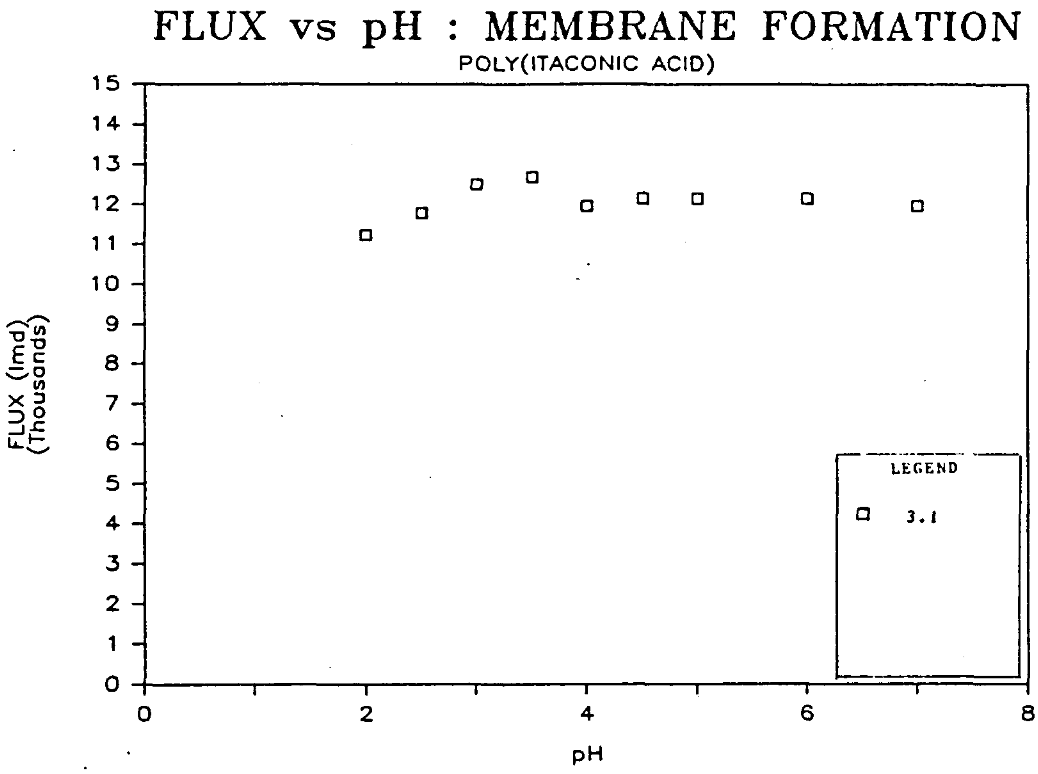


Fig. 5.3.11

and 5.3.11).

The effect of the second carboxylic group on the rejection behaviour is that it causes the rejection to "level off" at pH 6,00. This is due to the increasing charge density that increases the flux to such an extent that the membrane rejection suffers. Hydrated salts are now able to pass through the membrane more easily.

(v) Poly(acrylic acid-co-methacrylic acid)

The $\overline{R_f}$ value is 0,75 for these membranes, and there is a marked flux decrease from pH 5,0 to 6,0.

The high $\overline{R_f}$ value cannot easily be explained. The flux behaviour is expected, as the pK values for poly(acrylic acid) and poly(methacrylic acid) are very similar (4,25 and 4,50) so that a flux decrease at pH = pKa+1 is to be expected. (See Figs. 5.3.12

and 5.3.13).

The $\overline{K_f}$ value for any membrane with a copolymer as polyelectrolyte will depend to the following:

- Which monomers make up the copolymer, i.e. do they contain ionisable groups?
- What are the pKa values for the monomers (if they are both ionisable)?
- What is the copolymer composition?

It therefore depends on the above three factors to what degree of ionisation the polymer will have at any given pH value below neutral.

(vi) Poly(acrylic acid-co-vinyl acetate)

The rejection (See Fig. 5.3.15) is influenced in this case by the presence of hydrophobic groups. The initial rejection is high,

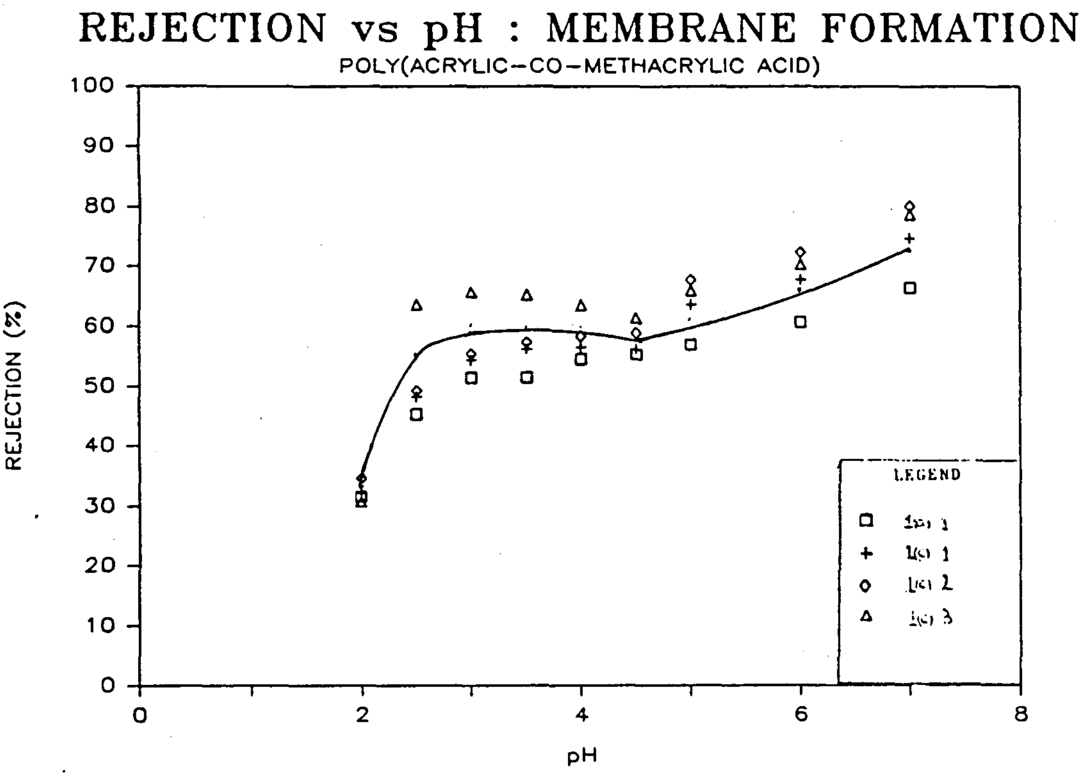


Fig. 5.3.12

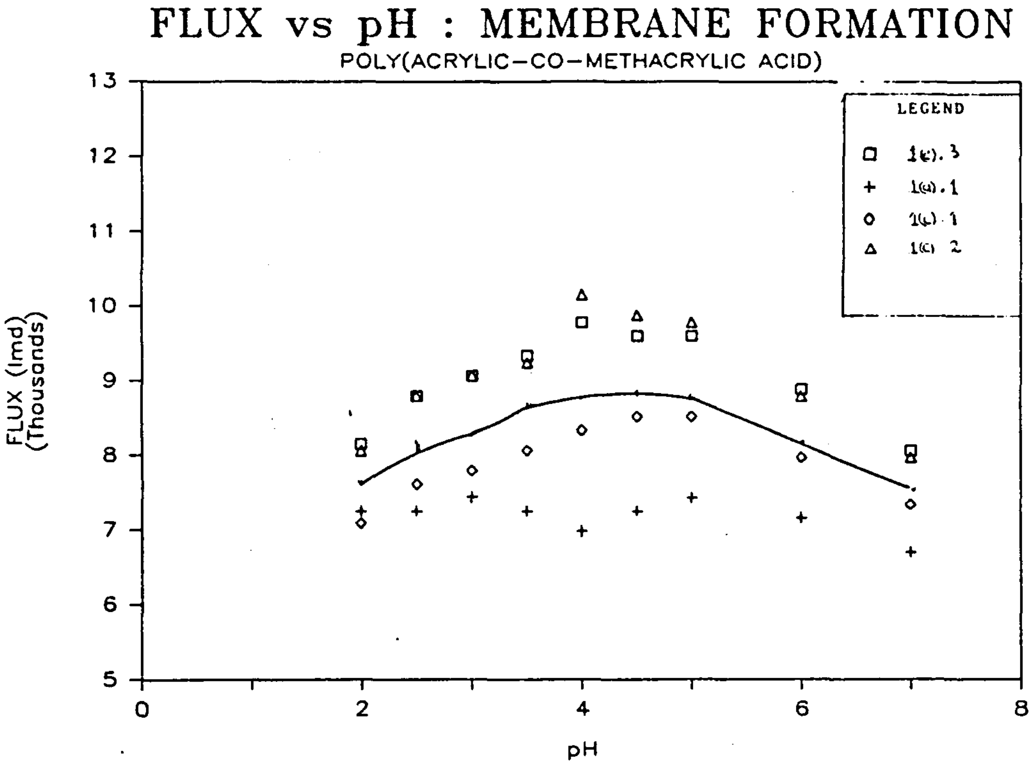


Fig. 5.3.13

with $\overline{K_f}$ = 0.80. This is because this membrane is not only a ion-exchange membrane, but has some properties of a neutral membrane as well. Thus the rejection will not depend be solely on the charge density.

As we have only a single type of carboxylic group in this copolymer, it is to be expected that the flux behaviour would be similar to that of the zirconium oxide-poly(acrylic acid) membranes. As can be seen from figure 5.3.14, this is indeed the case.

(vii) Poly (acrylic acid-co-itaconic acid)

Some of the results are shown in Figures 5.3.16 and 5.3.17. As can be expected in the case of a polymer with three different carboxylic groups, the flux and rejection behaviour is not as easily explained as in the case of the homopolymers.

The flux increased for this membrane from pH 3,0 to 3,5, probably due to the ionisation of the first itaconic acid carboxylic group (pKa = 3,83). The flux stayed steady from pH 4,0 to pH 5,0, due to the ionisation of the acrylic acid carboxylic group (pKa = 4,25). Only after the pH has reached 6,0 is a noticeable decrease in flux seen. The point where the flux decreases occurs only when the second itaconic acid carboxylic group ionises. This must cause the polymer to be more than 50% ionised, and swelling becomes the ruling factor in the flux behaviour.

The rejection behaviour does not show any discernable trends that could be explained in terms of acid strengths or degrees of ionisation.

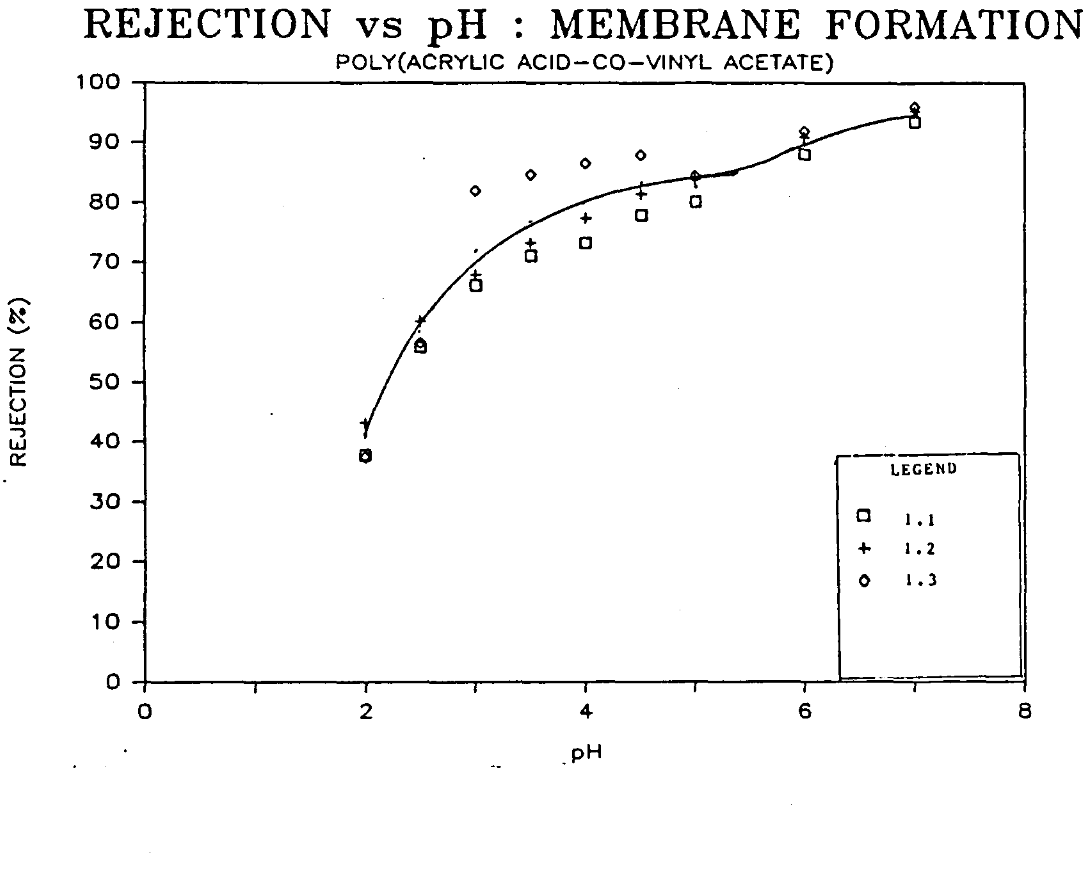


Fig. 5.3.14

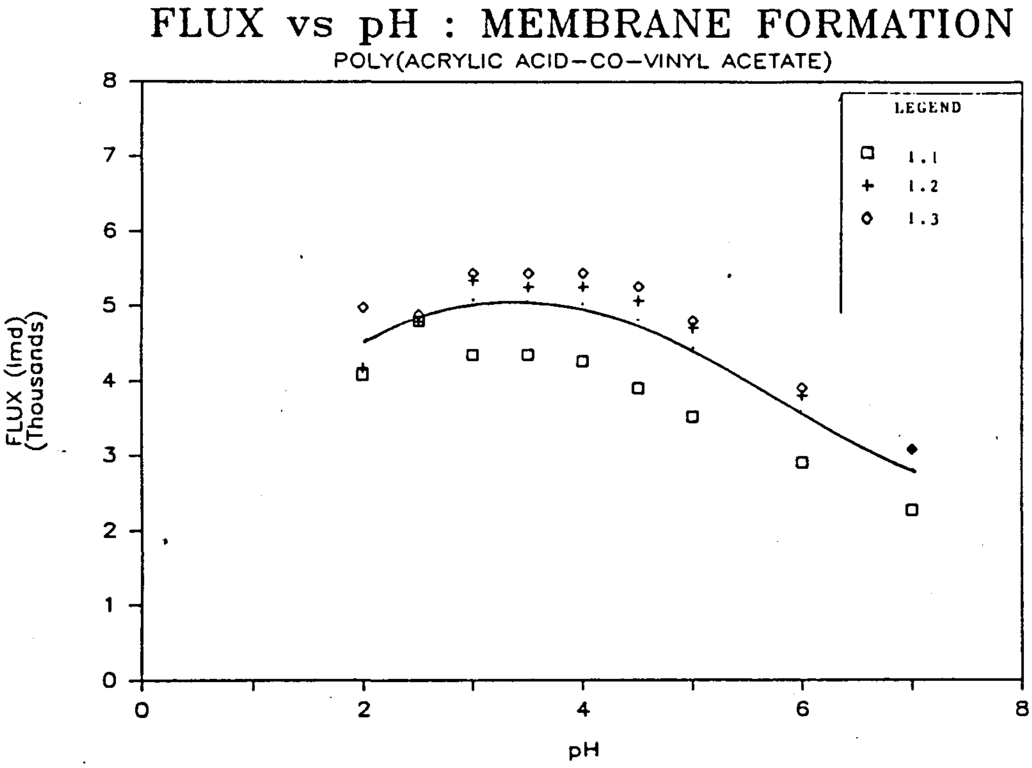


Fig. 5.3.15

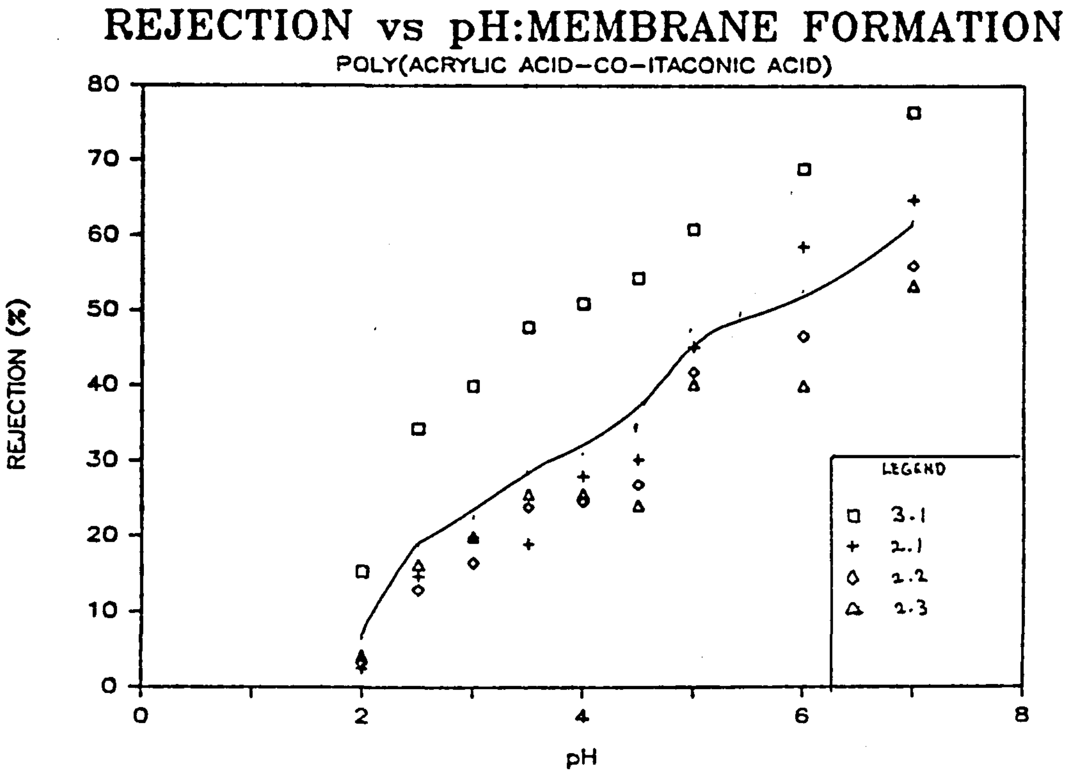


Fig. 5.3.16

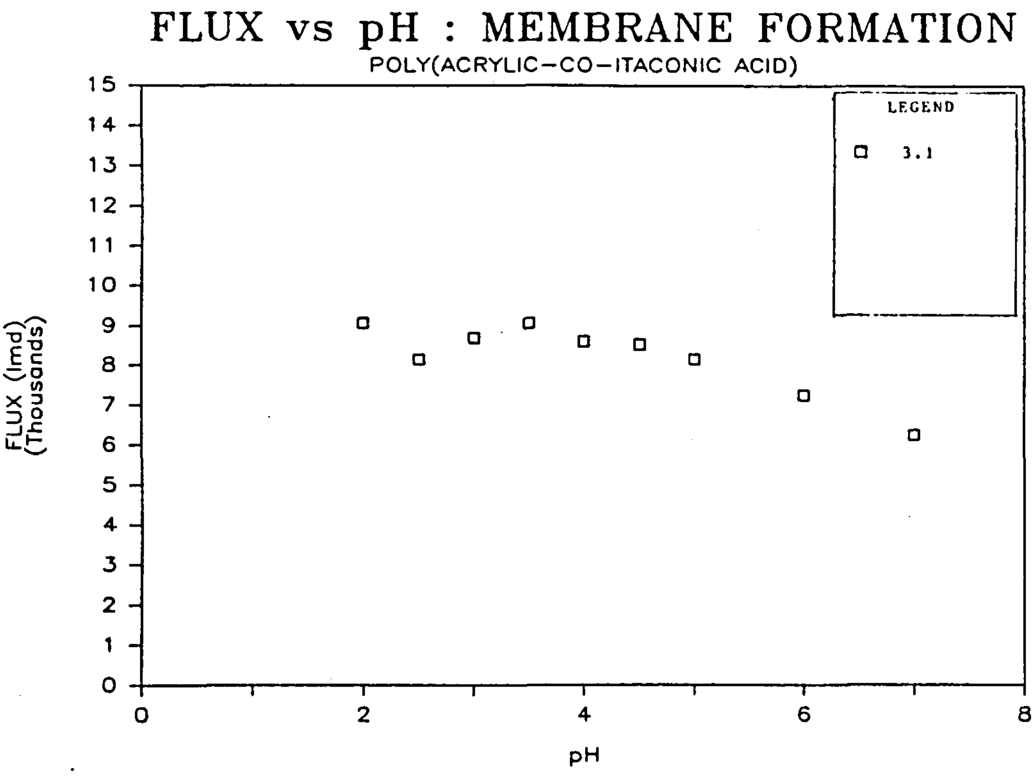


Fig. 5.3.17

5.3.2.3 CHLORINE-CONTAINING POLYMERS

(i) Poly(2-chloro acrylic acid)

Figs. 5.3.18 and 5.3.19 show that:

- The $\overline{R_f}$ is very high for the zirconium-poly(2-chloro acrylic acid) membranes, being 0,95. As the pKa value is 2,76 for 2-chloro acrylic acid, this is to be expected. This is because the polymer is above its pKa at pH 3,50, and is therefore over 50% ionised.

- As far as the rejection behaviour is concerned, it is noticeable that there is a decrease in rejection at pH 4,0 to 6,0, followed by an increase in rejection at pH 6,0 to 7,0.

- The flux decreases at pH 4,0 to 6,0 while the rejection decreases. This has no simple explanation. Since one possible explanation is that the polymer crosslinks, a solution of poly(2-chloro acrylic acid) was allowed to stand at pH 5,0. Crosslinking was proved to have occurred as the polymer came out of solution and formed a precipitate which dried into a tough, flexible film.

- At first, a free radical mechanism was suspected, but subjecting a solution of 2-chloro acrylic acid to a liberal dose of hydroquinone had no effect as precipitation still persisted. The other reasonable explanation lies in the occurrence of a nucleophilic substitution reaction (See Fig. 5.3.20).

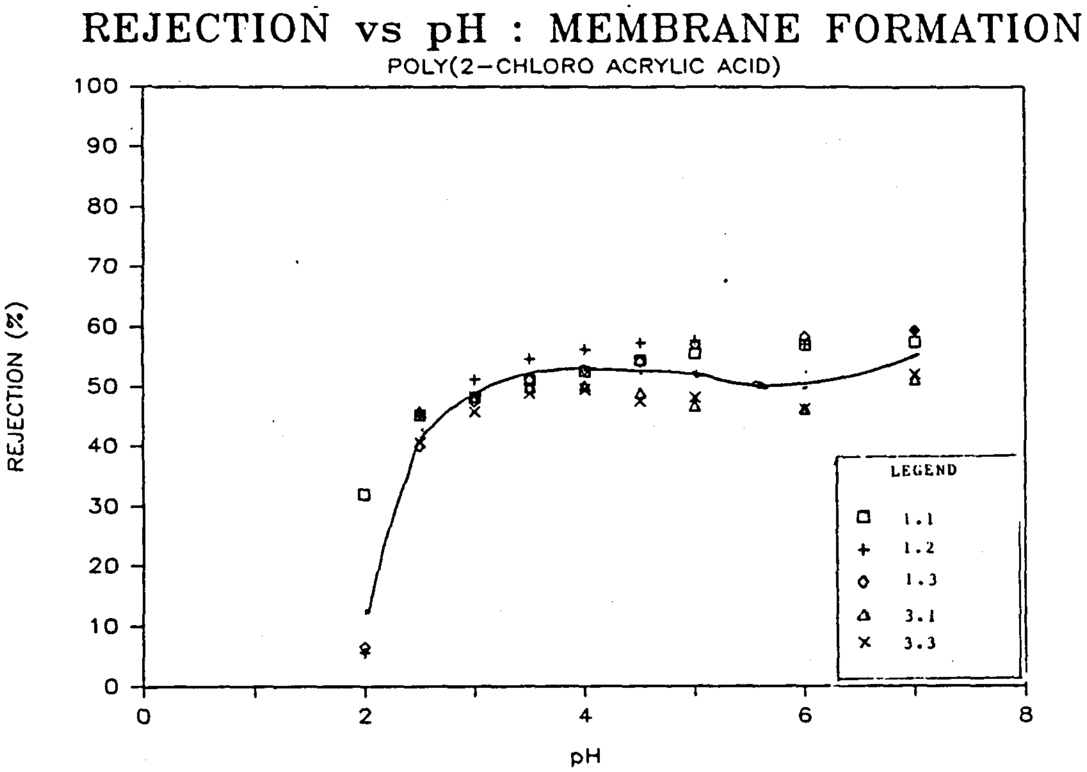


Fig. 5.3.18

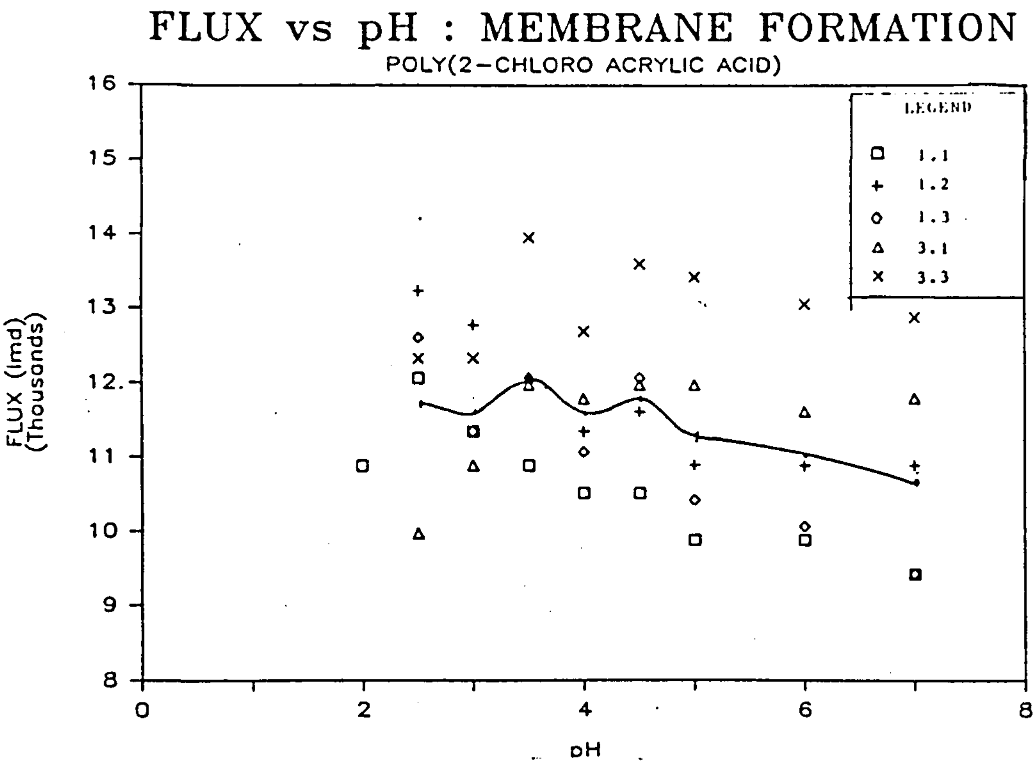


Fig. 5.3.19

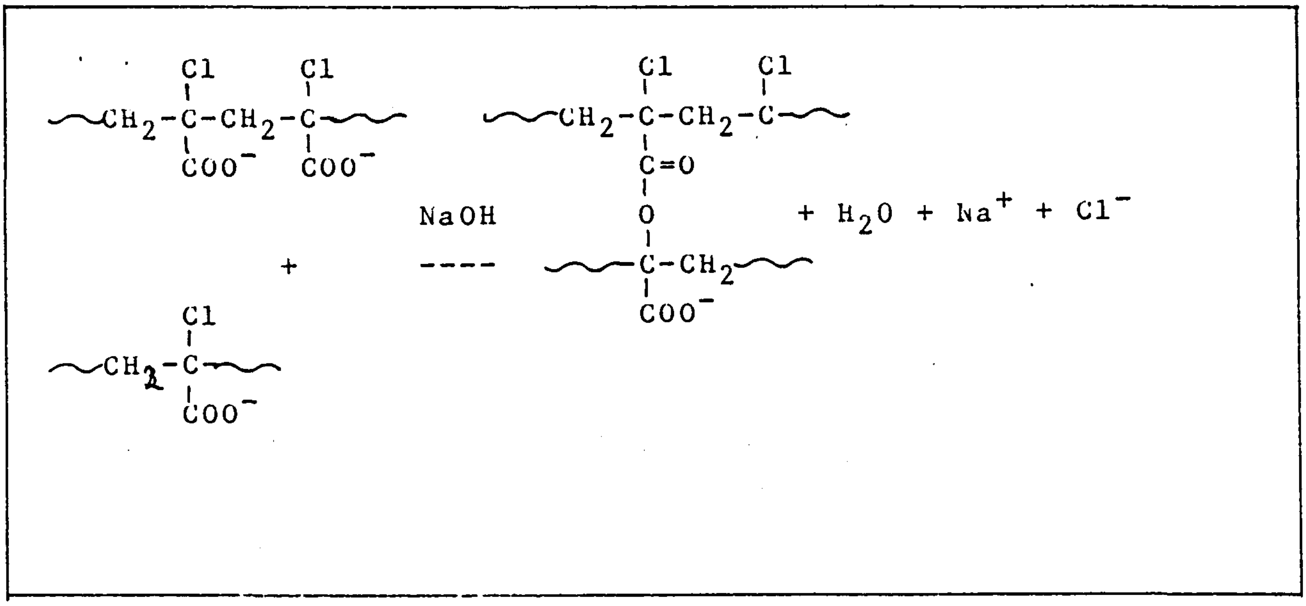


Fig. 5.3.20: Possible crosslinking reaction through esterification.

As will be seen in a later section, (5.5) the increase in rejection at pH 6,0 to 7,0 continues to pH 8,0 and 9,0, accompanied by a decrease in flux. This points to the fact that the number of charged sites on the membrane is increasing. This could be caused by the saponification of the formed ester bonds. (See Fig. 5.3.21).

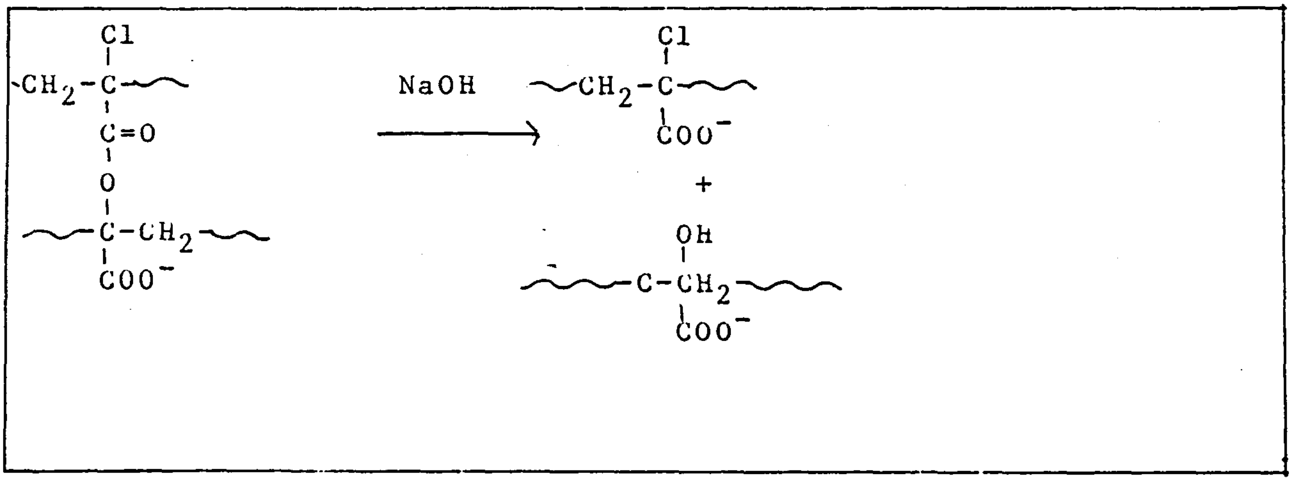


Fig. 5.3.21: Saponification of the formed esters.

The saponification was proved to a certain extent to have occurred by subjecting a formed precipitate of poly(2-chloro acrylic acid) to an excess of sodium hydroxide. The precipitate redissolved eventually. The situation at the membrane is one in which the reaction products are contantly being removed, while fresh NaOH is constantly being fed through the membrane. This has the effect of shifting the equilibrium shown in Fig. 5.3.21 to the right, making the reaction possible [35].

This theory explains the membrane behaviour. Due to crosslinking via carboxylic groups, at pH 4,00 to 6,00, we have an effect of charges "disappearing" from the membrane and thus a decrease in rejection (these are ion exchange membranes [17]). At the same time, the hydrophylic character of the membrane decreases, due to lower effective charge density. Swelling should not decrease because of the crosslinking as elastic resistance would be counteracting which is taking place. The flux decrease may be explained in this way.

(ii) Poly(acrylic acid-co-2-chloro acrylic acid)

The R_f value is 0,77. The initial high value (See Fig. 5.3.22) is ascribed to the ionisation of the 2-chloro acrylic acid. The $\overline{R_f}$ value of 0,77 is due to the 2-chloro acrylic acid being more than 50% ionised (pKa = 2,76) at pH 3,5. As these are ion-exchange membranes [101] the rejection depends on the fixed charge density.

The slow increase in rejection at pH 3,5 to 5,0 can be explained as follows. Two factors play a role here. First, there is the crosslinking reaction due to the 2-chloro acrylic acid taking place and, second, there is the ionisation of the acrylic acid reaching 50% in this pH range. As there is only 40% 2-chloro acrylic acid in the copolymer, the acrylic acid ionisation must play the major role, and there is thus a slight increase in rejection at pH 3,5 to 5,0.

The flux remains fairly steady up to pH 6.0 (See Fig. 5.3.23). This is due to the crosslinking reaction causing charges to disappear and thus decreasing the hydrophylicity on the one hand, and the increase in hydrophilicity due to acrylic acid ionisation

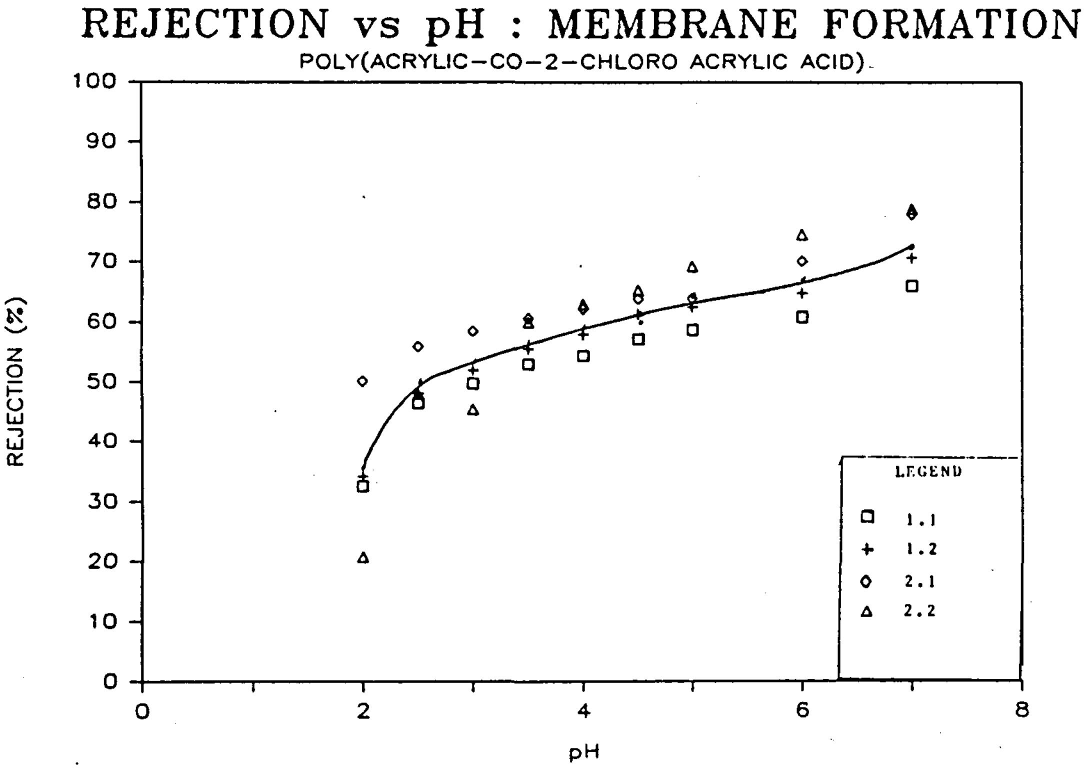


Fig. 5.3.22

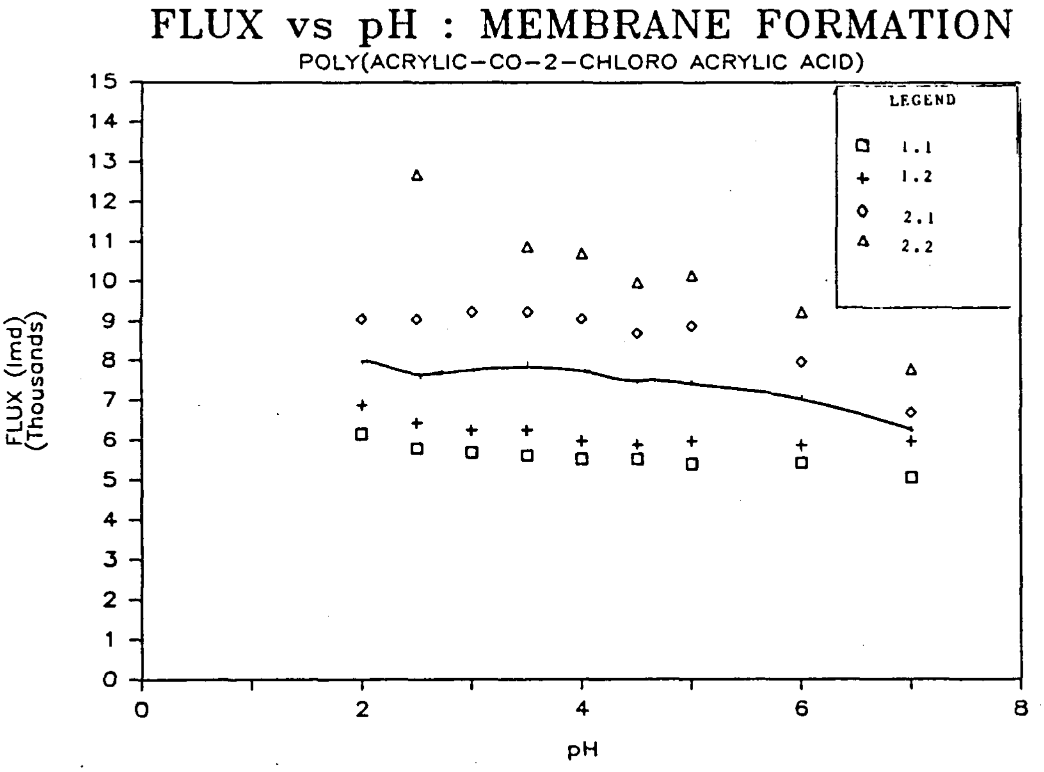


Fig. 5.3.23

on the other hand. Coupled to this is the fact that the swelling of the polymer is severely inhibited by the crosslinking reaction.

As the crosslinks are broken by saponification at above pH 6,00, the charge density increases rapidly. This causes an increase in rejection and a noticeable decrease in flux (See Figs. 5.3.21 and 5.3.22).

(iii) Poly(acrylic-co-methacrylic-co-2-chloro acrylic acid)

The $\overline{K_f}$ value is 0,81. The same "plateau"-effect, referred in the previous section, occurs for rejection by these membranes at pH 3,5 to 5,0. The explanation for this phenomenon is the same as in the previous Section (See Fig. 5.3.24).

The flux behaviour is essentially the same for these zirconium-poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid) membranes, as for the zirconium-poly(acrylic acid-co-2-chloro acrylic acid) membranes and the explanation for this is the same (See Fig. 5.3.25).

(iv) Poly(methacrylic acid-co-2-chloro acrylic acid)

Hydrous zirconium (iv) oxide-poly(methacrylic acid-co-2-chloro acrylic acid) membranes were formed, but due to experimental error the flux figures taken during formation were not reliable and thus no figures are reported or discussed.

5.3.3 ACID STRENGTH AND REJECTION

For the membranes having homopolymers as polyelectrolytes, there is a definite relationship between the pKa and the $\overline{Rf}$ values. This relationship is shown in Fig. 5.3.26.

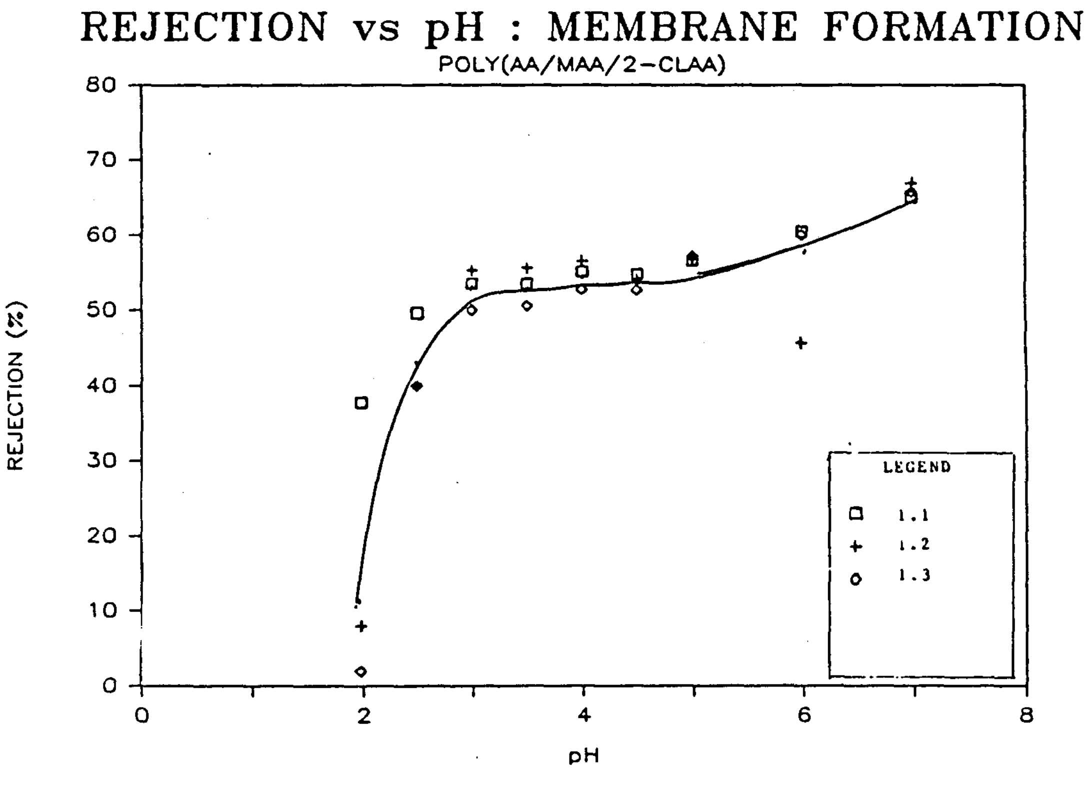


Fig. 5.3.24

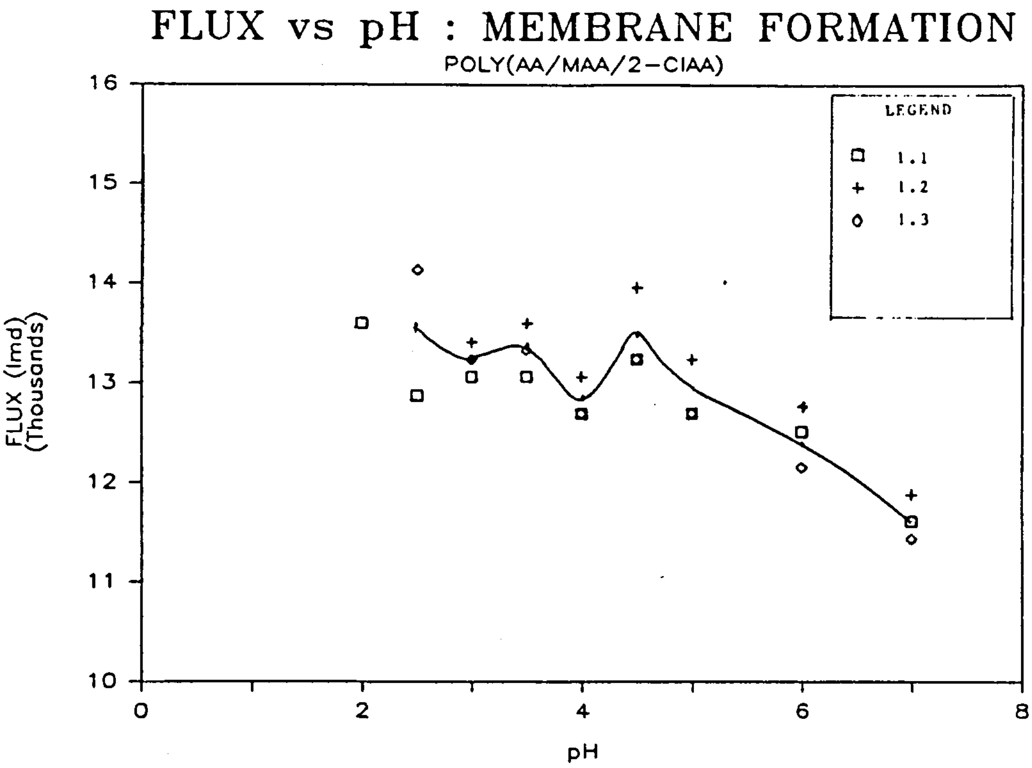


Fig. 5.3.25

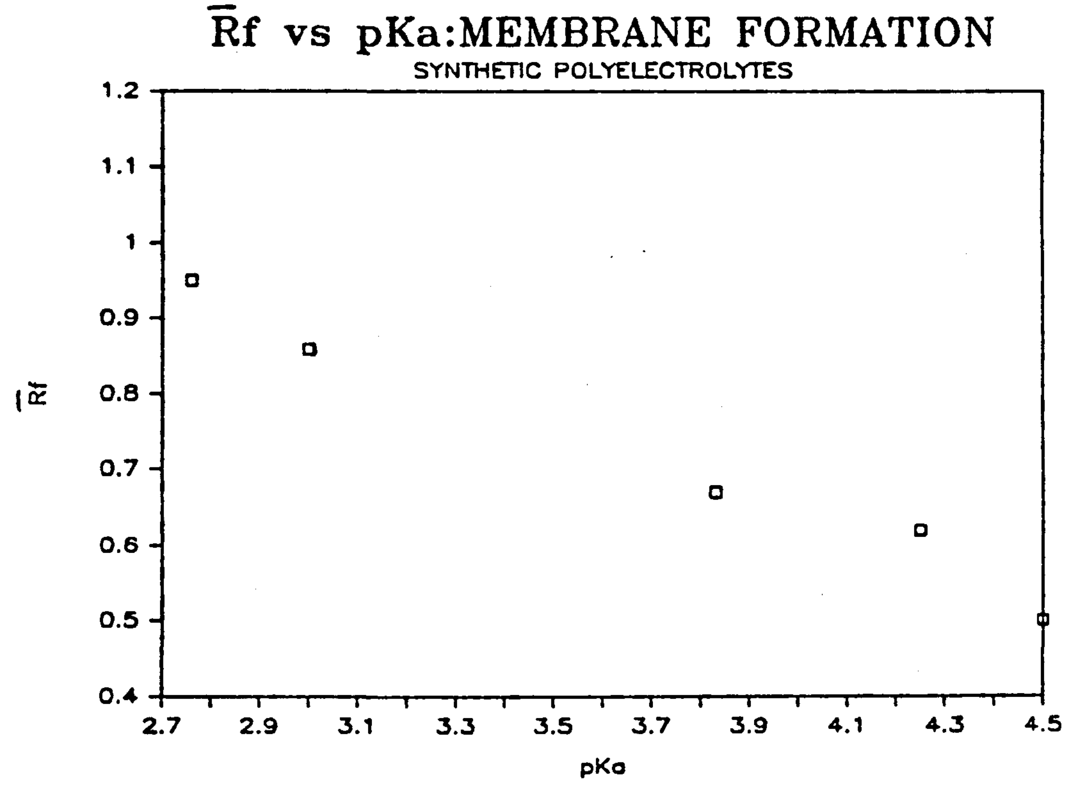


Fig. 5.3.26

There is a definite increase in the $\overline{Rf}$ values as the pKa decreases. This is due to the increasing degree of ionisation at pH 3,5 as the pKa values decrease.

As these are ion-exchange- type membranes, the above relationship is to be expected.

5.4 MEMBRANE PERFORMANCE

Membranes were evaluated, in terms of Lonsdale's figures of merit [54], in the following cases:

- Membrane performance in terms of time, as an indication of membrane stability.
- Membrane performance as a function of pH, 18 hours after the completion of formation.

5.4.1 MEMBRANE STABILITY

The results are reported below.

Membrane	A^2/B					
no.	1		2		3	
Time (h)	0	18	0	18	0	18
Zr-PAA-1	0,15	0,26	0,12	0,31	0,17	0,32
Zr-PAA-2	0,39	0,60	0,58	0,27	0,21	0,69
Zr-PMAA-1	0,45	0,37	0,53	0,39	0,49	0,39
Zr-PMMA-3	0,17	0,17	0,20	0,16	0,18	0,17
Zr-PMMA-4	0,24	0,85	1,22	0,85	1,15	0,87
Zr-PCIAA-3	0,44	0,38	0,49	0,39	-	-
Zr-PCIAA-1	0,45	0,37	0,56	0,49	0,48	0,48
Zr-PIA-1	0,38	0,42	0,52	0,47	0,37	0,41
Zr-PIA-2	0,49	0,45	0,49	0,49	0,52	0,45
Zr-PVSA-1	0,21	0,26	0,24	0,31	0,22	0,29
Zr-PAA/MAA-1a	0,47	0,43	-	-	-	-
Zr-PAA/MAA-1b	0,62	0,54	-	-	-	-
Zr-PAA/MAA-1c	0,76	0,61	1,12	0,89	1,05	0,83
Zr-PAA.CIAA-1	0,35	0,31	0,51	0,40	0,46	0,40
Zr-PAA/CIAA-2	0,82	0,70	1,07	1,13	1,07	0,92
Zr-PAA/IA-2	0,24	0,48	0,25	0,54		
Zr-PAA/IA-3	0,83	0,85	0,71	0,74		
Zr-PMAA/CIAA-1	0,78	0,61	0,62	0,63	0,60	0,54
Zr-TERP-1	0,77	0,65	0,86	0,76	0,78	0,69

Table 5.4.1: Membrane performance figures. Times given are from the completion of formation

The membranes were evaluated in terms of Lonsdale's [66] figures of merit, which take into consideration flux, rejection, pressure and feed salt concentration figures, rather than in terms of rejection figures alone, which are influenced by factors such as feed salt concentration.

The testing was short-term, being done after only 18 hours, and therefore no long-term predictions as regards membrane stability could be made. Comparisons were drawn only as the increase or decrease in the A^2/B values after 18 hours of testing.

Using the increase or decrease in A^2/B values, and assuming

$$\Delta \text{FOM} = [(A^2/B)_t/(A^2/B)_f]-1$$

where

ΔFOM = Change in figures of merit

$(A^2/B)_t$ = Figure of merit after 18 hours

$(A^2/B)_f$ = Figure of merit after completion of formation and assuming

$\overline{\Delta \text{FOM}} = \Sigma \Delta \text{FOM}/n$

where

n = number of membranes evaluated, the following table can be completed listing membranes in their comparative relative stabilities.

Membrane	$\overline{\Delta \mathrm{FOM}}$	Stability
Zr-PAA	+0,915	+
Zr-PVSA	+0,283	+
Zr-PAA/IA	+0,042	+
Zr-PIA	-0,017	+/-
Zr-PMAA/ClAA	-0,101	-
Zr-PMAA	-0,107	-
Zr-PAA/ClAA	-0,108	-
Zr-PClAA	-0,129	-
Zr-TERP	-0,129	-
Zr-PAA/MAA	-0,165	-
Zr-PAA/VAc	-0,288	-

Table 5.4.2: Relative membrane stabilities for Zr-polyelectrolyte composite membranes, determined over a period of 18 hours.

Membrane stability is a function of the strength of the hydrous zirconium (iv) oxide-polyelectrolyte bond. Assuming chelation to be the mechanism of bonding between the hydrous zirconium oxide and the polyelectrolyte, the following points are of importance:

- 5- and 6-membered rings are the most stable in chelate ring formations. (See Section 2.4.)
- With poly(acrylic acid) as model, the structure of the chelate ring would have to be the following (Fig. 5.4.1):

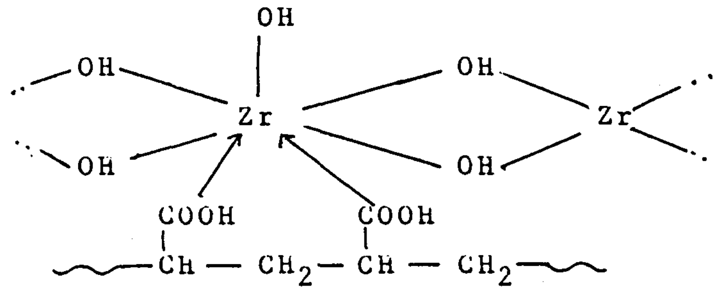
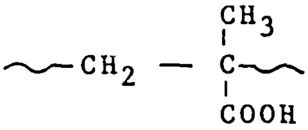


Figure 5.4.1 : Schematic representation of chelate ring formation

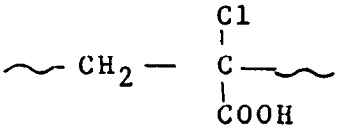
Thus, in the case of poly(acrylic acid) there is a 6-membered ring and both carboxylic groups must be on the same side as the polymer chain. Whereas this is undoubtedly sterically less favourable than for them to be trans to each other, there are no other groups involved to make it sterically even less favourable. It would, therefore be, expected that with polymers of -substituted poly(acrylic acids), the added steric hindrance of the groups in the -position would lessen the degree of chelation, or the strength of the chelate bond.

Thus membranes of polymers containing (i) methyl groups;



$$\sim CH_2 - \underset{COOH}{\overset{CH_3}{C}} \sim$$

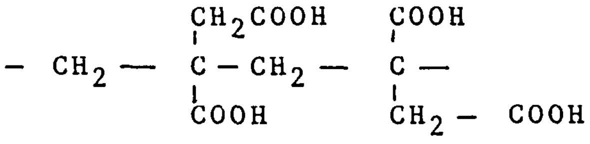
and (ii) chloro groups,



$$\sim CH_2 - \underset{COOH}{\overset{Cl}{C}} - \sim$$

would be expected to be less stable than the poly(acrylic acid) membrane. As can be seen from Table 5.4.1 this is so.

As far as poly(itaconic acid) is concerned, it would, in the light of the above argument alone, be expected to be extremely unstable. It can however, be described as fairly stable.



$$- CH_2 - \underset{COOH}{\overset{CH_2COOH}{C}} - CH_2 - \underset{CH_2 - COOH}{\overset{COOH}{C}} -$$

The above representation shows, however, that there are four different possibilities for chelation, including 5-, 6-, 7- and 8-membered rings.

For the acrylic acid copolymers, the question of stability would be clarified by answers to two questions:

- What is the percentage of acrylic acid in the copolymer
- What is the structural composition of the copolymer (i.e. random or alternating)

In the case of a copolymer which consists of two monomers, the homopolymers of which form stable membranes with hydrous Zr (iv) oxide, it would be expected that a stable membrane would be formed with the hydrous zirconium (iv) oxide-co-polymer system. This happens with the poly(acrylic acid-co-itaconic acid) copolymer. In a copolymer where one of the monomers forms a stable membrane as a homopolymer, whereas the other does not, membrane stability will be affected by:

- The amount of the "stable" monomer
- The degree to which the "unstable" monomer will disrupt the sequence of "stable" monomers in the polymer chain

Thus, with acrylic acid-monomer(x) copolymers, membrane stability will depend on copolymer composition. Looking at the "unstable" membranes containing acrylic acid and then at the composition of these copolymers, it is noticeable that none of these copolymers contain more than 65% acrylic acid. Studies could well be done on the effect of increasing the acrylic acid content.

5.5 THE EFFECT OF PH ON MEMBRANE PERFORMANCE

After 18 hours of testing, of the membrane the pH was adjusted to 6,0 and conditions were allowed to stabilize, and the flux and rejection values then taken. The pH was then adjusted to pH 9,0 and the above repeated. The time allowed for stabilization of conditions was 0,75 hours.

The results are reported below:

Polymer	Rejection (%)			Flux ($l.m^{-2}.d^{-1}$)			A^2/B ($x10^5$)		
pH	7,0	8.,	9,0	7,0	8,0	9,0	7,0	8,0	9,0
PAA-2.1	89,2	91,8	89,4	2080	1900	1990	0,60	0,75	0,59
PAA-2.2	73,1	63,2	71,9	2810	2990	2170	0,27	0,18	0,87
PAA-2.3	90,4	93,2	90,2	2080	1810	1900	0,69	0,87	0,61
PMAA-4.1	71,6	77,6	75,4	9060	7790	7790	0,80	0,94	0,83
PMAA-4.3	71,8	77,1	75,2	9780	8335	8520	0,87	0,98	0,90
PCIAA-3.1	48,3	53,4	58,7	11420	10870	9870	0,38	0,44	0,49
PCIAA-3.3	47,9	52,1	57,4	11960	11660	10510	0,39	0,45	0,50
PCIAA-2.1	41,9	52,1	54,3	7970	7520	7430	0,21	0,29	0,31
PCIAA-2.2	41,5	51,8	54,0	8880	8150	8070	0,22	0,31	0,34
PCIAA-2.3	40,2	50,8	53,0	8340	7700	7520	0,20	0,28	0,30
PCIAA-1.1	55,1	61,7	63,2	8430	8060	7790	0,37	0,46	0,48
PCIAA-1.2	59,7	63,6	65,0	9330	8770	8600	0,49	0,56	0,57
PCIAA-1.3	60,6	64,1	65,6	8880	8520	8340	0,48	0,54	0,56
PVSA-4.1	39,4	44,0	45,2	11415	11230	12140	0,26	0,31	0,35
PVSA-4.2	40,1	43,7	44,7	13050	13050	13050	0,31	0,36	0,37
PVSA-4.3	40,4	43,7	44,7	12330	12140	13050	0,29	0,33	0,37

Table 5.5.1: The effect of pH on membrane performance

Assuming a purely ion-exchange mechanism as method of rejection, an increase in rejection points to an increase in charged sites on the membrane.

(1) Homopolymers

At neutral pH, one would expect the polymer, to be nearly fully ionised after 18 hours subsequent to membrane formation. However: of the homopolymers, all five showed an increase in rejection at pH 7.0 to pH 8.0, indicating an increase in charged sites on the membrane.

Zirconium oxide-poly (acrylic acid) and zirconium oxide-poly (methacrylic acid) membranes show:

- An increase in rejection at pH 7,0 to 8,0, but a decrease in rejection at pH 8,0 to 9,0
- At the same time, there is a decrease in flux at pH 7,0 to 8.0, and increase in flux at pH 8,0 to 9,0

This points to: (i) an increase in charge on these polymers at pH 7,0 and 8,0
(ii) removal of the polymer from the zirconium at pH values higher than 8.0

The latter is to be expected from the literature [37], for poly(acrylic acid), and by assumption, due to similarity, for poly(methacrylic acid).

However, it would appear that some of the ionizable sites on these polymers are not ionised at pH 7,0. This could be due to some shielding of carboxylic groups by charged sites on the membranes. (Donnan exclusion effect.)

The zirconium oxide - poly(itaconic acid) membranes show:

- An increase in rejection at pH 7,0 to pH 8,0
- An increase in rejection at pH 8,0 to pH 9,0
- Sustained decrease in flux at pH 7,0 to pH 9,0

The increase in rejection at pH 7,0 and pH 8,0 is to be expected, in the light of the behaviour of the zirconium oxide-poly (acrylic acid) and zirconium oxide-poly (methacrylic acid) membranes. The increase in rejection at pH 8,0 to pH 9,0 can be explained as follows: because of the two different carboxylic groups present, which ionize at different rates, the effect of shielding will be greater for these membranes, which have as a polyelectrolyte a polymer with an unsaturated, dicarboxylic acid as monomer, than for the membranes which have as polyelectrolyte a polymer, with an unsaturated, monocarboxylic acid as monomer. The fact that they are not removed at pH 8 also points to stronger attraction to the Zirconium oxide in this pH range.

The zirconium oxide-poly(2-chloro acrylic acid) membranes all show a sustained increase in rejection at pH 7,0 to 9,0, with a simultaneous decrease in flux. This unquestionably indicates an increase in charged sites. This membrane has as its polyelectrolyte a polymer with an unsaturated, monocarboxylic acid as monomer. In this case, ester crosslinks made during membrane formation and testing were saponified by the addition of sodium hydroxide, which led to the formation of -hydroxy carboxylates, and thus an increase in charge on the membrane.

It is at this stage possible to predict in terms of the behaviour of the membranes with homopolymers as polyelectrolytes, the behaviour of the membranes with copolymers as polyelectrolytes at elevated values of pH.

In the light of the above results, and their explanation, all the membranes with co- and terpolymers as their polyelectrolyte components should show a continued increase in rejection at pH 7,0 to 9,0, if both the comonomers have ionizable groups. If one of the comonomers is neutral, the membrane should behave in exactly the same way as the membrane with the homopolymer of the ionizable monomer.

(ii) Copolymers

The rejection results for membranes having copolymers or terpolymers as polyelectrolyte components, show that:

Five of these membranes sustained an increase in rejection at pH 7,0 to 9,0, and simultaneously, a decrease in flux.

The five polymers showing a sustained increase in rejection were:

Zr-poly(acrylic acid-co-methacrylic acid)
Zr-poly(acrylic acid-co-2-chloro acrylic acid)
Zr-poly(acrylic acid-co-itaconic acid)
Zr-poly(methacrylic acid-co-2-chloro acrylic acid)
Zr-Poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid)

All these membranes therefore have as polyelectrolytes co- or terpolymers having two or more different carboxylic groups.

One membrane showed an increase in rejection at pH 7,0 to 8,0, then a decrease in rejection at pH 8,0 to 9,0. The flux behaviour is consistent with the rejection, showing an increase at pH 8,0 to 9,0, and a decrease at pH 7,0 to 8,0. This was:

Zr-poly(acrylic acid-co-vinyl acetate)

Comparison showed its behaviour was identical to that of the Zr-poly(acrylic acid) membranes.

Thus, the theory propounded in Section A is correct.

The anomaly here is the behaviour of the zirconium-poly(vinyl sulphonic acid) membranes. These membranes show a sustained increase in rejection from pH 7,0 to pH 9,0. This is in spite of the repeat unit of the polyelectrolyte having only one ionisable group. No reason can be offered.

5.6 CHARGE DENSITY EVALUATIONS

The charge density evaluations were done on seven membranes. The evaluations were due as described in Section 4.5. The results are given below:

Membrane	Rejection (%)	Flux ($l/m^2/d$)	A^2/B (x 10^5)	C.D (x 10^4)
Zr-PAA-2.1	89,2	2 080	0,60	10,55
PMAA-4.1	71,6	9 060	0,80	2,00
Zr-PAA/IA	78,0	5 980	0,74	4,86
Zr-PAA/MAA-1.4	60,9	9 780	0,54	6,32
Zr-TERP-1.2	64,0	12 140	0,76	4,15
Zr-PMAA/ClAA-1.1	58,2	12 500	0,61	3,27
Zr-PAA/ClAA-2.2	73,5	7 250	0,75	2,35

Table 5.7.1: Figures of flux, rejection, membrane performance and charge density (C.D.) of Zr-polyelectrolyte membranes

As can be seen from the table, there seems to be no direct linear relation between the thermodynamically effective charge density of the membranes tested, and the flux and rejection values attained.

As regards the membrane performance figures, however, there is a trend, not a definite relationship. It does appear that the membranes become "worse" as the charge density increases.

This is, however, just a general trend observed in the evaluation of seven different membranes, and, as such, no specific relationship can be shown to exist. A general explanation for this is that an increase in charge density might affect the flux adversely through more charge repulsion and swelling, while not affecting the rejection in as favourable a degree. The flux decrease is therefore a more important factor in this case than the rejection increase.

CHAPTER 6

CONCLUSIONS

6.1 POLYMERS

(i) Insight was required in terms of the complex behaviour of polyelectrolytes with zirconium in order to understand dynamic membrane formation. This study, though initial, is providing trends between chemical structure and membrane performance.

(ii) Accomplished, therefore, was:

- Synthesis of monomers: 2-chloro acrylic acid

- Techniques for the polymerization of acidic monomers of different pKa values in homopolymer form and in copolymer form, although no prior knowledge exsists in some of these cases. Totally novel systems includes poly(methacrylic acid-co-2-chloro acrylic acid) and poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid), whereas a modified system is poly(acrylic acid-co-2-chloro acrylic acid).

- Techniques for characterization developed, in cooperation with N. Dowler [94]. These techniques, though the scheme is accepted have hitherto not been applied to carboxylic copolymer systems.

- A converted technique for the calculation of charge densities developed, in cooperation with N. Dowler [94], from literature descriptions that apply to inorganic and liquid film membranes.

- Polymers of varying molecular mass, conversion and copolymer ratios were synthesized.

6.2 MEMBRANE FORMATION

The following polymers form dynamic hydrous zirconium(iv) oxide-polyelectrolyte composite membranes:

- -Poly(acrylic acid)
- -Poly(methacrylic acid)
- -Poly(2-chloro acrylic acid)
- -Poly(itaconic acid)
- -Poly(vinyl sulphonic acid)
- -Poly(acrylic acid-co-methacrylic acid)
- -Poly(acrylic acid-co-2-chloro acrylic acid)
- -Poly(acrylic acid-co-itaconic acid)
- -Poly(methacrylic acid-co-2-chloro acrylic acid)
- -Poly(acrylic acid-co-vinyl acetate)
- -Poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid)

The majority of these polymers have never been used to form zirconium-polyelectrolyte composite membranes. Exceptions are poly(acrylic acid), poly(methacrylic acid) and poly(vinyl sulphonic acid).

6.2.2 FLUX DURING FORMATION

Membrane flux depends on the charge density, or degree of ionisation of the polymer. The flux behaviour for homopolymers of unsaturated, monocarboxylic acids is governed by two mechanisms: first, the increase in flux due to increase in charge density as the polymer ionises (due to increasing hydrophylicity) and, second, the decrease in flux due to pore size decrease due to polymer swelling caused by like-charge repulsion.

These two factors remain more or less in balance until such time as the degree of ionisation on the polymer exceeds 50%, and at pH pKa+1 the swelling factor becomes dominant and there is a marked decrease in flux.

Although not clear-cut, the theory could be expanded to include homo-polymers of unsaturated dicarboxylic acids and copolymers. In these cases, the presence of the two or more different carboxylic groups make quantitive evaluations of flux behaviour virtually impossible, expecially as the degree of ionisation of a given pH would also, in copolymers, depend on the copolymer composition. However, it would seem that the same does apply, in broad terms; when the polymer reaches a level when more than 50% of its ionisable sites are ionised, swelling takes over the major role in governing flux behaviour.

6.2.3 REJECTION BEHAVIOUR

The rejection behaviour of the non-chloro-containing polymer is linked directly to the degree of ionisation of the polymer. This was established from figures relating to the membranes having as their polyelectrolyte component a homopolymer with a unsaturated vinyl monomer containing only one ionisable group. This must apply to the rejection of Zr-copolymer membrane as well, although the relationship is not as clearly defined.

For the chloro-containing polymers, the rejection behaviour is influenced by the "disappearance" of charge sites on the membrane due to crosslinking reactions involving the carboxylic groups. These reactions lead to the formation of ester bonds (inter-chain) and thus a decrease in the number of ionisable sites. At pH values above 6,0 these ester bonds are broken by saponification. This leads to an increase in rejection values.

6.3 MEMBRANE PERFORMANCE

6.3.1 MEMBRANE STABILITY

Evaluation of membrane stability in terms of the average charge in A^2/B values for the first 18 hours after completion of membrane formation reveals the following:

The following three membranes form "stable" membranes.

Zirconium oxide-poly(acrylic acid)
Zirconium oxide-poly(itaconic acid)
Zirconium oxide-poly(acrylic acid-co-itaconic acid)

These membranes show an increase in performance figures or stable performance figures.

All the other membranes evaluated show a decrease in performance figures which range from 10% to 23% over a period of 18 hours.

6.3.2 PEAK PERFORMANCE

Comparisons between hydrous zirconium(iv) oxide-poly(acrylic acid) membranes and other hydrous zirconium)iv) oxide-polyelectrolytes membranes were done in terms of the average figures of merit after 18 hours of testing. The best two membranes of each polymer was taken into consideration. Under the conditions of formation and testing as they were, the following membranes performed better than the Zr-PAA-2 membranes:

-Zr-PAA/VAC-1
-Zr-PAA/CIAA-2
-Zr-PMAA-4
-Zr-PAA/MAA-1
-Zr-TERP-1
-Zr-PAA/IA-3

Of these the hydrous zirconium(iv) oxide-poly(acrylic acid-co-vinyl acetate) (Zr-PAA/VAC-1) membranes were outstanding, being some 70% better than the next best membrane and 175% better than the hydrous zirconium(iv) oxide-poly(acrylic acid) membrane (Zr-PAA-2).

6.3.3 pH DEPENDENCE

6.3.3.1 REJECTION BEHAVIOUR

Rejection behaviour evaluated at given pH values confirm that:

- Because of shielding by charged sites the polyelectrolytes in composite membranes are not fully ionised at neutral pH.
- In the case of homopolymers the effect of shielding is greater for polymers of unsaturated dicarboxylic acids than for polymers of unsaturated monocarboxylic acids [poly(2-chloro acrylic acid) excluded].
- The effect of shielding of carboxylic groups is further borne out by the rejection behaviour of the co- and terpolymers evaluated as polyelectrolytes, particularly the trend of behaviour of the zirconium oxide-poly(acrylic acid-co-vinyl acetate) membranes and the zirconium oxide-poly(acrylic acid) membranes.

6.3.3.2 FLUX BEHAVIOUR

The flux behaviour of the membranes at evaluated values of pH is consistent with the theory propounded in Section 6.2.3.1.

6.3.3.3 THE CHLORO-POLYMERS

Due to saponification of ester bonds during the evaluation of the pH dependence, the rejection for membranes having these polymers as polyelectrolyte component increases with increase in pH.

6.4 CHARGE DENSITY

Two trends were observed in the charge density measurements.

First, there was an increase in rejection figures with the increase in charge density for the membranes evaluated. Second there was a decrease in the figures of merit [54] for these membranes. This brought to the fore a very important distinction in the interpretation of membrane results, namely, the judgement of membranes in terms of their rejection capabilities above, or in terms of their figures of merit, which take factors such as flux, feed concentration and pressure into account. (It is theoretically possible to reform a dynamic membrane in order to lower the flux and increase the rejection).

(Increased charge density would cause more polymer swelling, of course, and thus a lower flux value, which would decrease the membrane performance.)

The work done in this study helps to provide a better understanding of the process of dynamic composite membrane formation.

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APPENDIX A

A.1 Table of results

The complete results of formation and performance for the zirconium-polyelectrolyte composite membranes are tabled below. (Table A.1) The polymers used as polyelectrolyte component are denoted by their assigned symbol (See Chapter 4) followed by a period and a number, e.g. PAA-2.1. The number after the period denotes the number of the membrane formed with that polymer.

POLYMER	pH 2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PAA-1.1									70.6*** (1810)** [0.15]*	82.8 (1540) [0.26]		
PAA-1.2									70.8 (1450) [0.12]	86.3 (1360) [0.30]		
PAA-1.3									78.1 (1360) [0.17]	87.2 (1360) [0.32]		
PAA-2.1	15.0 (4890)	35.0 (3900)	47.1 (4170)	54.1 (3400)	62.0 (3800)	62.0 (3530)	74.6 (3260)	84.5 (2450)	85.3 (1900) [0.39]	89.2 (2080) [0.60]	91.8 (1900) [0.75]	86.1 (1990) [0.59]
PAA-2.2	3.7 (36240)	13.7 (12300)	24.8 (9510)	58.4 (4410)	66.2 (3990)	72.6 (3800)	77.8 (3530)	88.0 (2540)	89.2 (1990) [0.58]	73.1 (2810) [0.27]	63.2 (2990) [0.18]	91.9 (2170) [0.86]
PAA-2.3	4.0 (28360)	9.4 (9510)	37.5 (5080)	45.3 (4070)	53.4 (3900)	65.9 (3440)	73.7 (3170)	85.1 (2360)	76.3 (1810) [0.21]	90.4 (2080) [0.69]	93.2 (1810) [0.87]	90.2 (1900) [0.61]
PMAA-1.1	15.2 (7800)	21.1 (7070)	17.5 (7340)	24.4 (7340)	34.7 (8150)	45.5 (7520)	50.7 (7620)	58.2 (7160)	65.6 (6610) [0.45]	59.7 (7070) [0.37]		

pH

	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PMAA-1.2	14.3*** (11330)**	22.7 (8430)	20.6 (8340)	28.2 (8150)	44.5 (7970)	50.1 (7880)	54.9 (7880)	62.9 (7440)	67.7 (7160) [0.53]*	58.6 (7790) [0.39]		
PMAA-1.3	18.9 (9240)	25.6 (7520)	19.8 (7700)	25.2 (7520)	45.0 (7610)	48.9 (7610)	53.7 (7610)	61.2 (6900)	67.2 (6700) [0.49]	57.4 (7520) [0.39]		
PMAA-4.1	25.1 (10870)	34.2 (10500)	45.4 (10330)	50.6 (9980)	53.4 (9780)	60.0 (9970)	66.1 (9970)	73.1 (9140)	81.4 (7170) [1.21]	71.6 (9060) [0.80]	77.6 (7790) [0.94]	75.4 (7790) [0.83]
PPMAA-4.2	21.9 (13600)	32.2 (12140)	45.0 (11050)	51.7 (10330)	54.7 (10330)	61.1 (10330)	68.9 (10150)	74.1 (9600)	80.9 (340) [1.22]	71.2 (9780) [0.85]	76.6 (8340) [0.95]	
PMAA-4.3	5.9 (18120)	25.7 (13050)	39.7 (11420)	46.8 (11230)	51.0 (10330)	58.4 (10510)	68.7 (10690)	73.4 (9970)	79.1 (8700) [1.15]	71.8 (9780) [0.87]	77.1 (8340) [0.98]	75.2 (8520) [0.90]
PClAA-1.1	32.4 (10870)	45.2 (12050)	48.2 (11330)	51.0 (10870)	52.5 (10510)	54.4 (10510)	55.5 (9880)	57.0 (9880)	57.4 (9420) [0.45]	55.1 (8430) [0.37]	61.7 (8060) [0.46]	63.2 (7790) [0.48]
PClAA-1.2	5.6 (20840)	45.4 (13230)	51.1 (12770)	54.6 (12050)	56.2 (11330)	57.3 (11600)	57.7 (10880)	57.0 (10870)	59.3 (10870) [0.86]	59.7 (9330) [0.49]	63.6 (8970) [0.56]	65.0 (8600) [0.57]

	pH											
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PCIAA-1.3	6.6 (20930)	40.0 (12600)	47.5 (11330)	51.0 (12050)	52.8 (11050)	54.1 (12050)	57.0 (10420)	58.3 (10060)	59.3 (9420) [0.48]	60.6 (8880) [0.48]	64.1 (8520) [0.54]	65.6 (8335) [0.56]
PCIAA-3.1		45.9 (9970)	48.3 (10570)	49.8 (11960)	50.1 (11870)	48.9 (11960)	46.8 (11960)	46.3 (11600)	51.5 (11780) [0.44]	48.3 (11420) [0.38]	53.4 (10870) [0.44]	58.7 (9780) [0.49]
PCIAA-3.2		40.6 (12320)	45.8 (12320)	48.8 (13950)	49.5 (12680)	47.6 (13590)	48.2 (13410)	46.3 (13050)	52.0 (12870) [0.49]	47.9 (11960) [0.39]	52.1 (11000) [0.45]	57.4 (10010) [0.50]
PCIAA-2.1	29.8 (7430)	38.9 (7610)	43.8 (8340)	46.0 (8700)	46.6 (8520)	45.8 (8520)	40.2 (8520)	33.1 (8480)	37.5 (8700) [0.19]	41.9 (7970) [0.21]	52.1 (7520) [0.29]	54.3 (7430) [0.35]
PCIAA-2.2	22.7 (11050)	39.8 (8700)	44.8 (9060)	47.2 (9330)	48.1 (9330)	47.6 (9330)	41.1 (9330)	35.6 (9200)	37.1 (9700) [0.20]	41.5 (8880) [0.22]	51.8 (8130) [0.31]	54.6 (8070) [0.34]
PCIAA-2.3	34.2 (10870)	45.6 (7700)	47.2 (8430)	47.5 (8790)	47.1 (8700)	45.6 (8520)	36.7 (8430)	36.1 (8500)	36.7 (8740) [0.18]	40.2 (8340) [0.20]	50.8 (7700) [0.28]	53.1 (7520) [0.30]

	pH											
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PJA-3.1	20.8 (11230)	33.5 (11780)	42.0 (12500)	45.4 (12680)	47.1 (11960)	48.6 (12140)	51.4 (12140)	51.4 (12140)	53.4 (11960) $\boxed{0.49}$	54.7 (10510) $\boxed{0.45}$	57.8 (10150) $\boxed{0.49}$	61.0 (9600) $\boxed{0.53}$
PIA-3.2	3.3	11.4	16.5	24.3 (31980)	29.2 (25900)	38.0 (18750)	38.1 (18750)	51.4 (13590)	47.3 (15400) $\boxed{0.49}$	53.1 (12410) $\boxed{0.49}$	57.8 (11415) $\boxed{0.56}$	61.4 (10510) $\boxed{0.59}$
PIA-3.3	28.2	28.3 (26480)	31.9 (21700)	35.1 (17400)	44.6 (13230)	46.1 (12865)	42.2 (14686)	49.8 (13410)	53.4 (12865) $\boxed{0.52}$	51.9 (11800) $\boxed{0.45}$	55.0 (11230) $\boxed{0.49}$	61.4 (10150) $\boxed{0.52}$
PIA-2.1	28.2 (10240)	33.3 (10060)	42.4 (9780)	44.7 (9330)	49.6 (8880)	51.7 (8430)	51.6 (8340)	53.9 (8340)	56.5 (8340) $\boxed{0.38}$	58.3 (8520) $\boxed{0.42}$		
PIA-2.2	14.7 (20930)	39.8 (9880)	48.6 (9880)	50.5 (9880)	53.7 (9880)	53.7 (9880)	54.7 (9880)	56.3 (9880)	58.5 (10420) $\boxed{0.52}$	56.1 (10420) $\boxed{0.47}$		
PIA-2.3	34.2 (10420)	47.4 (9515)	49.2 (9515)	51.1 (9330)	53.4 (8880)	49.0 (9060)	50.7 (8790)	52.3 (9060)	52.8 (9510) $\boxed{0.37}$	55.7 (9330) $\boxed{0.41}$		
PVSA-4.1	15.2	31.7 18480	34.9 18120	38.0 17400	37.6 16700	35.9 16300		30.0 (17760)	25.1 (17400) $\boxed{0.21}$	39.4 11420 $\boxed{0.26}$	44.0 (11230) $\boxed{0.31}$	45.2 (12140) $\boxed{0.35}$

pH

	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PVSA-4.2	16.0	26.9 22640	31.0 25730	32.7 22830	38.8 20290	34.1 21020		28.5 (21400)	26.0 (18840) [0.24]	40.1 13050 [0.31]	43.7 (13050) [0.36]	44.7 (13050) [0.37]
PVSA-4.3	5.8	24.5 21340	24.3 24640	32.2 19570	33.2 18480	18120		24.8 (18480)	23.8 (19930) [0.22]	40.4 (12230) [0.29]	43.7 (12140) [0.33]	44.7 (13050) [0.37]
PAA/IA-2.1	2.5 (8150)	14.7 (6250)	19.8 (5530)	18.9 (5340)	28.0 (5070)	30.2 (4980)	40.2 (4710)	58.2 (4350)	64.7 (3800) [0.25]	77.8 (4350) [0.54]		
PAA/IA-2.2	3.3 (9970)	12.9 (6890)	16.4 (6250)	24.0 (5530)	24.7 (5340)	26.9 (5340)	41.8 (4980)	46.6 (4800)	56.0 (4440) [0.20]	75.3 (4440) [0.48]		
PAA/IA-2.3	3.3 (5890)	16.2 (4890)	19.8 (4340)	25.7 (4080)	25.7 (4340)	24.2 (4890)	40.2 (4170)	40.0 (4340)	53.4 (3620) [0.15]	73.1 (3620) [0.35]		
PAA/IA-3.1	15.6 (9060)	34.3 (8150)	40.6 (8700)	47.8 (9060)	51.0 (8600)	54.4 (8520)	60.8 (8150)	68.8 (7250)	76.5 (6250) [0.71]	78.0 (5980) [0.74]	81.9 (5250) [0.83]	85.9 (4350) [0.92]

	pH										
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PAA/IA-3.2	11.2	25.8	31.7	38.2	42.6	45.1	51.1	63.7 (10510)	73.5 (8650) [0.83]	75.6 (7880) [0.85]	78.3 (7700) [0.97]	83.5 (5700)
PAA/IA-3.3	3.3	30.1	33.0	40.0	43.3	47.2	53.3	60.0	75.1 (6520) [0.66]	77.1 (5990)	79.8 (5300)	84.0 (4440)
PAA/ClAA -1.1	32.6 (6160)	46.4 (5800)	49.7 (5700)	52.9 (5620)	54.5 (5530)	57.2 (5530)	58.7 (5440)	60.8 (5440)	65.9 (5070) [0.35]	62.0 (5440) [0.31]		
PAA/ClAA -1.2	34.2 (6885)	48.1 (6430)	51.9 (6250)	55.5 (6250)	58.0 (5980)	61.3 (5980)	62.5 (5980)	64.8 (5980)	70.6 (5980) [0.51]	65.2 (5980) [0.40]		
PAA/ClAA -1.3	29.2 (6700)	44.5 (6250)	48.6 (6160)	52.6 (6070)	55.2 (5890)	58.7 (5800)	62.6 (5800)	64.7 (5800)	70.6 (5440) [0.46]	65.2 (5890) [0.40]		
PAA/ClAA -2.1	50.1 (9060)	55.9 (9060)	58.5 (9240)	60.7 (9240)	63.2 (9060)	63.8 (8700)	63.9 (8880)	70.1 (7970)	77.9 (6700) [0.82]	73.5 (7250) [0.70]	76.8 (6700) [0.78]	80.9 (6160) [0.91]

	pH											
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
PAA/CIAA -2.2	20.8	29.6					68.0 (10870)	72.7 (4330)	78.2 (8520) $\boxed{1.07}$	79.2 (8520) $\boxed{1.13}$	79.8 (7970) $\boxed{1.10}$	84.5 (7250) $\boxed{1.38}$
PAA/CIAA -2.3	20.8 (25370)	47.9 (12680)	45.4 (16130)	60.0 (10870)	63.0 (10690)	65.3 (9970)	69.2 (10510)	74.6 (9240)	78.9 (7790) $\boxed{1.02}$	75.8 (8430) $\boxed{0.92}$	78.9 (7520) $\boxed{0.98}$	83.9 (6800) $\boxed{1.24}$
PMAA/ CIAA-1									63.4 (12870) $\boxed{0.78}$	58.1 (12500) $\boxed{0.61}$	60.1 (11960) $\boxed{0.63}$	63.6 (11050) $\boxed{0.68}$
PMAA/ CIAA-1.2									52.6 (15950) $\boxed{0.62}$	57.2 (13410) $\boxed{0.63}$	59.5 (13050) $\boxed{0.67}$	62.6 (11960) $\boxed{0.70}$
PMAA/ CIAA-1.3									55.6 (13590) $\boxed{0.60}$	53.9 (13230) $\boxed{0.54}$	56.2 (12680) $\boxed{0.57}$	59.6 (11600) $\boxed{0.60}$
TERP-1.1	37.9 (13590)	49.8 (12870)	53.7 (+£=%=)	53.7 (13050)	55.4 (12680)	55.0 (13230)	56.8 (12680)	60.7 (12500)	65.4 (11600) $\boxed{0.77}$	61.7 (11420) $\boxed{0.65}$	66.8 (10700) $\boxed{0.76}$	69.2 (10330) $\boxed{0.82}$

	pH											
	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	7.0^1	8.0^2	9.0^3
TERP-1.2	8.0 (27180)	40.1 (17400)	55.5 (13400)	55.8 (13590)	56.8 (13050)	54.5 (13950)	57.1 (13230)	45.9 (16850)	67.2 (11870) [0.86]	64.0 (12140) [0.76]	66.5 (11420) [0.80]	68.9 (10870) [0.85]
TERP-1.3	2.0 (36240)	40.1 (14130)	50.2 (13230)	50.8 (13230)	53.0 (12680)	52.9 (13230)	57.4 (12680)	60.3 (12140)	66.0 (11420) [0.78]	63.4 (11330) [0.69]	66.0 (10870) [0.75]	68.8 (13300) [0.80]
PAA/VAC-1.1	37.8 (4080)	55.9 (3990)	66.2 (4430)	71.2 (4350)	73.3 (4260)	78.0 (3900)	80.2 (3530)	88.1 (2900)	93.5 (2270) [1.14]	88.2 (2720) [0.71]	91.8 (2360) [0.92]	88.6 (2450) [0.67]
PAA/VAC-1.2	43.2 (4710)	60.2 (4800)	67.8 (5350)	73.3 (5260)	77.5 (5260)	81.5 (5070)	83.9 (4710)	90.9 (3800)	95.2 (3080) [2.13]	92.8 (3800) [1.71]	95.4 (3350) [2.43]	93.3 (3440) [1.68]
PAA/VAC-1.3	37.5 (4980)	56.6 (4890)	82.0 (5440)	84.7 (5440)	86.5 (5440)	88.0 (5260)	84.5 (4806)	91.9 (3900)	96.0 (3080) [2.57]	93.2 (3900) [1.87]	95.4 (3350) [2.43]	93.5 (3530) [1.78]

* Figures in round brackets : Flux in $1.m^{-2}\ d^{-1}$

** Figures in square brackets : A^2/B (xw5)

*** Figures of rejection (%)

1. After 18 hours of use
2. After 18,75 hours of use at pH 8.00
3. After 18,75 hours and 45 minutes at pH 9.00

A.2 Graphs

The graphs give a representation of some results tabled in Chapter 5. Figures A 2.1 to A 2.10 give graphic representations of membrane figures as pH, while Figures A 2.11 to A 2.13 give representations of charge density vs flux, rejection and membrane performance figures.

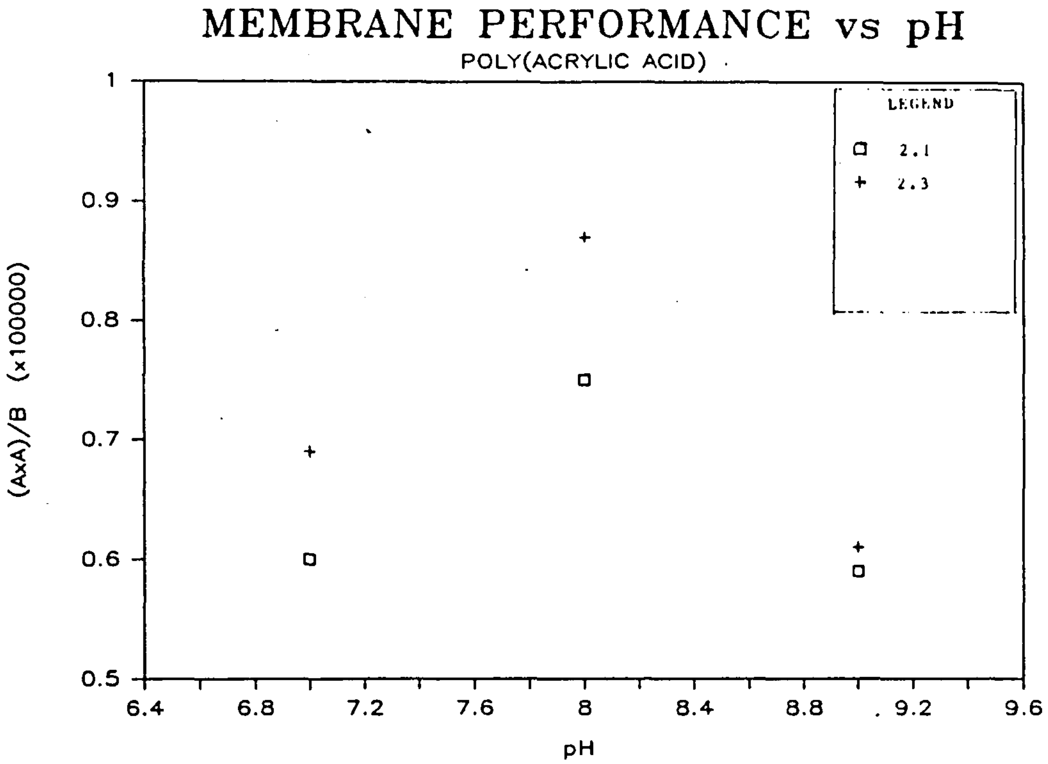


Fig. A.2.1

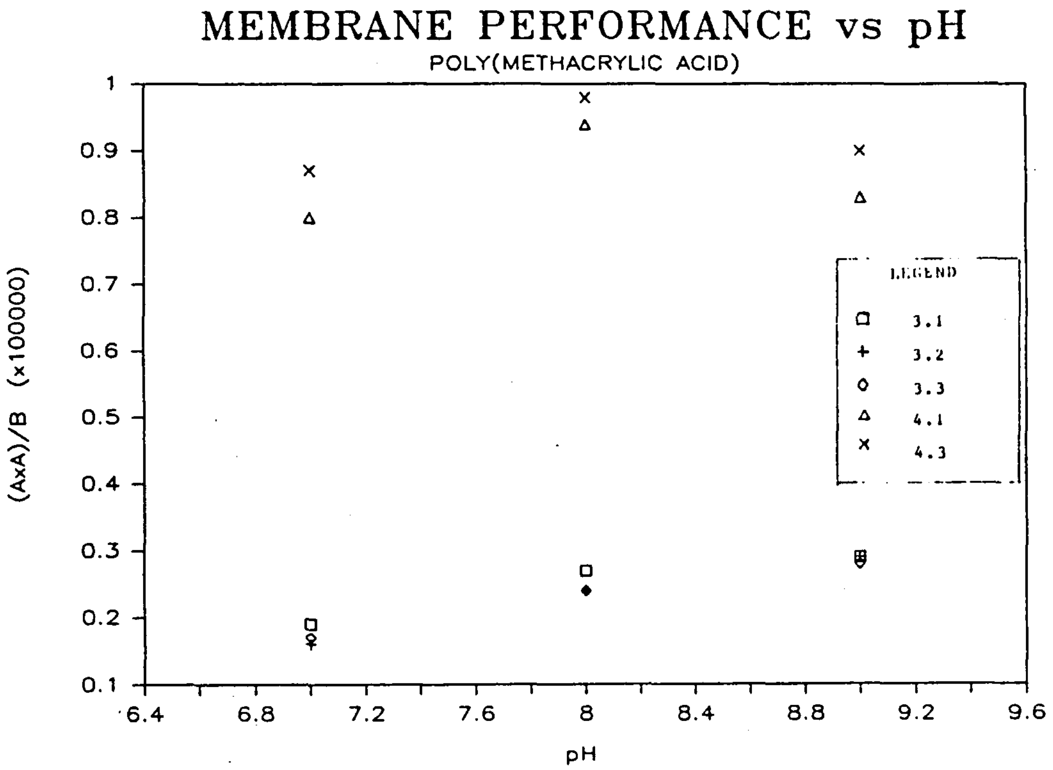


Fig. A.2.2

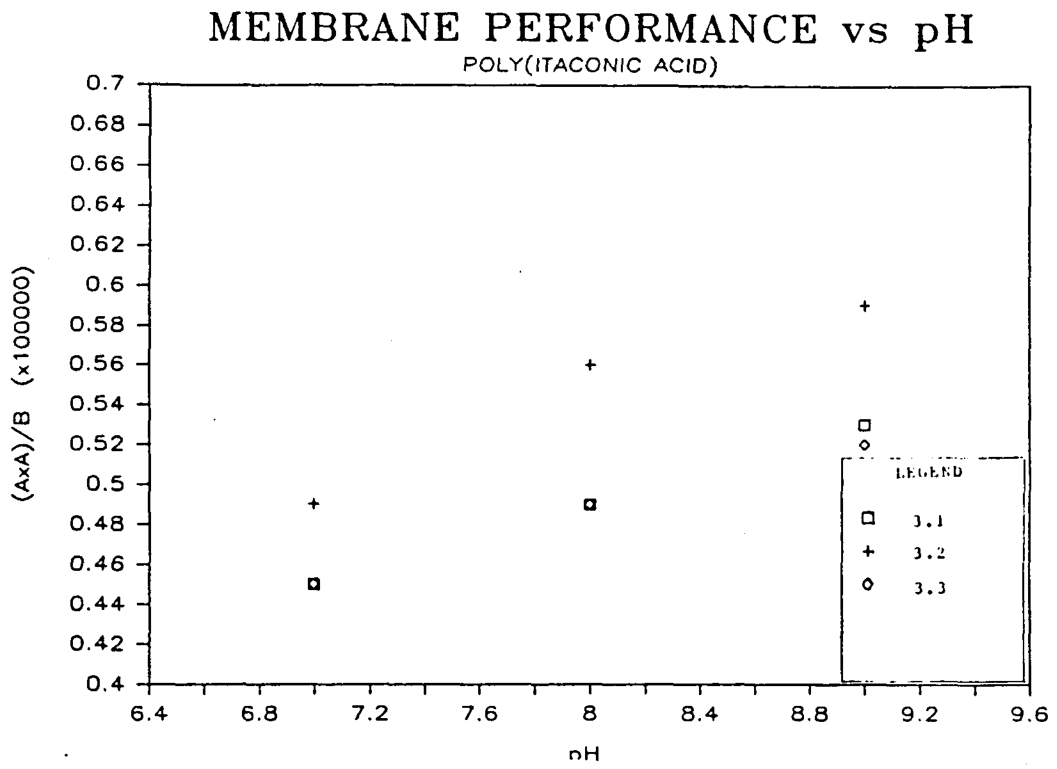


Fig. A.2.3

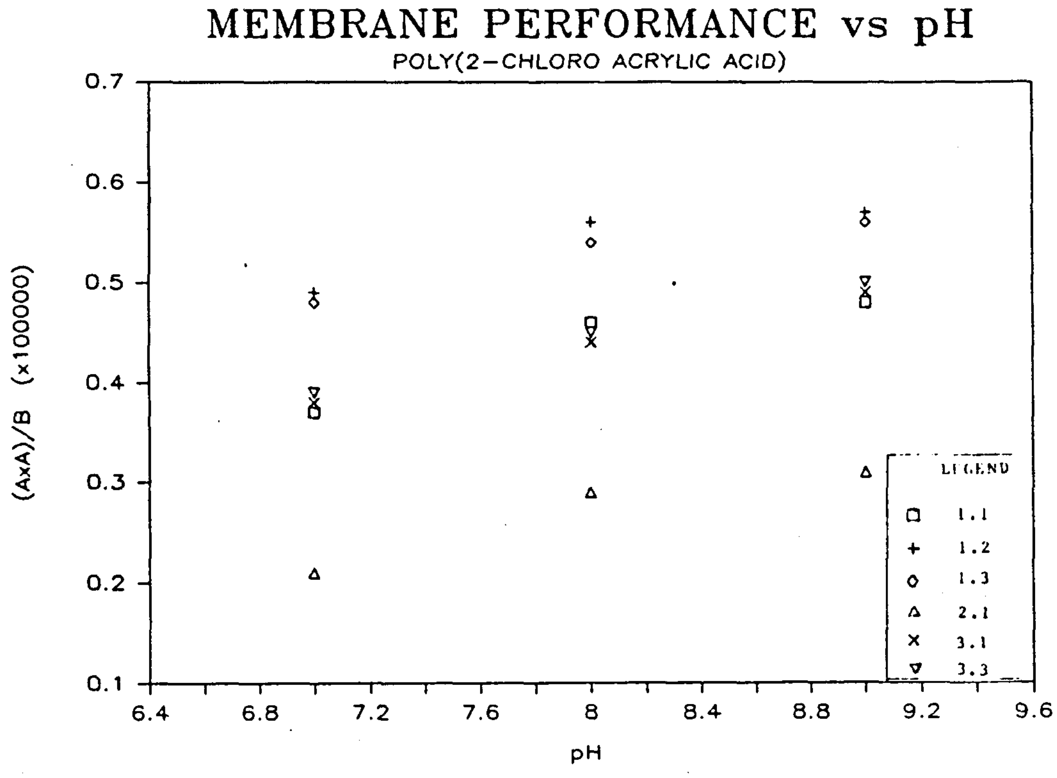


Fig. A.2.4

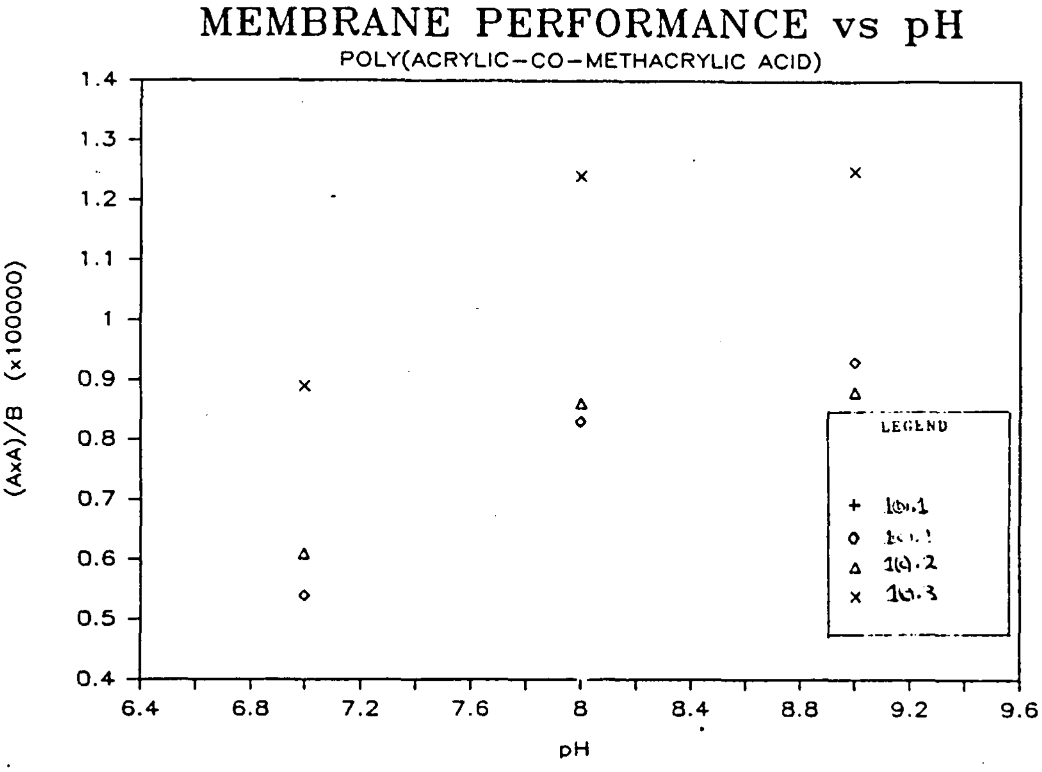


Fig. A.2.5

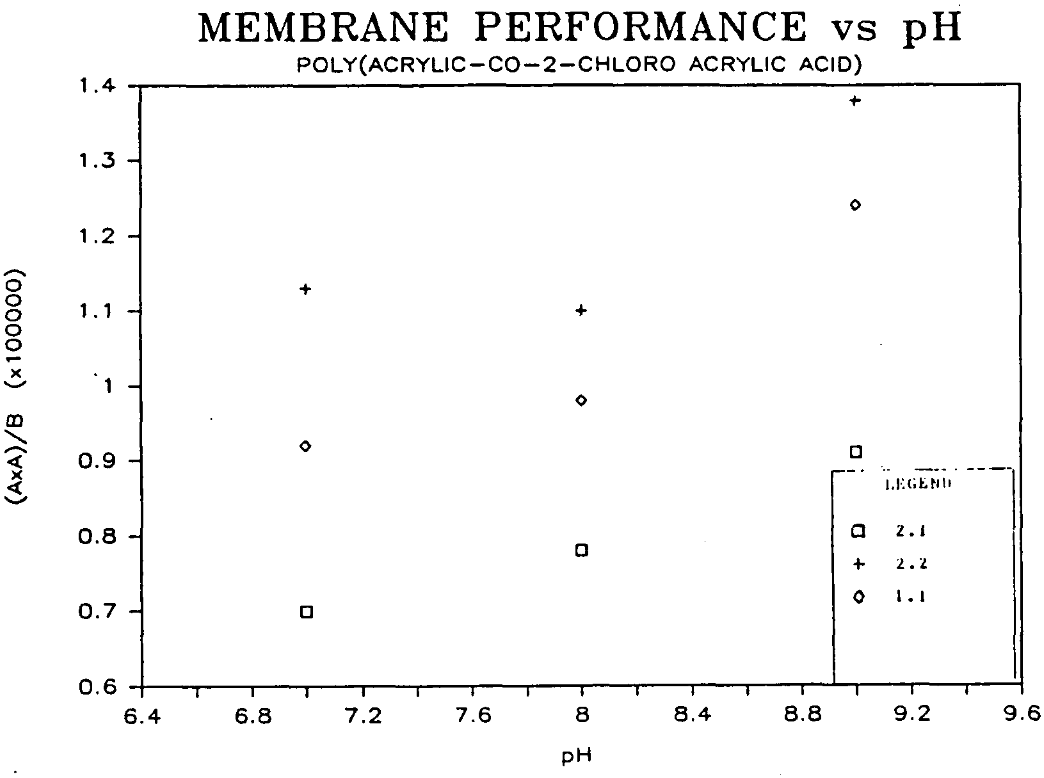


Fig. A.2.6

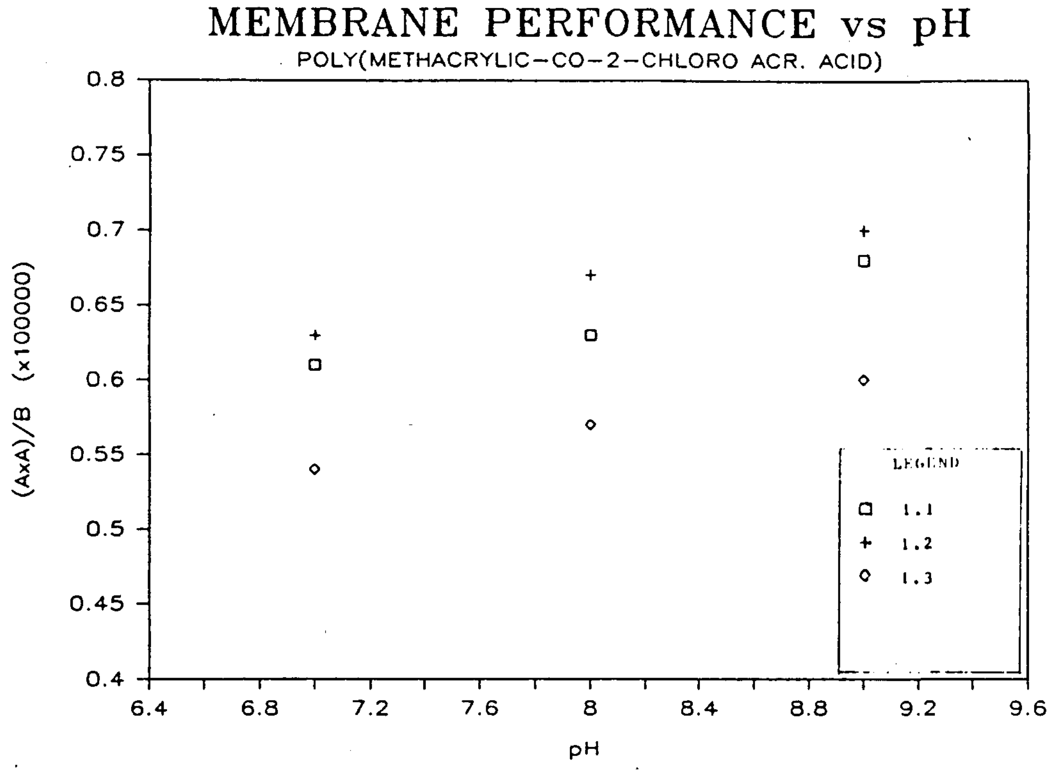


Fig. A.2.7

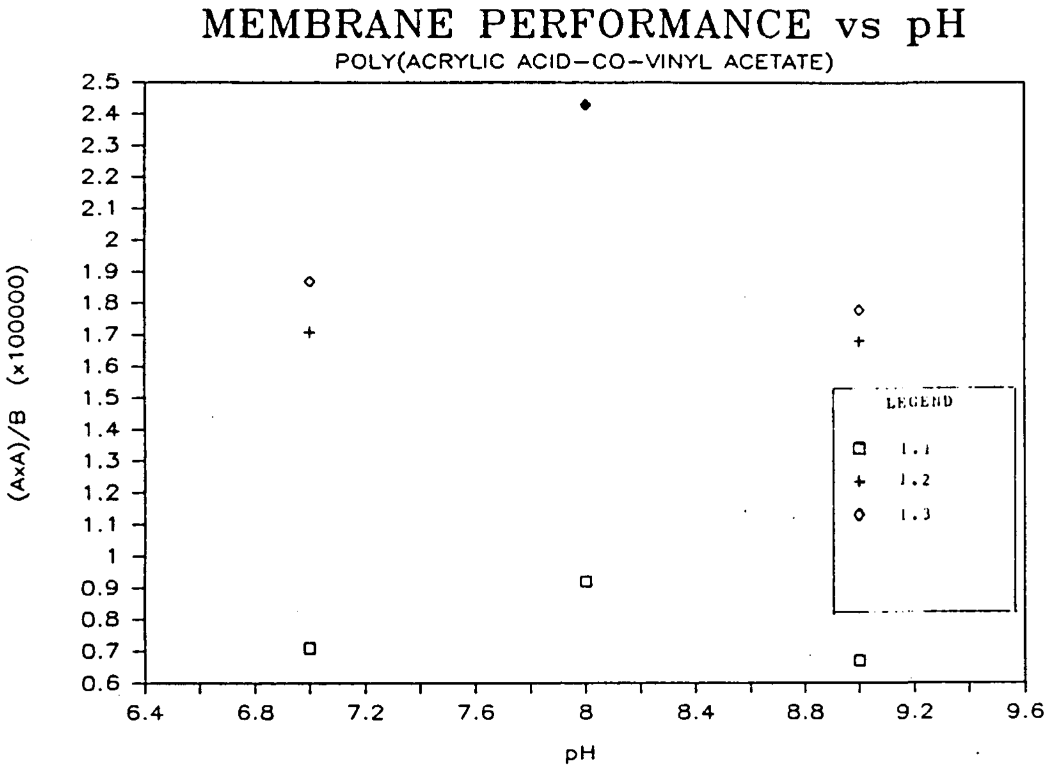


Fig. A.2.8

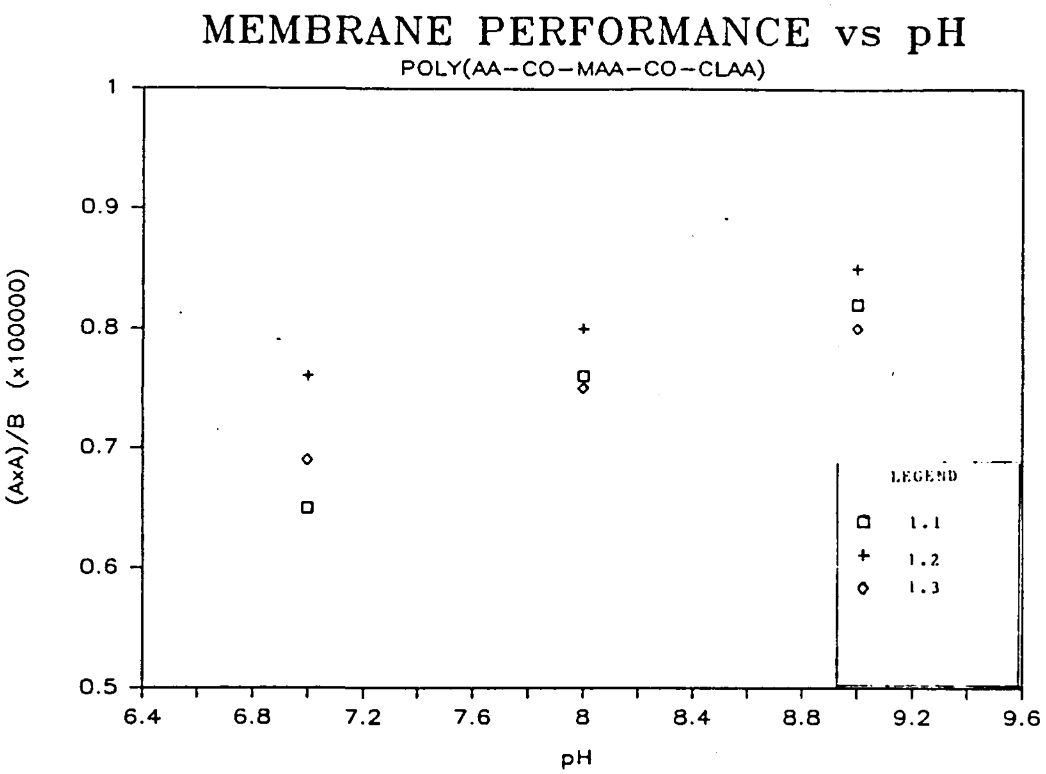


Fig. A.2.10

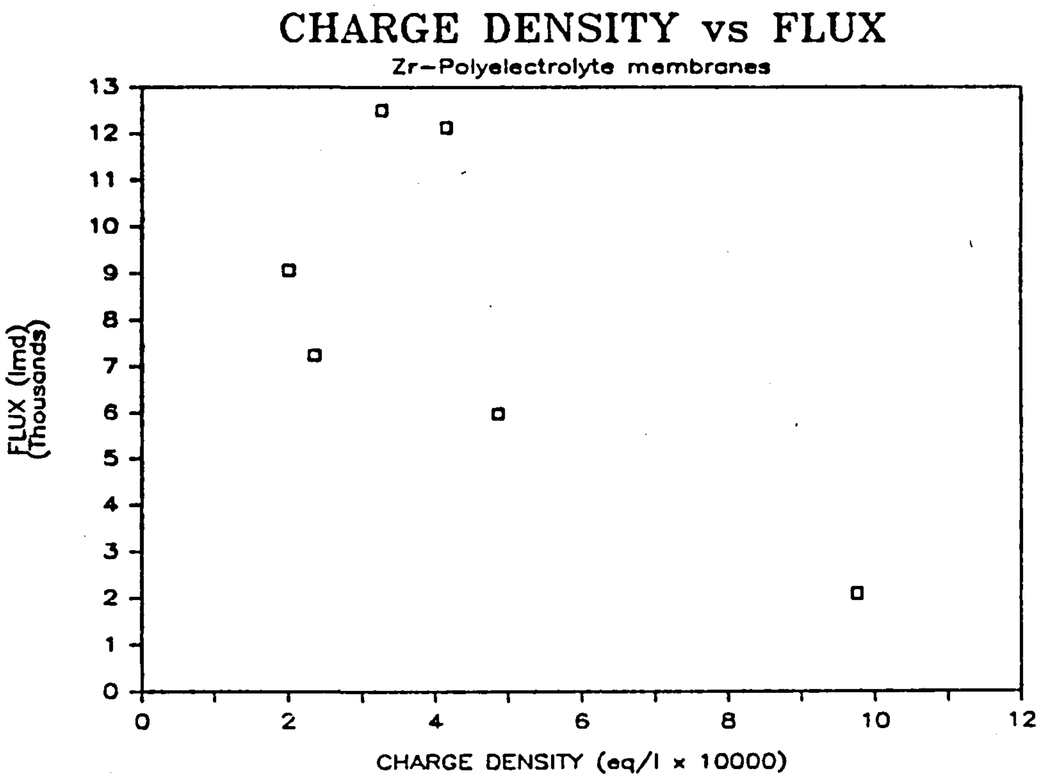


Fig. A.2.11

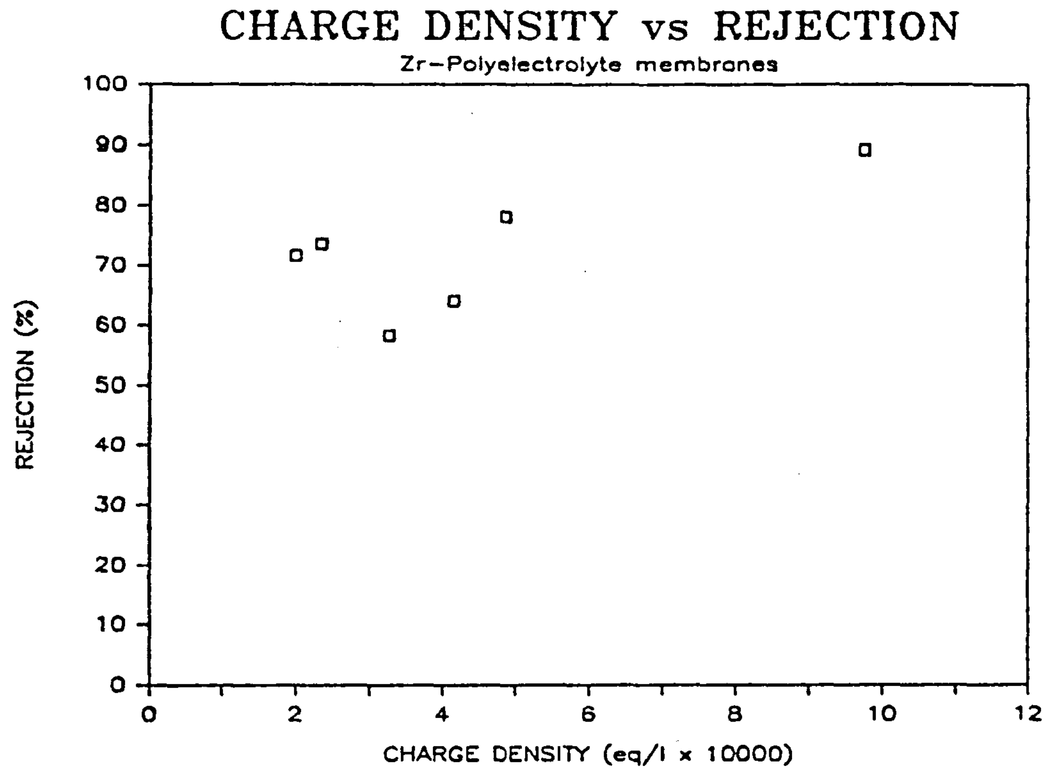


Fig. A.2.12

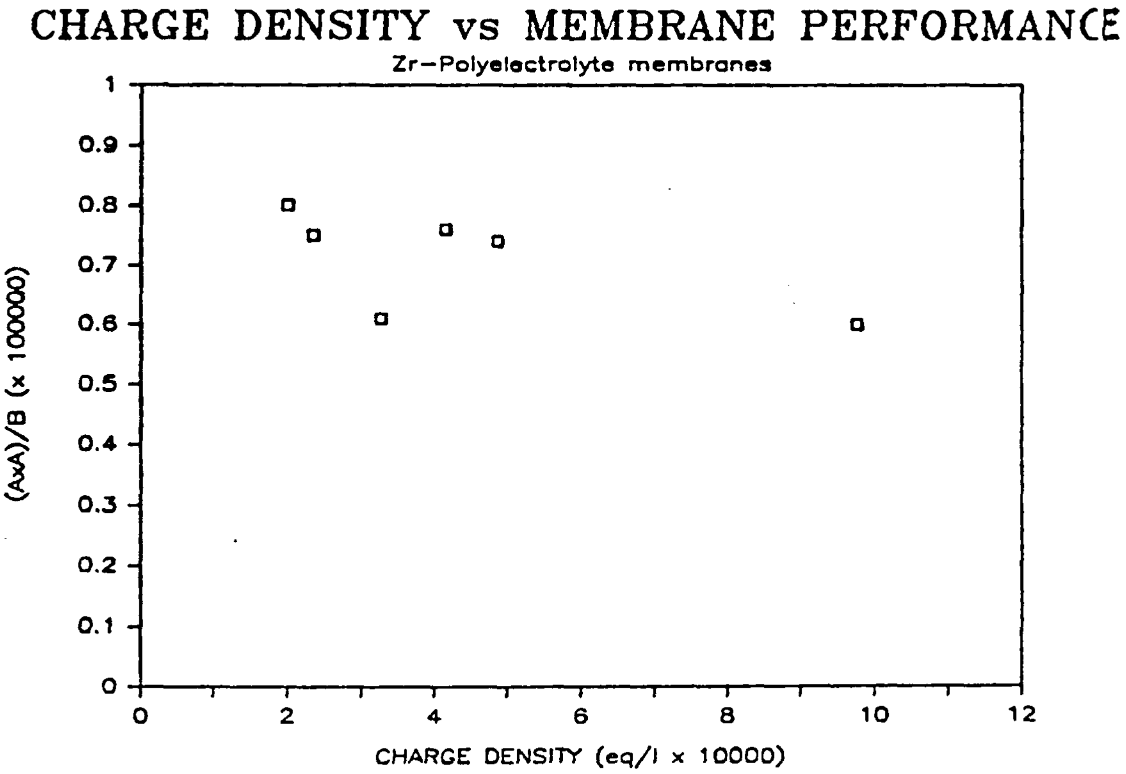


Fig. A.2.13

APPENDIX B

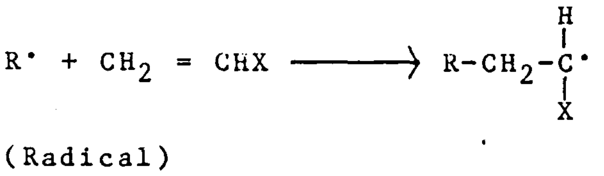
B.1 POLYMERIZATION

The formation of radicals was discussed in Section 2.6.

B.1.1 CHAIN INITIATION

It is important at this stage to discern between a catalyst and an initiator. Whereas a catalyst promotes a reaction and does not itself become part of the reaction, i.e. it is recoverable, an initiator starts a chain reaction and in doing so becomes incorporated in the reaction products (Billmeyer).

Generally, in the case of an unsaturated monomer (such as acrylic acid, x = COOH): see Fig. B.1:

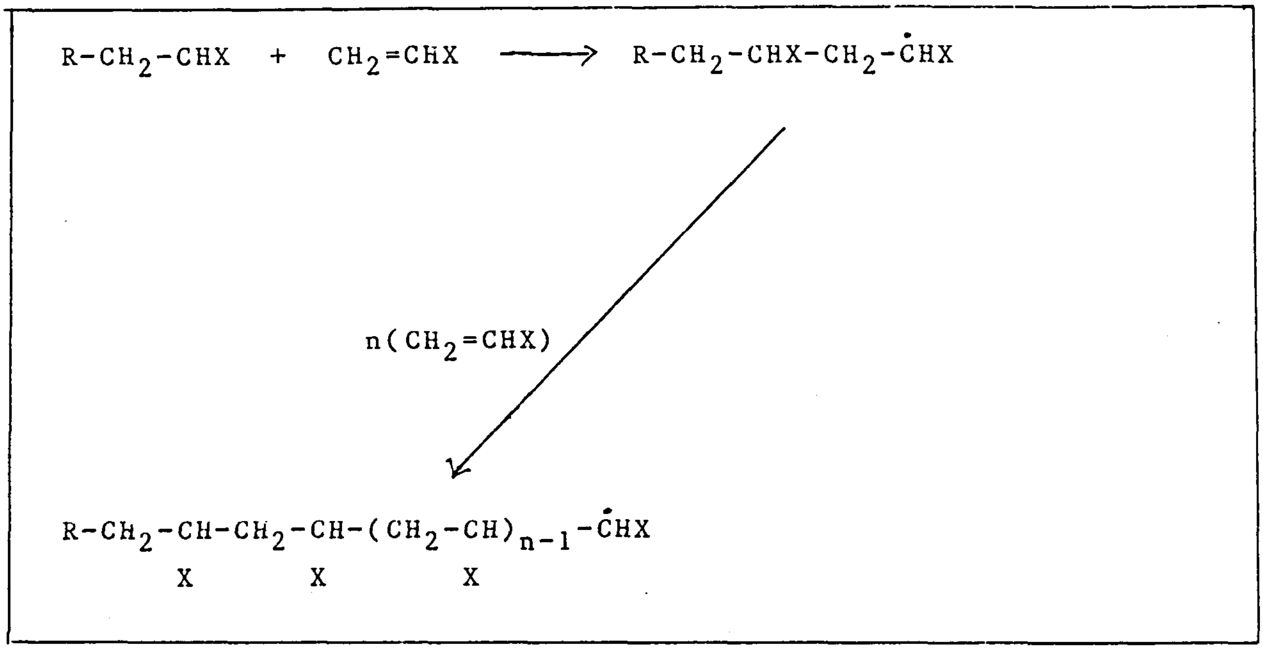


$$\underset{\text{(Radical)}}{R^\bullet} + CH_2 = CHX \longrightarrow R\text{-}CH_2\text{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^\bullet$$

Fig. B.1: The radical reads with the monomer, and in so doing creates a new radical.

B.1.2 CHAIN PROPAGATION

The radical formed (see Fig. B.1) after the initiating radical has reacted with the monomer can now in it's own turn react with other monomers: (see Fig. B.2)



$$R\text{-}CH_2\text{-}\dot{C}HX + CH_2{=}CHX \longrightarrow R\text{-}CH_2\text{-}CHX\text{-}CH_2\text{-}\dot{C}HX$$

$$\xrightarrow{n(CH_2=CHX)} R\text{-}CH_2\text{-}\underset{X}{CH}\text{-}CH_2\text{-}\underset{X}{CH}\text{-}(CH_2\text{-}\underset{X}{CH})_{n-1}\text{-}\dot{C}HX$$

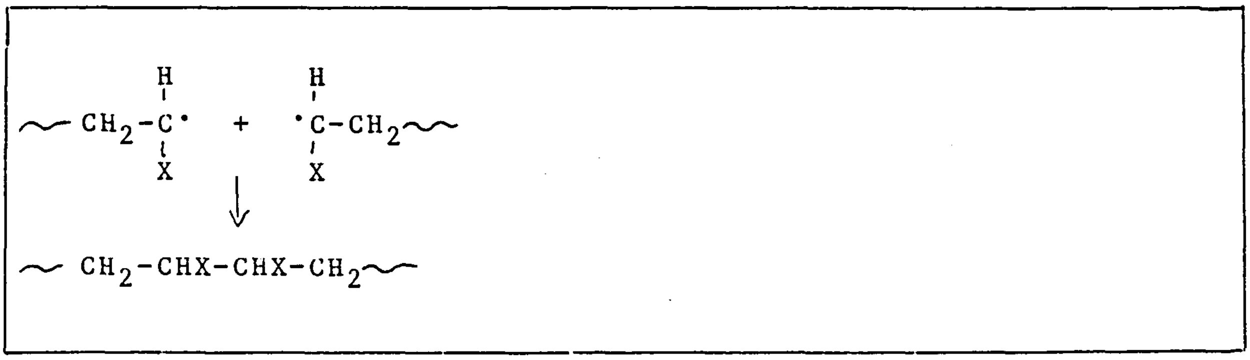
Fig. B.2: Chain propagation of a vinyl polymer

B.1.3 CHAIN TERMINATION

This can occur either through combination or disproportionation.

B.1.3.1 Combination

Combination or coupling occurs when 2 chain-ends meet and couple (see Fig. B.3).



$$\sim CH_2\text{-}\overset{H}{\underset{X}{C}}\cdot + \cdot\overset{H}{\underset{X}{C}}\text{-}CH_2\sim \longrightarrow \sim CH_2\text{-}CHX\text{-}CHX\text{-}CH_2\sim$$

Figure B.3: Termination by Combination

B.1.3.2 Disproportionation

In this case, opposed to the case of coupling where two chains are terminated with the formation of 1 chain, disproportionation leads to the formation of 2 chains. (See Fig. 5.4).

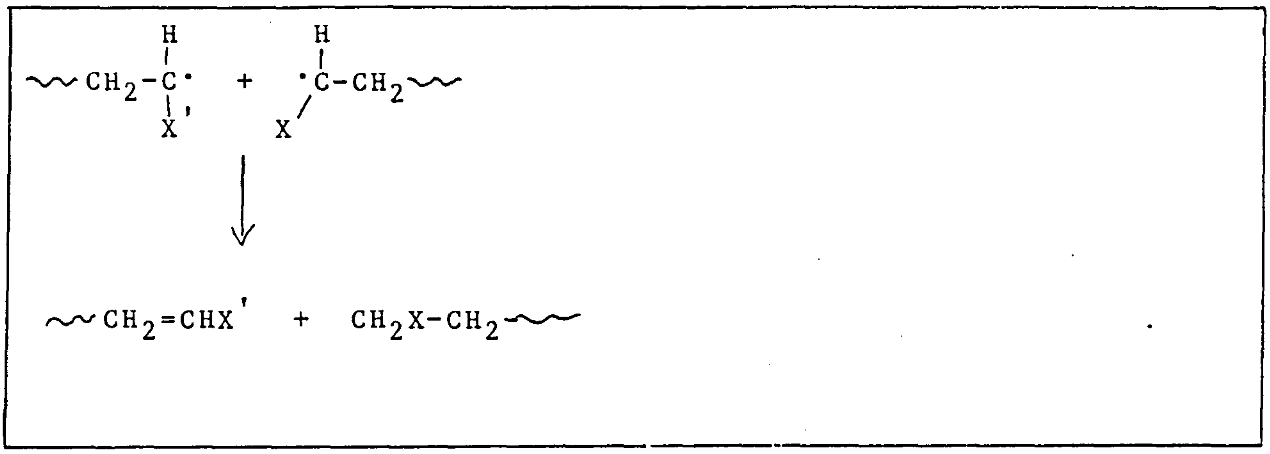


Figure B.4: Termination by Disproportionation

This mechanism takes place at higher temperature, or when steric effects play a role.

B.1.4 CHAIN TRANSFER REACTIONS

As the active centre of the radical polymerisation is highly reactive, there is always a possibility of side reactions. The radical can thus be transferred to other species, [60] including monomer, preformed polymer, initiator or added transfer agents.

While these reactions do not normally retard the polymerisation rate, they do affect the molecular mass of the polymers formed.

However, if impurities are present, such as O_2 they can, as the result of side reactions (see Fig. B.5) create species which are not active enough to promote polymerisation and thus retards the reaction.

$$\sim\sim R^{\bullet} + O_2 \longrightarrow \sim\sim RO_2^{\bullet}$$

Figure B.5: Radical Transfer to Oxygen

This is the primary reason for degassing all reaction mixtures prior to polymerisation (see Section 4.1).

B.2 STEADY STATE KINETICS [100]

Let. I = Initiator
M = Monomer
M = Chain Radical, where radical x = 1, 2, 3, etc.
M = Chain Radical Concentration
R = Radical Fragment
= Rate Constant,
V = Rate of Reaction

B.2.1 INITIATION

As we can write :

$$I \xrightarrow{k_d} 2R^{\cdot} \qquad (1)$$

$$R^{\cdot} + M \xrightarrow{k_a} M_1^{\cdot} \qquad (2)$$

Thus the rate of initiation :

$$v_i = (d[M^{\cdot}]/dt) = 2fk_d[I] \qquad (3)$$

Where f is the fraction of radicals which successfully initiate chains. Thus (2) can be disregarded.

B.2.2 PROPAGATION

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \xrightarrow{k_p} M_3^{\bullet}\ldots \xrightarrow{k_p} M_x^{\bullet}$$

$$v_p = -d[M]/dt = k_p[M][m^{\bullet}]$$

B.2.3 TERMINATION

$$M_x^{\bullet} + M_y^{\bullet} \xrightarrow{k_{tc}} M_{xy} \qquad \text{(coupling)}$$

OR

$$M_x^{\bullet} + m_y^{\bullet} \xrightarrow{k_{td}} M_x + M_y \qquad \text{(disproportionation)}$$

$$v_t = -(d[M]/dt)_t = 2k_t[M^{\bullet}]^2$$

(Assume $k_t = k_{tc} = k_{td}$)

Early in the reaction $[M^{\bullet}]$ becomes essentially consistent in many cases and thus

$$v_i = v_t$$
$$2fk_d[I] = 2k_t[M^{\bullet}]^2$$

and $[M^{\bullet}] = (fk_d[I]/k_t)^{0.5}$

thus

$$v_p = k_p[M] \text{ x } (fk_d[I]/k_t)^{0.5}$$

$$= k_p(fk_d[I]/k_t)^{0.5}$$

Thus the propagation rate is proportional to [T] 0.5 and [M]. It can further be shown that

$$1/\overline{DP}n = C_m + C_i([I]/[M]) + Av_p$$

where DP_n = average degree of polymerisation
C_m = monomer transfer constant
C_i = initiator transfer constant

and

$$A = (k_{tc}+k_{td})/(k_p{}^2[M^2]) = \text{constant}$$

Thus, the degree on polymerisation, DP_n is dependent on the initiator concentration [I] and the monomer concentration [M]. Thus, at a given temperature, and a given monomer concentration, an increase in the initiator concentration will lower the molecular mass, and vice versa.

This is of importance, as this method was used to tailor molecular processes in the polymerization of the polyelectrolytes used in this study.

B.3 COPOLYMERIZATION [61]

In general, we can discern between three types of copolymers. These are:

Random copolymers
Graft copolymers
Block copolymers

Of interest in this study are the random copolymers. These occur normally in free radically initiated polymerizations. Theoretically for a copolymer poly (A-CO-B) the structure (random) would be.

- AABABBAABBBABABBABAA -

etc.

As the structure will not be completely random, i.e., some sequences will occur either of monomer A or monomer B, it is better to refer to these copolymers as conventional, rather than random, copolymers.

The copolymer composition will be determined by the ease with which the respective monomers polymerize.

Dostal, in 1936, made the first attempts at laying the theoretical basics to the kinetics of copolymerization reactions. He assumed that only two types of chain radials could form, that the reactivities would be unaffected by perultimate report unit effects, or by chain length. Thus he was able to propose the following four ways of monomer addition:

RATE

1. $\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1^{\bullet}$ $\quad k_{11}[M_1^{\bullet}][M_1]$

2. $\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_2^{\bullet}$ $\quad k_{12}[M_1^{\bullet}][M_2]$

3. $\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim M_1^{\bullet}$ $\quad k_{21}[M_2^{\bullet}][M_1]$

4. $\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim M_2^{\bullet}$ $\quad k_{22}[M_1^{\bullet}][M_2]$

In 1944, 3 different groups published the so-called copolymerization equation.

The following assumption laid basis for the equation:

1) Copolymerization involves a chain reaction for the formation of a relatively long chain.

2) Reaction is a lengthy process compared to the growth period of individual molecules. Thus an equilibrium is assumed to set in rapidly after the reaction is started.

3) Dostals 4 equations are a satisfactory propogation model.

Then the copolymerisation reaction rates of two monomers M_1 and M_2 can be expressed as follows:

$$-d[M_1]/dt = k_{11}[M_1^{\cdot}][M_1] + k_{21}[M_2^{\cdot}][M_1 \qquad (5)$$

$$-d[M_2]/dt = k_{12}[M_1^{\cdot}][M_2] + k_{22}[M_2^{\cdot}][M_2] \qquad (6)$$

In the equilibrium assumption the rate of convension of a M_1 type radical to a M_2 type radical must be equal to the rate of a M_2 type to a M_1 radical.

Thus $$k_{12}[M_1^{\cdot}][M_2] = k_{21}[M_2^{\cdot}][M_2] \qquad (7)$$

(5)/(6) and substitute by (7)

$$r_1 = r_2(m_1M_2^2/m_2M_1^2) + (M_2/M_1) \qquad (8)$$

Where $r_1 = {}^{k11}/_{k12}$ and $r_2 = {}^{k22}/_{k21}$ (9)

And the copolymerization equation is derived

$$dM_1 = (r_1M_1^2 + M_1M_2)/(r_2M_2^2 + M_1M_2) \qquad (10)$$

This eq. gives the composition of the copolymer at any specific instant since

$d[M_1]/d[M_2]$ is the relative rate of the two monomers entering the copolymer

r_1 and r_2 are the relative reactivity ratios. They indicate the tendency for homopolymerization vs the cross-over reaction, i.e. the presence for like monomer against the unlike monomer.

B.4 VISCOMETRY [81]

A number of the important physical properties of polymers are related to their molecular mass and molecular mass distribution. In a polymerizing system, polymer molecules with varying molecular weights are formed.

All polymers increase the viscosity of solvents in which they are dissolved and this increase provides the most convenient method for the calculation of the molecular mass of polymers consisting of flexible chain molecules. It should be noted that this method is not based on rigorous physical laws such as those which allow M_n to be obtained from osmotic pressure measurements, and M_w from light scattering measurements. It should be emphasized that viscosity measures molecular size (which may be different in different solvents), not mass, and any correlation with molecular mass is empirical and restricted to systems in which there is a one-to-one relation between size and mass. The viscometric method must, therefore, be calibrated by samples having narrow molecular mass distributions and which have already been characterized by a primary method, such as osmotic pressure or light-scattering.

The frictional resistance of liquids to shear is characterized by the coefficient of viscosity, n, as defined by

$$\eta = \dot{Y}T \qquad (1)$$

where T is the shearing stress per unit of surface and $\dot{Y}$ is the velocity gradient perpendicular to the shearing stress. With T in dynes/cm^2 and Y in sec^{-1}, η is given in poise. The viscosity of solvents decreases with increasing temperature. Thus if we want to determine accurately small viscosity increases brought about by dissolving small amounts of polymer in solvents, it is critical to measure viscosities at closely controlled temperatures.

The simplest experimental method for the determination of viscosity is the measurement of the time, t, required for the passage of a volume, V, through a capillary of length, l, with a circular cross-section of radius, r. The relationship between n and t is given by:

$$\eta/p = At + B/t \qquad (2)$$

where p is the density of the liquid while A and B depend on the dimensions of the capillary. A is defined as:

$$A = h\ g\ \eta\ r^4/8\ V \qquad (3)$$

where h is the mean hydrostatic head of the fluid and g is the gravitational constant. The B term, the so-called "kinetic energy correction" arises from the back pressure produced by the deceleration of the fluid as it emerges from the capillary. For comparison of two fluids with similar densities and for reasonably long flow times (above 100 sec.), we may assume that the viscosities are proportional to the flow times by neglecting the B/t term.

In interpreting the comparison of the viscosity of the pure solvent, η_o, and the viscosity, η, of a polymer solution, the terms in Table 1 are commonly used.

Table 1: Viscometric terms in common use.

Common Name	IUPAC Name	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_o$
Specific viscosity	---	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \ln \eta_{sp}/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/c)_{c=o}$

Here the concentration of the polymer is given in g/100 ml, but some authors use c in g/ml as proposed by the IUPAC. Note that $[\eta]$ has the dimension c^{-1}, thus $[\eta]$ will be given either in dl/g(dl = deciliter, i.e., 100 ml) or ml/g depending on the units used for c. In dilute solution, η_{sp}/c is linear in c and $[\eta]$ may, therefore, be obtained by extrapolating a plot of η_{sp}/c vs. c to c = 0.

By using Huggins' empirical equation

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \qquad (2)$$

And Kreamers' empirical equation

$$(\ln \eta r)/c = [\eta] + k^{11}[\eta]^2 c \qquad (3)$$

Where k^{l} = Huggins constant
k^{ll} = Kreamer constant

we can derive the Mark-Houwink relationship

$[\eta] = KM^{a}$, where the constants K and a are characteristic of a polymer-solvent pair at a given temperature.

B.5 pH TITRATIONS

B.5.1 pKa VALUES

In order to obtain the pKa values for monomeric acids that are not available in the literature, it was necessary to calculate these by pH titration.

As, by definition

$$pK = \log(Ka)$$

ka = dissociation constant of acids or corresponding bases

and

$$pH = pKa + \log\ (Ab/Aa)$$

Where Ab = base activity, Aa = acid activity and assuming activity = concentration ;

Ab = concentration of base and Aa = concentration of acid

And as, in the case of a pH titration, the pKa corresponds to a point on the pH titration curve, K, where $VK = VE/2$, VE = end-point volume of base added, if the concentrations of acid and base are approximately equal.

Thus we can determine the pK for a given acid by titrating it with a base of equal concentration, and then using the pH titration curve to calculate VE, K and to obtain pKa.

B.5.2 COPOLYMER COMPOSITION

If we have a situation where there are two acidic monomers (A and B) within a copolymer, and we wish to obtain their relative compositions, this can be done by titration, if the monomeric acids have pKa values that are far enough apart (differing by 0,7 - 1 unit at least). If a given mass of the copolymer is dissolved and titrated against base, a first endpoint is reached, corresponding to the neutralization of the first acidic species in the copolymer. Thus, the mole concentration of the first monomer can be calculated, and thus the mass are therefore the mole percentage of the second monomer.

As some of the monomer with the higher pKa value, (say monomer B) will be ionised as number A becomes fully neutralised, this method is approximate only, Thus the values obtained in this way are not definite, but give an indication of copolymer composition only.

APPENDIX C

C.1 COMPUTER PROGRAMS

The programs written for the purpose of this study are listed below.

C.1.1 VISCOMETRY

```
5 CLS
7 KEY OFF
10 PRINT TAB(33) "Viscometry"
20 PRINT:PRINT:INPUT "Polymer: ";P$:PRINT:INPUT "Solvent run time (s): ";RS
30 PRINT:INPUT "Number of data points: ";N:PRINT
45 I=I+1
48 PRINT:PRINT
50 INPUT "Run time: ";R(I):INPUT "Concentration (g/dl): ";C(I)
55 NR(I)=R(I)/RS:NSP(I)=NR(I)-1:NSPC(I)=NSP(I)/C(I)
60 X(I)=10*C(I):Y(I)=10*NSPC(I)
65 Q(I)=X(I)*62.9+80:P(I)=289-(Y(I)*27.9)
70 XA=XA+(C(I)^2):YA=YA+(C(I)*NSPC(I)):XGA=XGA+(X(I)^2):YGA=YGA+(X(I)*Y(I))
75 X=X+C(I):Y=Y+NSPC(I):XG=XG+X(I):YG=YG+Y(I)
77 IF I<N THEN 45 ELSE 80
80 L=X*Y:O=N*YA:R=X^2:T=N*XA:LG=XG*YG:OG=N*YGA:RG=XG^2:TG=N*XGA
90 B=-((O-L)/(R-T)):BG=-((OG-LG)/(RG-TG))   :AG=(YG-(BG*XG))/N
100 A=(Y-(B*X))/N:A1=AG*27.9:A2=289-A1:A3=B*279:A4=A2-A3
110 CLS
112 LPRINT "POLYMER: "P$:LPRINT:LPRINT "Run time" TAB(25) "nr" TAB(43) "Conc"
B(65) "nsp/c":LPRINT
120 FOR I=1 TO N:LPRINT R(I) TAB(20) NR(I) TAB(40) C(I) TAB(60) NSPC(I):NEXT
130 LPRINT:LPRINT "Slope: ";B:LPRINT:LPRINT "Intercept: ";A:LPRINT
140 INPUT "Graphic display ? (Y/N) : ";H$:IF H$="Y" THEN 400 ELSE 150
150 END
400 CLS
410 SCREEN 2
420 LINE (80,10)-(709,289),,B
425 LOCATE 2,24:PRINT "PLOT OF CONCENTRATION vs SPECIFIC VISCOSITY/C"
430 FOR W=1 TO 9:LINE (80,10+(28*W))-(85,10+(28*W)) :NEXT
440 FOR V=1 TO 9:LINE (80+(63*V),289)-(80+(63*V),284):NEXT
450 LINE (80,A2)-(709,A4)
460 FOR I=1 TO N:CIRCLE (Q(I),P(I)),4:NEXT
465 LOCATE 23,35:PRINT "CONCENTRATION (g/dl)"
467 LOCATE 12,1:PRINT "nsp/c"
468 LOCATE 22,9:PRINT "0":LOCATE 22,16:PRINT "0.1":LOCATE 22,23:PRINT "0.2"
469 LOCATE 22,30:PRINT "0.3":LOCATE 22,37 :PRINT "0.4":LOCATE 22,44:PRINT "0.
470 LOCATE 22,51:PRINT "0.6":LOCATE 22,58:PRINT "0.7":LOCATE 22,65:PRINT "0.
OCATE 22,72:PRINT "0.9"
475 FOR I=1 TO 9:LOCATE 1+I*2,6:PRINT "0"+RIGHT$(STR$(1-I/10),2):NEXT
480 LOCATE 1,1
490 GOTO 150
```

C.1.2 CHARGE DENSITY

```
10 X=0:Y=0:X1=0:Y1=0:F=96489!:V=8.31441
20 CLS
30 PRINT "                           CHARGE DENSITY"
40 PRINT:INPUT "Operator: ";V$:PRINT:INPUT "Date: ";A$
50 CLS
60 PRINT "The experimental data is now required":PRINT
70 INPUT "Experiment no: ";B$:PRINT:INPUT "Polymer: ";Z$:PRINT
80 INPUT "Temperature (K): ";U:PRINT:INPUT "Electrolyte: ";E$
90 PRINT:INPUT "Number of sets of values obtined experimentally: ";N:PRINT
```

```
100 INPUT "Concentration Ratio: ";M:PRINT
110 INPUT "If you want to reenter any of the above type in 13 (else 1): ";A8
115 PRINT
120 IF A8=13 THEN 40
130 CLS
140 PRINT "Now enter the membrane potential and concentration (C1) starting wi
 the lowest":PRINT
145 I=I+1
150 PRINT:INPUT "Membrane potential (mV): ";S(I)
160 INPUT "Concentration (mole/l) : ";C(I):PRINT
165 INPUT "If you want to reenter any of the above type in 13 (else 1): ";A9
166 IF A9=13 THEN 150
170 S(I)=S(I)*(-.001):A1=F/(V*U):A2=1/(2*LOG(M)):A3=A2*A1
180 E(I)=(A3*S(I))+.5:Q(I)=1/C(I):P(I)=1/E(I):QG(I)=Q(I)/25:PG(I)=P(I)/8
185 XXG(I)=QG(I)*62.9+80:YYG(I)=289-56.6*PG(I)
190 SY=SY+(Q(I)*P(I)):SYG=SYG+(QG(I)*PG(I)):SXG=SXG+(QG(I)^2):YG=YG+PG(I)
191 SX=SX+(Q(I)^2):XG=XG+QG(I)
192 Y=Y+P(I)
193 X=X+Q(I)
200 IF I<N THEN 145
210 L=X*Y:O=N*SY:R=X^2:T=N*SX:LG=XG*YG:OG=N*SYG:RG=XG^2:TG=N*SXG
220 B=-((O-L)/(R-T)):A=(Y-(B*X))/N:AG=(YG-(B*XG))/N:A6=A*56.6:A7=289-A6
222 BG=-((OG-LG)/(RG-TG)):A8=BG*269:A9=A7-A8
240 A4=1-(1/A):A5=(1-A4)/A4::M1=M*LOG(M):M2=M1/(M-1)
250 Z=A5*M2*ABS(B)
260 CLS
270 LPRINT "CHARGE DENSITY DETERMINATION":LPRINT
280 LPRINT "Operator " TAB(30) V$:LPRINT:LPRINT "Date" TAB(30) A$:LPRINT:LPRIN
"Experiment no" TAB(30) B$
290 LPRINT:LPRINT "Polymer" TAB(30) Z$:LPRINT:LPRINT "Electrolyte" TAB(30) E$
300 LPRINT:INPUT "Enter 1 to continue: ";A10
310 IF A10=1 THEN 320 ELSE 300
320 LPRINT:LPRINT "Membrane pot. (V)" TAB(35) "t-" TAB(50) "1/C" TAB(65) "1/t-
325 LPRINT :FOR I=1 TO N:LPRINT S(I) TAB(35) E(I) TAB(50) Q(I) TAB(65) P(I):NE

330 LPRINT:LPRINT "In the plot of 1/t vs 1/C1 the following is obtained":LPRIN
340 LPRINT "Slope" TAB(30) B:LPRINT:LPRINT "Intercept" TAB(30) A:LPRINT
342 LPRINT "Charge density (eq/l)" TAB(30) Z:LPRINT
345 PRINT :INPUT "Graphic display of plot (Y/N): ";ANS$
347 IF ANS$="Y" THEN GOSUB 1000
350 END
360 R$="* * "
370 FOR H=1 TO 20:PRINT R$;:NEXT H
400 END
1000 CLS
1005 KEY OFF
1100 SCREEN 2
1200 LINE (80,20)-(709,289),,B:UNITX=629/10:UNITY=269/19:FOR E=1 TO 19:LINE(8
*UNITY+20)-(85,E*UNITY+20):NEXT
1300 FOR E=1 TO 9:LINE (E*UNITX+80,289)-(E*UNITX+80,284):NEXT
1400 FOR E=1 TO 9:LOCATE 22,E*7+8:PRINT 25*E:NEXT
1500 FOR E=1 TO 4:LOCATE 1+E*4,6:PRINT 5-E*1:NEXT
1550 LOCATE 1,35:PRINT "PLOT OF 1/C vs 1/t"
1600 LOCATE 23,43:PRINT "1/C":LOCATE 11,1:PRINT "1/t":LOCATE 1,1
1700 FOR I=1 TO N:CIRCLE (XXG(I),YYG(I)),4:NEXT
1800 LINE (80,A7)-(709,A9)
1900 RETURN
```

C.1.3 MEMBRANE PERFORMANCE

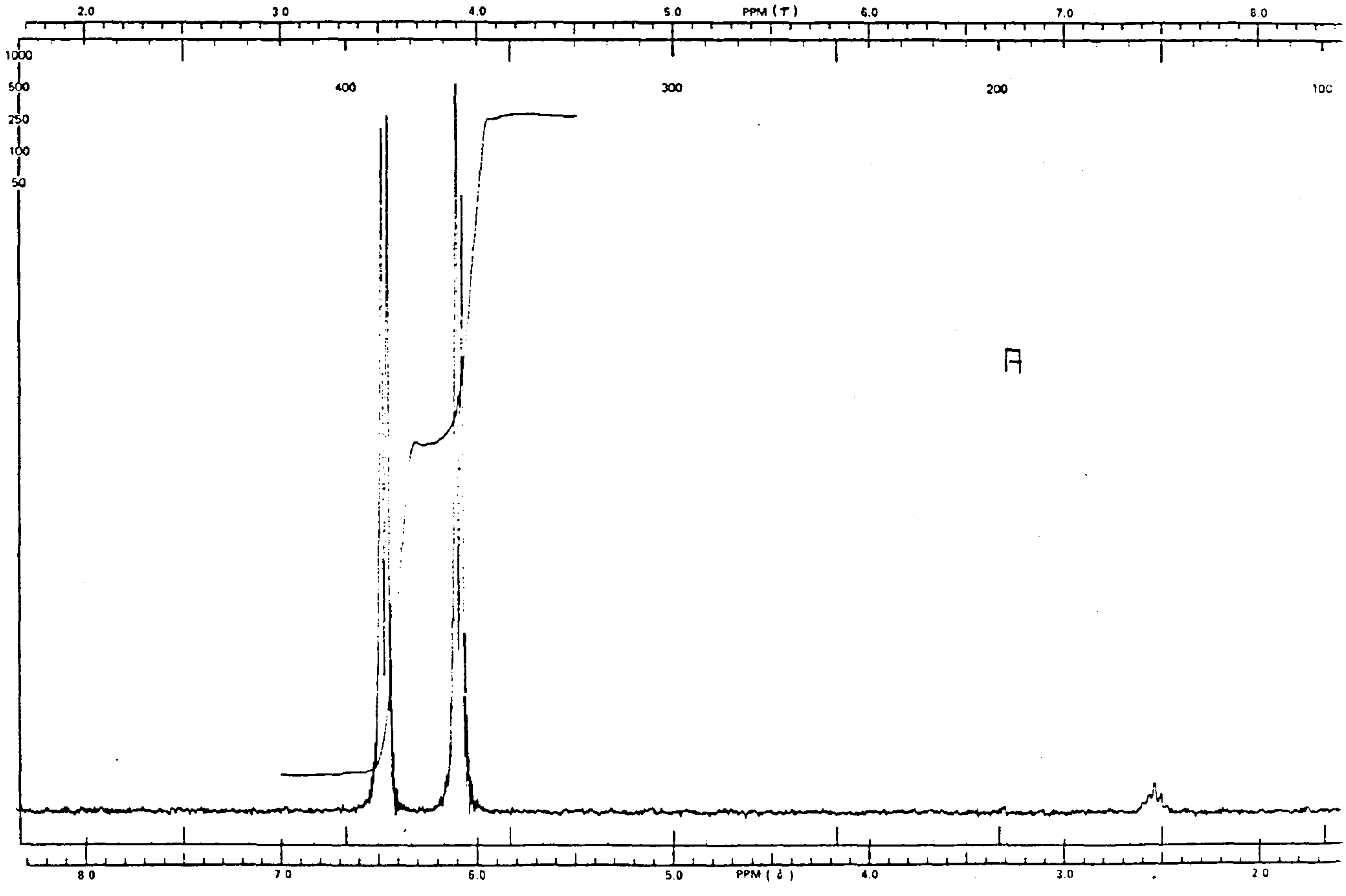
```
5 KEY OFF
10 CLS
20 PRINT TAB(39) "THE":PRINT TAB(33) "DETERMINATION":PRINT TAB(39) "OF":PRINT
B(32) "FIGURES OF MERIT"
30 PRINT TAB(39) "FOR":PRINT TAB(32) "DYNAMIC MEMBRANES"
40 PRINT TAB(30) "----------------------":PRINT
45 PRINT:INPUT "Printout ? (Y/N) ";F$:CLS
50            :KV=8.929999E-03:AC=.962112:G=.15875
55 D=.35
60 INPUT "Polymer: ";A$
70 PRINT:PRINT"The following values are set:":PRINT:PRINT "Salt Molecular Mass
85":PRINT "Pressure: 59.20 (atm)":PRINT "Feed flow rate: 3.67 (l/min)"
77 PRINT"Temperature: 308 K":PRINT
78 INPUT "If you want to change any of tham enter Y:";CH$
80 IF CH$="Y" THEN 100
85 M=85:V1=3.67:P=59.2:T=308
90 GOTO 107
100 INPUT "Salt Molecular Mass(g/l): ";M:PRINT :INPUT "Feed flow rate (l/m): "
1:PRINT:INPUT "Pressure (atm): ";P:PRINT
105 PRINT:INPUT "Temperature: ";T
107 PRINT:INPUT "Feed Concentration (mg/l):";C
108 CLS
110 M1=M*1000
120 Z=0
130 LOCATE 1+K,10:INPUT "Cell number: ";Z:LOCATE 3+K,10:INPUT "Flux (ml/min):
F2(Z):LOCATE 3+K,40:INPUT "Rejection (%): ";R1(Z):K=K+5
140 FOR I=1 TO 40 :PRINT "--";:NEXT
145 F(Z)=F2(Z)*906
150 V=V1*16.667:U=V/AC:R(Z)=R1(Z)/100:F1(Z)=F(Z)*1.157E-06:
160 D1(Z)=1/(1-R(Z))
170 Q1(Z)=1/D1(Z):Q5(Z)=1-1/D1(Z):Q2(Z)=F1(Z)*(KV^.5)*(D^.17):Q3(Z)=.023*(U^.

175 Q4(Z)=Q2(Z)/Q3(Z):Q6(Z)=EXP(Q4(Z)):Q7(Z)=Q5(Z)*Q6(Z):Q(Z)=Q1(Z)+Q7(Z)
190 L=L+1
200 P1=(G*T*C)/M1
210 A1(Z)=P-(P1*Q(Z)+P1/D1(Z)):A(Z)=F1(Z)/A1(Z):A2(Z)=A(Z)^2
212 B1(Z)=D1(Z)*(Q(Z)-1/D1(Z)):B(Z)=F1(Z)/B1(Z)
215 A3(Z)=A2(Z)/B(Z)
220 GOSUB 900
225 A31(Z)=A3(Z)*100000!
235 IF L=3 THEN 240 ELSE 120
240 CLS
245 IF F$="Y" THEN 250 ELSE 310
250 LPRINT "Polymer " A$:LPRINT:LPRINT TAB(15) "A" TAB(30) "B" TAB(40) "Rejec
n % " TAB(53) "Flux (lmd)" TAB(65)" Asq/B (*10^5)":LPRINT
260 FOR Z=1 TO 3:LPRINT "Cell "Z TAB(10) A(Z)  TAB(25) B(Z)  TAB(43) R1(Z) TA
3) F(Z) TAB(65) A31(Z):NEXT
261 LPRINT
265 GOTO 400
270 LPRINT "------------------------------------------------------------------
-------------":LPRINT
```

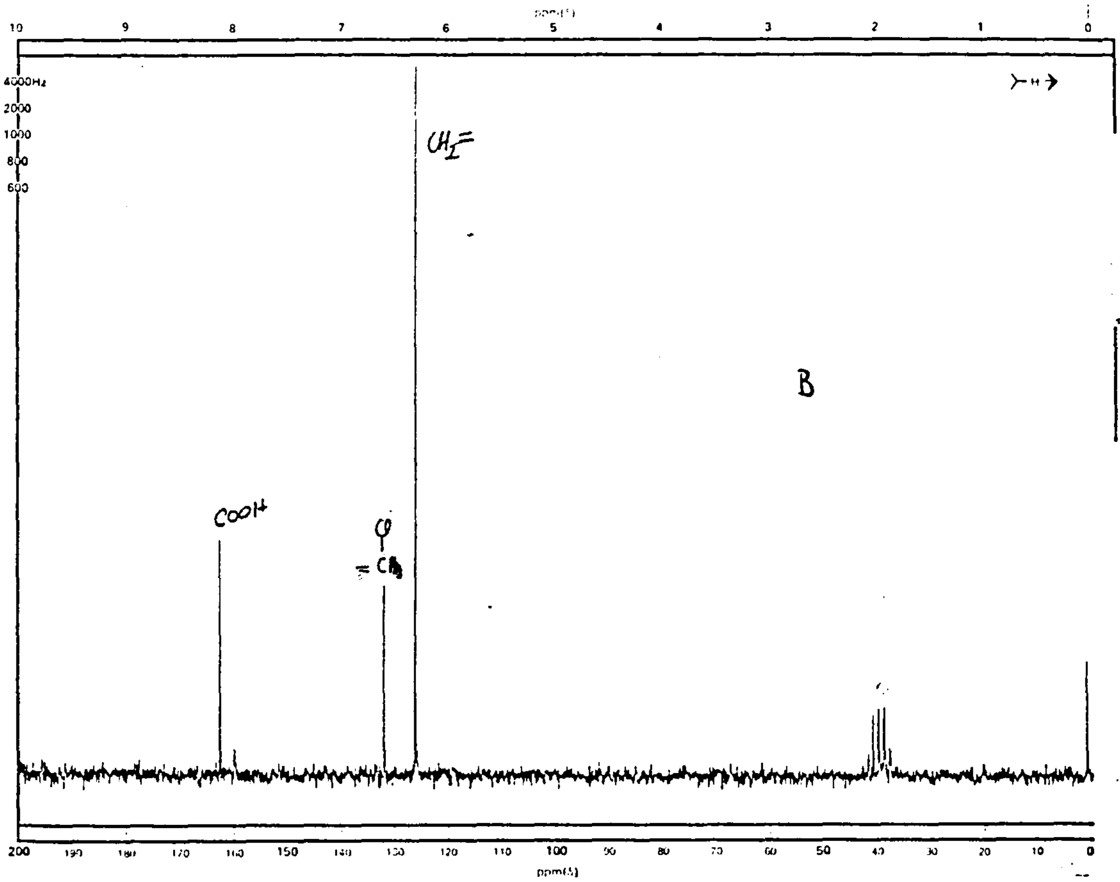
```
300 END
310 PRINT "Polymer " A$:PRINT:PRINT TAB(15) "A" TAB(30) "B" TAB(40) "Rejection
 " TAB(53) "Flux (lmd)" TAB(65)" Asq/B (*10^5)":PRINT
320 FOR Z=1 TO 3:PRINT "Cell "Z TAB(10) A(Z)  TAB(25) B(Z)  TAB(43) R1(Z) TAB(
) F(Z) TAB(65) A31(Z):NEXT
322 PRINT :PRINT TAB(30) "Normalized rejection":PRINT
323 FOR Z=1 TO 3:PRINT "Cell "Z TAB(35) RN(Z)*100:NEXT
330 GOTO 300
335 GOTO 400
370 LPRINT TAB(25) "Normalized rejection (%)":LPRINT
380 FOR Z=1 TO 3:LPRINT "CELL "Z TAB(35) RN(Z):NEXT
390 GOTO 330
400 LPRINT :LPRINT TAB(30) "Normalized rejection":LPRINT
405 FOR Z=1 TO 3:LPRINT "Cell "Z TAB(35) RN(Z)*100:NEXT
430 GOTO 330
900 F3=1.157E-06*1500
1100 DN1(Z)=-(P1^2)
1200 DN2(Z)=(1/A3(Z))*F3*Q(Z)
1300 DN(Z)=DN1(Z)/DN2(Z)
1350 CN1(Z)=-2*P1*(P-P1*Q(Z))
1400 CN(Z)=CN1(Z)/DN2(Z)
1500 BN1(Z)=(1/A3(Z))*F3
1600 BN2(Z)=(P-(P1*Q(Z)))^2
1700 BN3(Z)=-(BN1(Z)+BN2(Z))
1800 BN(Z)=BN3(Z)/DN2(Z)
1900 PN(Z)=CN(Z)-.333333*(BN(Z)^2)
2000 QN1(Z)=27*DN(Z):QN2(Z)=9*BN(Z)*CN(Z):BNA(Z)=ABS(BN(Z)):QN3(Z)=-(2*(BNA(Z)
))
2100 QN4(Z)=QN1(Z)-QN2(Z)+QN3(Z)
2150 QN(Z)=QN4(Z)/27
2200 PNA(Z)=ABS(PN(Z))
2300 RM(Z)=-((PNA(Z)/3)^3)+((QN(Z)/2)^2)
2400 DRN1(Z)=(-(QN(Z)/2)+(RM(Z)^.5))^.333333
2500 DRN2(Z)=(-(QN(Z)/2)-(RM(Z)^.5))^.333333
2600 DRN3(Z)=BN(Z)/3
2700 DRN(Z)=DRN1(Z)+DRN2(Z)-DRN3(Z)
2800 RN(Z)=1-(1/DRN(Z))
2900 RETURN
```

APPENDIX D

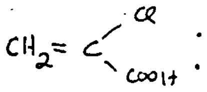
NMR SPECTRA

The monomer 2-chloro-2-propenoic acid was checked for purity and composition by nuclear magnetic resource spectrometry. The carbon-13, proton and multiplicity spectra are shown below.



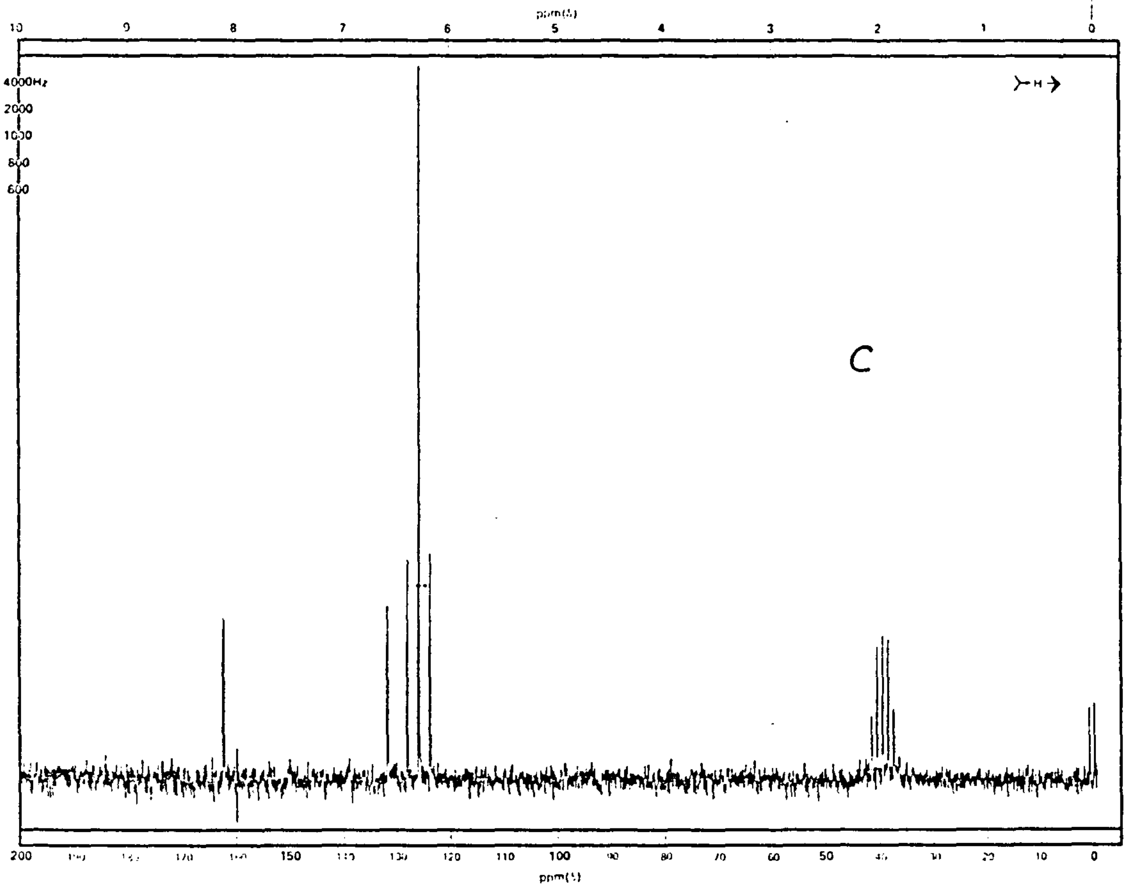


CFT 20
SPECTRUM NO 309
OPERATOR HSC DATE 1/11/85
SAMPLE AUR
TUBE OD [✓ 5mm] 8mm 10mm



$CH_2=C(Cl)COOH$

NUCLEI ☐1H ☒13C ☐19F ☐31P ______ ☐
LOCK ☐INTERNAL ☐EXTERNAL
LOCK SIGNAL DMSO-d6
SPIN RATE 28 rps TEMP 34 °C
ACQUISITION



CFT 20
SPECTRUM NO 310.
OPERATOR HSC. DATE 1/11/85
SAMPLE AVR001D4
TUBE OD [✓ 5mm] 8mm 10mm
HB.

SFORD.

NUCLEI ☐1H ☒13C ☐19F ☐31P ______ ☐
LOCK ☐INTERNAL ☐EXTERNAL
LOCK SIGNAL DMSO-d6.
SPIN RATE 8 rps TEMP 34 °C

ACQUISITION
SPECTRAL WIDTH (SW) ______ Hz
NO. OF TRANSIENTS (NT) ______
ACQUISITION TIME (AT) ______ sec
PULSE WIDTH (PW) ______ μsec
PULSE DELAY (PD) ______ sec
DATA POINTS (DP) ______

TRANSMITTER OFFSET (TO) ______
HIGH FIELD ______ LOW FIELD ______
RECEIVER GAIN (RG) ______

DECOUPLER MODE (DM) ______
DECOUPLER OFFSET (DO) ______
NOISE BANDWIDTH (NB) ______ kHz
ACQUISITION MODE (AM) ______

DISPLAY
SENS. ENHANCEMENT (SE) ______ sec.
WIDTH OF PLOT (WP) 4030 Hz
END OF PLOT (EP) -30 Hz
WIDTH OF CHART (WC) 4030 Hz
END OF CHART (EC) -30 Hz
VERTICAL SCALE (VS) ______
REFERENCE LINE (RL) ______

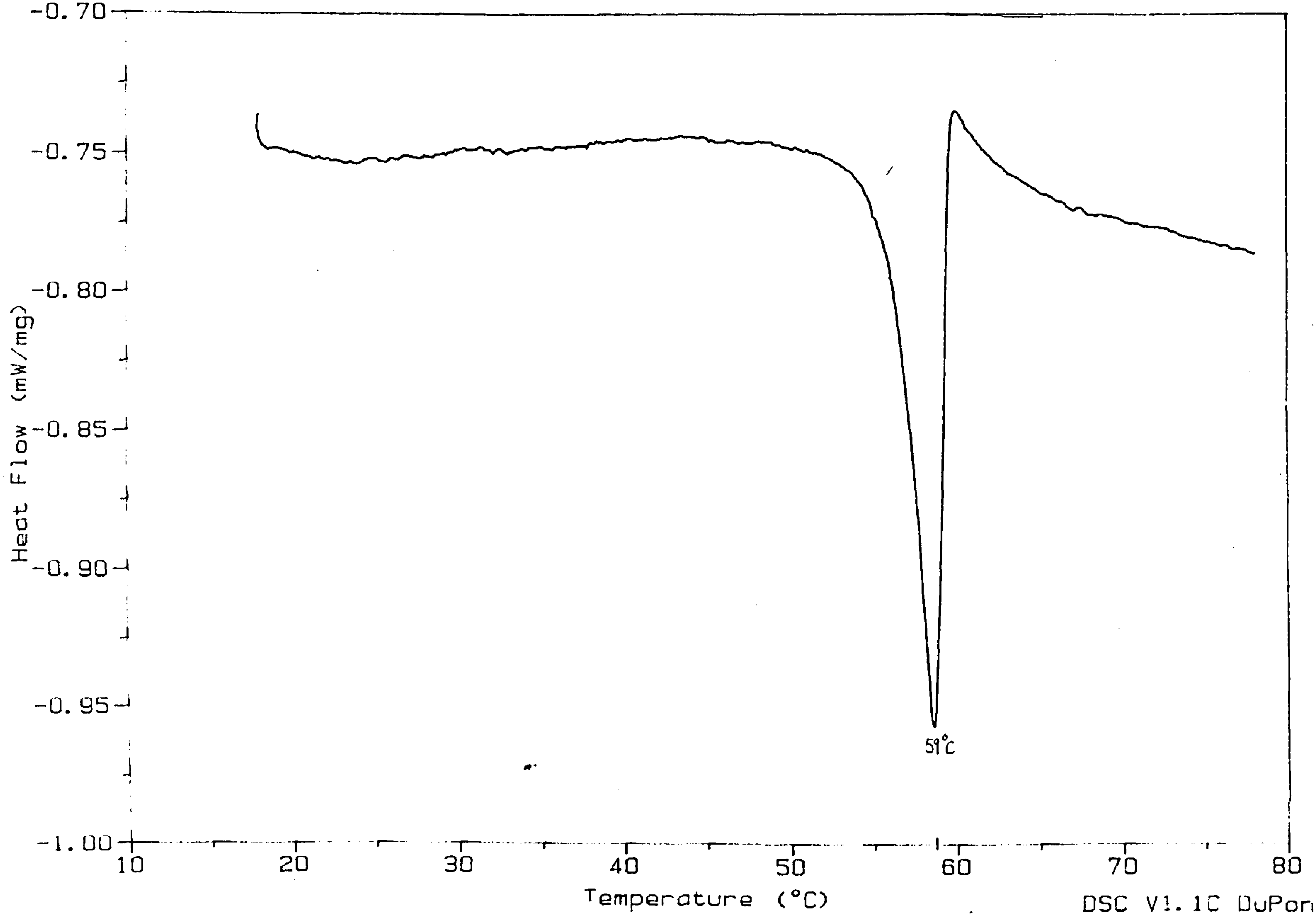
WILMAD GLASS CO. INC.

These spectra (A, B, C) are conclusive of the structure of the synthesized 2-chloro-2-propenoic acid. Also shown below is the plot of the melting point determination. The melting point is calculated to be 58-60°C. Literature gives the melting point at 60-62°C [70].

Sample: 2-CHLORO-2-PROPENOIC ACID
Size: 15.00 mg
Method: MPT
Comment: MELTING POINT DETERMINATION

DSC

File: AVR.01
Operator: A. VAN REENEN
Run date: 11/12/85 09:42



DSC V1.1C DuPont 9900