THIN FILM COMPOSITE MEMBRANES BASED ON POLYESTERAMIDES

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By
JAYARANI M. MUDALIAR

POLYMER SCIENCE AND ENGINEERING GROUP
DIVISION OF CHEMICAL ENGINEERING
NATIONAL CHEMICAL LABORATORY
PUNE 411 008

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CERTIFICATE

Certified that the work incorporated in the thesis **THIN FILM COMPOSITE MEMBRANES BASED ON POLYESTERAMIDES** submitted by Ms. Jayarani Mohan Mudaliar was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Sudhir Kulkarni

Dr. S. S. Kulkarni
Research Guide
National Chemical Laboratory
Pashan Road
Pune - 411 008

Dedicated to my Parents…

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(Jayarani M. Mudaliar)

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Abbreviations

ADTC	Adamantane-2,6-dione-1,3,5,7-tetracarbonyl chloride
AFM	Atomic Force Microscopy
m-AP	*m*-Aminophenol
p-AP	*p*-Aminophenol
Bis-A	Bisphenol-A
BP	Biphenol
BPS	Bisphenol-S
CA	Cellulose acetate
CMC	Critical micellar concentration
COSY	Correlation spectroscopy
CTA	Cellulose triacetate
DHDPE	4,4'-Dihydroxydiphenyl ether
ESCA	Electron spectroscopy for chemical analysis
HQ	Hydroquinone
FOCAS	Full optimization curve analysis software
FTIR	Fourier transform infrared
HT	Cyclohexane-1,3,5-tricarbonyl chloride
IPC	Isophthaloyl chloride
NF	Nanofiltration
o-PDA	*o*-Phenylene diamine
m-PDA	*m*-Phenylene diamine
p-PDA	*p*-Phenylene diamine
PBIL	Poly(benzimidazolone)
PSF	Polysulfone
PVA	Poly(vinyl alcohol)
PVI	Poly-2-vinylimidazoline
PVP	Poly(vinylpyrrolidone)
Res	Resorcinol
RO	Reverse osmosis
SLS	Sodium lauryl sulfate
TBAC	Tetrabutylammonium chloride
TBABr	Tetrabutylammonium bromide
TEA	Triethylamine
TEAC	Tetraethylammonium chloride
TEBAC(BTEAC)	Triethylbenzylammonium chloride
TDS	Total dissolved solids
THEIC	1,3,5-tris(hydroxyethyl)isocyanuric acid
TFC	Thin film composite
TMC	Trimesoyl chloride
TPC	Terephthaloyl chloride

ABSTRACT

INTRODUCTION

Thin film composite (TFC) type of membranes comprising of an ultra thin film of a permselective polymer deposited on a micro-porous support are being increasingly used for reverse osmosis (RO) applications. An ideal TFC membrane exhibits high salt rejection coupled with high water permeability. An aromatic polyamide TFC membrane formed from the reaction of *m*-phenylene diamine (*m*-PDA) with trimesoyl chloride (TMC) has excellent desalination performance. However, the membrane is degraded by chlorine attack which is used as a disinfectant. Research in this field is thus directed towards the formulation of high flux and high solute rejection membranes coupled with high chlorine tolerance.

There are few systematic studies in the open literature as a basis for design of the polymer structure. There is not even a clear picture of the mechanism of chlorine attack. The relationship between the polymer structure and the resulting membrane characteristics such as RO performance (water permeability, salt and organics rejection) and chlorine tolerance need to be studied in further details.

The present work is divided in two parts that includes both (i) a study of the chlorination resistance of various adducts as well as (ii) a study of various polyesteramide based TFC membranes.

EXPERIMENTAL

I) Adduct Study

Various adducts comprising of *o*-, *m*- and *p*-diamide, *m*- and *p*-diester and *m*- and *p*-esteramide linkages were synthesized by benzoylation of respective diamines, diols and aminophenols. These adducts were then exposed to different levels of chlorination within a fixed pH = 6 - 6.5. The first two levels involved single day exposures at chlorine concentrations of 10,000 ppm (A) and 35,000 ppm (B) respectively while the third level involved exposure upto seven days at chlorine concentration of 35,000 ppm (C). The chlorine treated and untreated adducts were then analyzed by melting point, IR and NMR studies.

II) Fabrication of TFC Membranes for RO

A standard polyamide membrane was formed by the reaction of *m*-PDA with TMC on a micro-porous polysulfone (PSF) support. Based on the adduct study, monomers such as *m*-aminophenol (*m*-AP), bisphenol-A (Bis-A) and hydroquinone (HQ) were selected for TFC membrane formation. In all cases, when only these monomers were reacted with TMC the resultant membranes gave high solute permeabilities coupled with high water permeabilities. Hence, TFC membranes were prepared as copolymers based on the reaction of TMC in the organic phase with the experimental monomers and *m*-PDA in varying proportions in the aqueous phase. The two diamine systems i.e. 1,5 naphthalene diamine and 2,6-diaminopyridine were investigated without the addition of *m*-PDA. TFC membranes were formed by coating a micro-porous PSF support with an aqueous solution followed by contacting with TMC dissolved in hexane. The aqueous solutions consisted of the following :

1) 90:10; 80:20; 70:30; 50:50 and 30:70 mole proportions of *m*-AP : *m*-PDA. The effect of a surfactant (SLS) in the aqueous phases was also examined;

2) 80:20; 70:30; 50:50 and 30:70 mole proportions of Bis-A : *m*-PDA;

3) 80:20; 70:30; 50:50 and 25:75 mole proportions of HQ : *m*-PDA;

4) 1,5-naphthalene diamine dissolved in 50:50 methanol : water; and

5) 2,6-diaminopyridine dissolved in water

The aqueous phase in addition also contained NaOH and a suitable phase transfer catalyst in cases 1-3. Generally, at each composition of the reacting phases, the dip times in each phase and the curing conditions were optimized so as to get the best performance corresponding to that particular composition.

All these TFC membranes in addition to the standard polyamide membrane were tested for their RO/nanofiltration (NF) characteristics using a solution of 2000 ppm NaCl + 5% sucrose at 2.7 MPa. The water flux through the membranes was measured and the feed and permeate samples were analyzed in order to determine the water and solute permeabilities.

III) Polymer Sample Preparation for FTIR Characterization Study

Since the reactivities of the aminophenols and the diols are lower than that of the diamines it was necessary to confirm the percent ester incorporated in the polyesteramides. For this, firstly, homopolymers were prepared by the reaction of TMC dissolved in hexane with an aqueous solution comprising of : 1) *m*-PDA , 2) *m*-AP , 3)

Bis-A, and 4) HQ. Physical mixtures were prepared based on 50:50 weight percent of homopolymers 2, 3 and 4 with polyamide 1. Following this, polyesteramide polymers were prepared by unstirred interfacial reaction between TMC and 50:50 mole ratios of *m*-AP : *m*-PDA, Bis-A : *m*-PDA and HQ : *m*-PDA. The physical mixtures were used to calibrate the area peaks observed in FTIR spectra in order to determine the percent ester incorporation in the polyesteramides.

IV) Chlorine Tolerance Studies

The chlorine exposure studies monitored the changes in the rates of water flux and salt passage through the TFC membrane after continuous exposure to chlorinated water. Chlorine exposure studies were conducted with the addition of NaOCl to the feed solution so that residual chlorine concentration in the feed was about 200 ppm followed by stabilizing the pH at 6 - 6.5 with HCl addition. The chlorine tolerance of the polyesteramide membranes, in each chlorine exposure run, was compared with the TFC membrane based on the standard polyamide formulation (*m*-PDA reacted with TMC) as a reference. The membrane samples for the reference polyamide and polyesteramide TFC membranes were chosen so as to have similar initial salt rejection values. Since high rejection TFC membranes could not be made using either 1,5-naphthalene diamine or 2,6-diaminopyridine, these were not included in the chlorine tolerance study. The polyesteramide TFC membranes chosen for the chlorine exposure studies were based on the reaction of TMC with the following aqueous phase compositions: 1) 50:50 *m*-AP : *m*-PDA , 2) 25:75 HQ : *m*-PDA, 3) 50:50 Bis-A: *m*-PDA, and 4) 50:50 HQ: *m*-PDA.

RESULTS AND DISCUSSIONS

I) Adduct Study

The structures of the adducts synthesized by benzoylation of various diamines, aminophenols and diols were confirmed by IR and NMR spectral analysis. The reactivity of these adducts when subjected to varying levels of chlorine treatment was monitored by NMR. Ring chlorination has been detected only at the positions either ortho or para or both to the amide function. N-chloro amide formation could not be specifically detected by NMR. But the overall results are consistent with N-chlorination followed by ring chlorination via Orton rearrangement.

The chlorine resistance of a particular class of adducts is greatly influenced by the substitution pattern. The diamide obtained from *o*-PDA could not be chlorinated even at the most severe chlorination conditions (treatment C). This is attributed to steric hindrance at the -NH- position and is consistent with the above postulated reaction mechanism. The other diamides obtained from *m*-PDA and *p*-PDA showed susceptibility to chlorination only on treatment C. The diamide obtained from *p*-PDA was chlorinated to a lesser extent compared to that formed from *m*-PDA. The NMR spectra of the diamide adduct formed from *m*-PDA subjected to treatment C on chlorination showed the presence of a tri-chloro derivative as the major product in addition to minor fractions of either mono- or di-chloro derivatives. The NMR spectra of the diamide adduct formed from *p*-PDA subjected to treatment C showed the presence of a major portion of unchlorinated adduct along with some mono- and di-chloro derivatives. The diamide adducts showed the following increasing order of chlorine tolerance :

diamide obtained from *m*-PDA < diamide obtained from *p*-PDA < diamide obtained from *o*-PDA.

In case of the esteramide adducts, the adduct obtained from *p*-AP was affected even at the mildest chlorination conditions (treatment A) where no change was observed with the adduct obtained from *m*-AP. Both the esteramide adducts are susceptible when exposed to more severe chlorination (treatment C); the extent of chlorination was more with the adduct formed from *m*-AP than that formed with *p*-AP. The NMR spectra of the esteramide obtained from *m*-AP indicated the formation of a di- and a tri-chloro derivative. In case of the esteramide obtained from *p*-AP, treatment C resulted in the formation of mixed mono- and di-chloro products that were confirmed from a COSY study.

The formation of these chlorinated products in both the diamides and the esteramides is attributed to the ortho para directing effect of the -NH- group.

All the diesters resisted chlorination even on most severe chlorination conditions (treatment C).

The above NMR study on the chlorine treated adducts is in turn supported by the melting point study.

II) TFC Membranes for RO

a) Polyesteramide TFC membranes formed from m-AP : m-PDA based compositions

In case of polyesteramide TFC membranes formed from varying compositions of *m*-AP : *m*-PDA it was observed that as the proportion of *m*-AP was decreased the salt rejection of the membrane increased. The best membrane obtained with 70:30 *m*-AP : *m*-

PDA composition exhibited complete sucrose rejection combined with a salt permeability of 0.6 x 10^{-6} m/s corresponding to a rejection of 91%. This was combined with a reasonable water permeability of 3.1 x 10^{-6} m/s-MPa. The membranes formed from 50:50 and 30:70 compositions showed overall lower solute permeabilities that were comparable with the standard polyamide membrane but with even lower water fluxes.

Addition of the surfactant SLS to this system caused all the permeability coefficients to decrease by 2-3x and there was no improvement in the separation ability of the membrane to compensate for the loss in water flux.

b) Polyesteramide TFC membranes formed from Bis-A : m-PDA based compositions

At the highest Bis -A : *m*-PDA ratios (>80:20), the membrane solute rejection was poor. The membrane performance was not found to be sensitive to the Bis-A proportion within a wide composition range of 80:20 to 30:70. In comparison to the standard polyamide membrane, the Bis-A : *m*-PDA membranes exhibited similar sucrose and water permeabilities; however, the salt permeabilities were at least 2x higher. The incorporation of ester functionalities via the Bis-A moiety is found to decrease the salt rejection of the resulting membranes as compared to the standard polyamide membrane. This effect could be related to the size of the Bis-A monomer.

c) Polyesteramide TFC membranes formed from HQ : m-PDA based compositions

The HQ : *m*-PDA system shows considerable potential for forming useful RO membranes. This system could be used to fabricate both loose RO or NF membranes as well as tighter RO membranes with NaCl rejections up to 98% at 2.76 MPa and 2000 ppm salt. The sucrose rejection was complete and the water permeability of these membranes was found to be only slightly lower being about 70% of the best values for the standard polyamide membrane samples. Though there was a slight trend towards increasing salt rejections with decreasing ratios of HQ : *m*-PDA, within a range from 80:20 to 25:75, the salt rejections were not very sensitive to this composition. The salt permeabilities of the membranes formed from 70:30 and 50:50 compositions were comparable to that of the standard polyamide membrane although the water permeabilities are slightly lower (70% of best values). As compared to membranes formed from the Bis-A : *m*-PDA system, those formed from HQ based compositions yield membranes with higher salt rejection values. This may be attributed either to the greater colinearity of the polymer chain with HQ compared to that with Bis-A (additional kink at the bridge carbon) or to the larger size of the Bis-A monomer compared to HQ, which thus allows a tighter polymer matrix packing in the HQ case.

d) Novel polyamide TFC membranes

The salt rejections for the novel polyamide membranes formed from the reaction of 1,5-naphthalene diamine with TMC, could not be improved beyond 85%. Even though the water permeability was very low, the sucrose rejections too could not be improved beyond 95%.

Novel polyamide TFC membranes formed from the reaction of TMC with 2,6-diaminopyridine also did not exhibit sufficiently high salt rejections to be considered for development as RO membranes (max. 89-92% NaCl rejection). Though the water permeability and sucrose rejection of these membranes were better than with the 1,5-naphthalene diamine system, they were much lower than that of the standard polyamide membrane. At certain conditions membranes could be made which exhibited reasonably high salt and water permeabilities with low sucrose permeabilities.

III) FTIR Study

A standard deconvolution package (FOCAS) was used to determine the area under the ester and amide signals for both the physical mixtures and the polyesteramide polymers. Approximately 10% incorporation of ester functionality through the use of aminophenol (*m*-AP) moiety and 22% in case of the diols (Bis-A and HQ) was observed in case of the polyesteramides.

IV) Chlorine Tolerance Studies

All chlorine exposure studies were conducted on polyesteramide systems based on 50:50 compositions. At the 50:50 composition ratio, FTIR analysis showed that the final membrane would contain 10% ester linkages in the *m*-AP case and 22% ester linkages in the case of the two diols. The adduct study had already shown that aromatic ring chlorination is less feasible for the diesters compared to adducts prepared with diamines or aminophenols.

Both the 50:50 *m*-AP : *m*-PDA system and the 25:75 HQ : *m*-PDA systems which contain a similar low proportion of ester linkages (10 - 11%) show low chlorination resistance, that is only slightly better than that of the standard polyamide membrane. The 50:50 *m*-AP : *m*-PDA composition exhibited a chlorine tolerance that was only 1.58x higher and 25:75 HQ : *m*-PDA composition showed 1.96x higher as compared to the standard polyamide membrane tested under the same conditions separately in each case. Doubling the percent HQ from 25 to 50%, gave a substantial increase in chlorination resistance.

Both the 50:50 Bis-A : *m*-PDA and HQ : *m*-PDA systems showed enhanced chlorine tolerance of about 4x as compared to the standard polyamide membrane. This is encouraging as useful RO membranes can be prepared from these systems at even higher levels of diol incorporation. Though the HQ system gives better salt rejection than the Bis-A system, there is no significant difference between either monomer in terms of the chlorine tolerance of the resultant membranes.

The study shows that the most important variable affecting the chlorination resistance of the polyesteramide membranes is simply the level of ester linkages incorporated into the copolymer. Unless there is a certain minimum level of ester functions (22%) incorporated in the polyesteramide membrane, no significant improvement in chlorine tolerance was seen. Diols are more effective than aminophenols in increasing chlorine tolerance due to two reasons, (i) twice the number of ester linkages are introduced into the structure per monomer unit, and, (ii) the aromatic rings contributed by the diols are not susceptible to chlorine attack as was evidenced from the adduct study. Both these factors have effectively reduced the available sites for chlorine attack thereby enhancing the chlorine tolerance of the membrane.

All membranes showed an initial rapid decline in the water permeability on initial chlorination which is indicative of rapid N-chlorination which destroys the H-bonding potential of the membrane. This was then followed by a more gradual ring chlorination process. Both these processes render the membrane hydrophobic. In certain instances, the reference standard polyamide membranes did show an increase in the water permeability values at higher chlorination times which is indicative of chain cleavage that results in polymer structural breakdown. Comparatively, the polyesteramide membranes do not show the increasing flux regime corresponding to structural degradation of the membrane.

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Traditional separation processes such as distillation, extraction, ion-exchange and adsorption have been supplemented by a class of processes that utilize semipermeable membranes. Today, membrane processes are widely used to produce potable water from the sea, to clean industrial effluents and recover valuable constituents, to concentrate, purify or fractionate macromolecular solutions in the food and drug industries and to remove urea and other toxins from the blood stream in an artificial kidney. Membranes can to a certain extent be “tailor made”, so that their separation properties can be adjusted to a specific separation task.

Reverse osmosis (RO) membrane technology is one such process that was initially developed for providing potable water from sea water. Today, the technology finds a wide variety of applications in waste water treatment, production of ultrapure water, water softening, food processing etc.. As compared to other desalination processes, RO has a number of advantages in that it involves no phase change and thus is a potentially low energy process, is compact in terms of space and can operate at mild temperatures.

In comparison to the traditional RO membranes, nanofiltration (NF) or “loose RO” membranes exhibit lower salt rejection with higher water fluxes at low pressures. The performance range of these NF membranes is between that of the RO and ultrafiltration membranes. These membranes are finding several applications in water treatment and in chemical and food industry processing.

1.1.1 Definitions

Osmosis is a natural phenomenon in which water passes through a semipermeable membrane from the side with lower solute concentration to the higher solute concentration side until the solvent chemical potential is restored to equilibrium. For the reverse phenomena, that is recovery of water from concentrated solutions, a pressure difference greater than the osmotic pressure difference, corresponding to the difference in chemical potential between the two solution phases, has to be applied. This phenomenon, also known as hyperfiltration, is termed as reverse osmosis.

The driving force in solute and solvent transport through RO membranes are the chemical potential gradients across the membrane which are defined in terms of the differences in concentration and pressure across the membrane. The process of RO is classified into three types : high pressure RO (5.6 - 10.5 MPa, 99+% NaCl rejection, e.g. seawater desalination), low pressure RO (1.4 - 4.2 MPa, 95% NaCl rejection, e.g. brackish water desalination) and nanofiltration also known as "loose RO" (0.3 - 1.4 MPa, 20 - 90% NaCl rejection, e.g. water softening).

Solute rejection through a membrane is defined as,

$$R = 1 - C_p/C_f \tag{1.1}$$

where R is the observed solute rejection, C_p is the concentration of the solute in the permeate and C_f is the solute concentration in the feed solution.

The water flux (J_w) through the membrane is defined as,

$$J_w = \text{volumetric rate/membrane area}$$

$$J_w = A\,(\Delta P - \Delta\pi) \tag{1.2}$$

where, A is the water permeability coefficient, ΔP is the applied pressure difference while $\Delta\pi$ is the osmotic pressure difference.

The solute flux is defined as,

$$J_s = B\,(C_f - C_p) \tag{1.3}$$

$$J_w.C_p = B\,(C_f - C_p) \tag{1.4}$$

where, J_s is the solute flux, B is the solute permeability coefficient, C_f is the solute concentration in the feed and C_p is the solute concentration in the permeate.

1.1.2 Applications of RO

The technology of RO has grown extensively over the recent years. As compared to the traditional cellulose acetate (CA) membranes, newer membrane materials have been developed that are more pH, temperature and chlorine resistant thereby resulting in many applications for the RO process. The most important application of RO membranes is in the desalination of sea and brackish water. Numerous RO desalination plants with varying capacities and feed waters have been installed in various locations around the world. The total capacity is exceeded only by multi-stage flash evaporation plants, which today is preferred for large units, especially in combination with power plants. However, for smaller units and brackish water sources, RO is clearly the more economical process for producing potable water mainly due to its lower energy requirements, lower capital and operating costs and low land and space requirements. RO also finds application in the treatment of waste water such as effluents from the metal plating industry, pulp and paper industry, other industrial and municipal waste waters. Food processing is another important application area for RO technology. These applications in the food industry include water treatment applications, recovery of food products, recovery and recycling of the chemicals required in food processing and concentration and dewatering applications. Yet another important application of RO is in the production of ultra pure water for the semiconductor industry.

NF membranes find applications in water softening, desalting, food processing as well as waste water treatment. These membranes can be used to separate salt from organics. Thus, in the processing of whey permeate, NF can simultaneously concentrate lactose and increase the lactose : ash ratio.

1.1.3 RO Membrane Materials

From the advent of CA as a RO membrane through the discovery of high flux membranes by Loeb and Sourirajan (1962, 1964), continuous research has identified several new polymer materials for RO. Various reviews (Parekh 1988; Koros *et al* 1988; Petersen 1993; Glater *et al* 1994; Soltanieh and Gill 1981; and Pusch 1986) have covered the development of RO membrane technology as also the membrane materials used, the transport mechanisms and applications of the same.

RO membranes are structurally divided into either asymmetric or thin film composite (TFC) structures. Both consist of a thin separation layer supported by a porous substructure; the difference is that in TFC membranes, the active layer and the porous support are formed from different polymers. TFC membranes are made either by (a) coating of a film forming polymeric layer on top of a porous support or, (b) by interfacial reaction of monomers to form a polymer in situ on the surface of a porous support.

The most widely used asymmetric membranes are based either on CA, cellulose triacetate (CTA) or on aromatic polyamides. CA membranes are best suited where continuous chlorination is desired. Aromatic polyamides have better desalination performance and better biological and thermal resistance. Other materials that have been used for preparing asymmetric membranes include poly(amidehydrazide), poly(piperazineamide), poly(benzimidazole), sulfonated polysulfone, and poly(sulfonamides).

TFC membranes are gradually gaining predominance since the choice of chemistries involving this fabrication technique is very wide. Today, the most widely used TFC membranes are based on aromatic polyamides. Other TFC membranes based on polyureas, poly(etherureas), poly(etheramides), sulfonated polymers and poly(vinyl alcohol) were developed but suffered from either hydrolytic or oxidative instability or from poorer desalination characteristics.

A significant advance in the development of TFC RO membranes was the FT-30 membrane that comprises of a crosslinked aromatic polyamide active layer. The salt rejection, water flux and pH resistance of this membrane is superior to any of the previously synthesized membranes. The main drawback of this membrane is its sensitivity to oxidizing agents and lack of chlorine tolerance. The membrane is also more costly per unit membrane area than the CA membrane.

NF membranes are often negatively charged so that the salt rejection is mainly due to anion repulsion. Several commercially successful NF membranes are based on crosslinked poly(piperazineamide) structures.

1.2 RATIONALE FOR WORK

The thesis investigates the potential use of polyesteramides as new TFC membrane materials. The rationale for this approach towards developing improved RO membranes and target membrane criteria are given below.

1.2.1 Criteria for RO Membrane Performance

It is desirable to identify materials that will yield membranes exhibiting a high flow capacity at low driving pressure with high levels of salt rejection. In addition, chlorine tolerance of the membranes is one of the most important factors affecting the performance of RO membranes. Some of the more successful attempts to increase chlorine tolerance has been the use of secondary amines, sulfonamides, piperazine based polyamides, etc.. However, these usually gave lower water permeability and higher salt passage as compared to the standard FT-30 polyamide based TFC membrane. To date, the chlorine tolerance of aromatic polyamide membranes has not been improved beyond 1000 ppm-hours. Chlorine concentration in the feed thus has to be controlled to minimal values of 0.05 ppm or lesser in cases where polyamide based membranes are employed.

As a target performance, it would be expected that new RO membranes should exhibit salt rejections >95% with correspondingly high water permeability of $>3 \times 10^{-6}$ m/s-MPa. The chlorine resistance should be higher than 1000 ppm-hours.

To be useful as a NF membrane, the water permeability should be higher than 10×10^{-6} m/s-MPa. This membrane should also have at least 10 times higher permeability for NaCl than sucrose. The chlorine resistance of an NF membrane should be higher than

2000 ppm-hours.

1.2.2 Improvements Possible with Polyesteramide as Compared to Polyamide based Membranes

Present efforts in the field of RO are aimed at generating high flux and rejection membranes with considerably higher degree of chlorine tolerance as compared to the standard polyamide membranes. Polyesteramide based membranes have not yet been comprehensively studied. Polyesteramide membranes would be expected to be slightly less hydrophilic as compared to the polyamide membranes; in addition, they should have improved chlorine tolerance. The amidic nitrogen in these polyamides is known to be vulnerable to chlorine attack. Thus, in case of polyesteramide membranes, it is expected that these sites would be reduced in proportion thereby contributing to an enhanced degree of chlorine tolerance as compared to the polyamide membranes.

Literature reports the synthesis of polyesteramide polymers by interfacial polymerization. It is known that the polyesteramide polymers are suitable for forming fibers, films or molded shapes.

Thus, both the RO/NF performance as well as chlorine tolerance characteristics of polyesteramide membranes need to be explored in detail.

1.3 SCOPE OF THE WORK

There are very few systematic studies in the open literature as a basis for design of the polymer structure for achieving the desired RO membrane properties. There is not even a clear picture of the mechanism of chlorine attack. The relationship between the polymer structure and the resulting membrane characteristics such as RO performance (water permeability, salt and organics rejection) and chlorine tolerance need to be studied in further details.

The present work involves two parts. It includes both (i) a study of the chlorination resistance of various adducts as well as, (ii) a study of various polyesteramide based TFC membranes.

The adduct study was conducted to get a clearer understanding of the relation between various chemical structures and their resistance to chlorination. This study was conducted with organic compounds as opposed to polymers and at severe chlorination conditions so as to more clearly identify the chlorination mechanisms and confirm the susceptibility towards chlorine of various types of chemical structures. The synthesis of model diamide, diester and esteramide adducts was followed by a study on the chlorine susceptibility of the various linkages in these model compounds at increasing levels of chlorination.

Based on the results thus obtained, several new polyamide and polyesteramide TFC membranes were chosen for study. The ability of these new chemistries to yield RO membranes with an increased degree of chlorine tolerance and without much loss in their RO performance characteristics as compared to a standard polyamide membrane (corresponding to FT-30) was investigated. The proportion of ester and amide linkages in the copolymer TFC membranes was varied in order to optimize both desalination performance and chlorine resistance. The RO/NF characteristics were studied by measuring the salt/sucrose rejections and the corresponding water permeability for the various membranes. The chlorine tolerance studies were carried out on selected compositions of polyesteramide membranes and the results were compared with those obtained for a standard polyamide membrane. In addition, synthesis and study of RO/NF performance of novel polyamide membranes based on the use of 1,5-naphthalene diamine and 2,6-diaminopyridine as amine monomers has also been explored.

1.4 OBJECTIVES

The objective of this thesis was to study systematically the effect of change of polymer structure on RO separation characteristics and to evaluate the chlorine resistance of the resulting TFC membranes. The first part comprises of synthesizing model compounds and studying the resistivity of these compounds towards chlorine. The detailed objectives for this study are as follows :

1) To synthesize model compounds comprising of *o*-, *m*- and *p*-diamide, *m*- and *p*-diester and *m*- and *p*-esteramide linkages.

2) To investigate the effect of *o*-, *m*- and *p*- substitution patterns of these adducts towards chlorine resistivity.

3) To compare the susceptibility of ester and esteramide linkages introduced via diols and aminophenols towards chlorination.

4) To analyze whether chlorination occurs by direct attack on aromatic rings or via N-chlorination mechanism.

The second part comprised of developing polyesteramide TFC membranes with improved chlorine tolerance as compared to existing polyamide membranes. The detailed objectives for this study are listed below:

5) To fabricate polyesteramide TFC membranes based on varying compositions of *m*-aminophenol, bisphenol-A and hydroquinone with respect to *m*-phenylene diamine.

6) To study the effect of ester incorporation induced through the use of the diol and aminophenol moieties on RO separation characteristics (solvent and solute permeabilities) of the resultant polyesteramide membranes and to compare this with that of the standard polyamide membrane.

7) To investigate the chlorine tolerance through chlorination study on selected compositions of polyesteramide membranes and compare this with that for a standard polyamide membrane.

8) To compare the effect of diol type (hydroquinone and bisphenol-A) that are used to incorporate the ester linkages on both RO separation characteristics and chlorine tolerance.

9) To analyze from chlorine tolerance studies the effect of combined ester and amide linkages on the same ring in case of the polyesteramide membrane formed by using *m*-aminophenol.

10) To draw comparisons based on the chlorine tolerance of the polyesteramide TFC membranes and to thus understand whether the chemistry through which the ester linkages are incorporated play any role whatsoever on the chlorine tolerance of these membranes.

11) To synthesize and study the separation characteristics of some novel polyamide TFC membranes that contain rings other than phenyl such as naphthalene and pyridine rings in the polymer backbone.

1.5 ORGANIZATION OF THESIS

The thesis is organized in six chapters :

Chapter 1 : Introduction

In this chapter the rationale for developing improved RO membranes with emphasis on objectives undertaken in this work is highlighted. RO technology in general with reference to applications, membrane materials and definition of various terms is also discussed. The organization of the thesis is also presented.

Chapter 2 : Literature review

This chapter reviews the literature on asymmetric and TFC RO membrane materials, their separation characteristics and mechanisms of chlorination of polyamides in addition to the effect of polymer structure on chlorine resistance. The literature on polyesteramides is also reviewed.

Chapter 3 : Experimental

In this chapter the experimental techniques involved in the synthesis and characterization of various model compounds and TFC membranes is discussed. The method of chlorination studies on the adducts in addition to the permeation and chlorination study through TFC membranes are described.

Chapter 4 : Chlorine resistance studies of diamide, diester and esteramide adducts : Results and discussion

This chapter discusses the experimental results of the adduct study in terms of substitution pattern on chlorine resistance and the susceptibility of ester and esteramide linkages in comparison to amide functionalities.

Chapter 5 : TFC membrane study : Results and discussion

In this chapter the RO/NF performance of the various polyesteramide, novel polyamide and standard polyamide TFC membranes that were synthesized is discussed. The RO performance of the polyesteramide and novel polyamide TFC membranes are compared with that of the standard polyamide TFC membrane. The chlorine tolerance of selected polyesteramide membranes is also compared with that of the standard polyamide membrane. The effect of incorporation of ester linkages through the use of aminophenol and diols on the chlorine resistivity are also compared and discussed.

Chapter 6 : Conclusions

This chapter summarizes the experimental data obtained and correlates the results from the adduct and TFC membrane studies.

CHAPTER 2

LITERATURE REVIEW

2.1 REVERSE OSMOSIS : INTRODUCTION

Reverse osmosis is a process wherein a semipermeable membrane is used to separate solutes from a solution by applying a pressure greater than the osmotic pressure of the feed solution, thereby forcing the solvent from the feed to flow through the membrane. The process of RO is simple to design and operate and also does not involve energy-intensive phase changes. In addition to seawater and brackish water desalination (Ko and Guy 1988), RO membranes find a wide variety of applications in waste water treatment (Bhattacharyya and Williams 1991), food processing (Cadotte *et al* 1988), paper and pulp industry (Chakravorty 1987), and production of ultrapure water (Imasu 1985).

RO membranes are either asymmetric or thin film composite structures where a porous matrix supports a dense skin layer also known as the active layer. Membrane permeability is governed by the solute solubility and diffusivity in the active layer (Pusch 1987). The diffusion coefficients of most solutes in nonporous membranes do not vary by orders of magnitude; thus, membrane selectivity is mainly controlled by solute partition coefficients. The membrane material is usually cellulosic or polyamide in nature.

2.2 ASYMMETRIC MEMBRANES

Asymmetric membranes are chemically homogenous and comprise of a dense skin layer on a micro-porous substructure which acts as a support. The selectivity and flux through the membrane is controlled by the dense skin layer while the porous substructure functions mainly as a physical support for the skin. These membranes are prepared by phase inversion techniques.

2.2.1 Preparation Procedure

Phase inversion membranes can be prepared from any polymer-solvent system which forms a homogenous solution under certain conditions of temperature and composition, and separates at a different temperature or composition into two phases. The polymer concentration is a significant parameter for tailoring a membrane in terms of its structure and separation properties. The following general preparation procedure is used to prepare asymmetric phase inversion membranes (Kesting 1955) :

1) The polymer is dissolved in an appropriate solvent to form a solution containing 10 - 30 weight percent polymer.

2) The solution is cast into a film of typically 100 to 500 μm thickness.

3) The film is quenched in a nonsolvent which for most polymers is typically water or an aqueous solution.

During the quenching process, the homogenous polymer solution separates into two phases i.e. a polymer rich phase that forms the membrane structure and a solvent rich liquid phase that forms the liquid filled membrane pores.

Certain membrane structures can be correlated with the rate of precipitation. Very high precipitation rates lead to a "finger" structure, slower precipitation rates lead to asymmetric membranes with a "sponge" structure and very slow precipitation rates often lead to symmetric membranes with no defined skin at the surface. Higher precipitation rates lead to finer pore structures (Frommer *et al* 1971). Detailed descriptions of membrane preparation techniques are given in literature (Merten 1966 and Manjikian 1967). Kimmerle and Strathmann (1990) have described the structure formation of phase inversion membranes by means of ternary phase diagrams, tie-lines and some kinetic considerations. The analysis can be applied to vapor-, diffusion- and thermal-induced phase separation processes.

2.2.2 Cellulose Acetate Membranes

The first asymmetric porous CA RO membrane was developed for desalination in 1960 (Loeb and Sourirajan 1962, 1964). A transition layer, with a density intermediate between that of the skin and the porous substructure, has also been identified to exist just below the skin layer in the asymmetric CA membranes (Panar *et al* 1973; Gittens *et al* 1973).

Early CA membranes were fabricated from cellulose diacetate which is subject to hydrolysis at either low or high pH conditions, biological attack and compaction at temperatures in excess of 29°C. A considerable amount of research was done to develop a membrane of CTA as this material is found to be more stable to temperature, pH and is better able to withstand chemical and biological attack (Mungle and Fox 1977; Joshi and Rao 1984). The ratio of water permeability to salt permeability also increases with increasing acetyl content (Lonsdale *et al* 1965). The main drawbacks of CTA were its poor solubility in solvents miscible with water, high crystallinity, and compaction at high pressures. A blend of cellulose diacetate and CTA was found to provide a better membrane which is more stable, exhibits a better flux and rejection value than cellulose diacetate membranes, and is more resistant to compaction than either di- or triacetate based membranes. Other cellulose esters (butyrate, propionate etc.) have also been examined as RO materials; however, the membrane properties have been inferior to the CA/CTA based membranes (Kesting 1985). CA type membranes can tolerate a limited concentration of 0.3 - 1.0 ppm of chlorine.

2.2.3 Other Asymmetric Membranes

Numerous polymers, other than CA, have been screened to determine their suitability for use in RO desalination. DuPont (Permasep) commercialized a series of asymmetric membranes based on aromatic polyamides (Aramid). Among these are the B-9 and B-10 Permasep (aromatic polyamide) hollow fiber permeators for brackish water and seawater applications respectively. These hollow fiber membranes contain a dense, semipermeable, outer skin (500 - 2500 A° thick) and a porous structure throughout the remainder of the fiber wall which supports the permselective skin. These membranes can be operated over a broad pH range of 4 - 11, and are reasonably resistant to hydrolysis and biodegradation. This membrane is less water permeable but more salt retentive than the CA membrane (Richter and Hoehn 1971). The transport properties of aromatic polyamide membranes have been reported (McKinney 1972).

Following the commercial success of the polyamide asymmetric membranes various other types of amide-containing polymers have also been investigated. Asymmetric membranes of aromatic polyamide hydrazide exhibit reasonably good RO performance (McKinney 1972; Satre and Ghatge 1993). Poly(piperazineamides) derived from various bicarboxylic acids also form skinned membranes exhibiting properties that approach that of CA (Credali *et al* 1974). Parrini *et al* (1983) have reported chlorine resistant asymmetric membrane compositions based on piperazine containing polyamides. Asymmetric membranes of poly(benzimidazolone) (PBIL) prepared by the phase inversion technique are reported to exhibit higher salt rejection than conventional CA membranes. The PBIL membrane also has improved stability to high temperature, and to acidic, alkaline and oxidative conditions (Hara *et al* 1977).

The use of sulfonated aromatic polymers for RO membranes began with work by Plummer *et al* (1970). The synthesis of asymmetric sulfonated polysulfone (PSF) membranes were reported by Rhone-Poulenc in 1973 (Quentin 1973; Bourganel 1977). The degree of sulfonation was limited so that the product would be water insoluble. Kinzer and Lloyd (1985) report the synthesis of asymmetric sulfonated PSF membranes by phase inversion using mixed nonsolvent casting systems. Casting solution components and compositions were selected based on Hansen's three-component solubility parameter. A further development was the asymmetric poly(sulfonamide) membranes (Gao *et al* 1991). These membranes were found to exhibit high salt rejection but very low fluxes. The increased chlorine tolerance of these membranes was attributed to the absence of amidic hydrogen.

2.3 THIN FILM COMPOSITE MEMBRANES

Unlike asymmetric membranes that are formed in a single step, TFC membranes comprise of a bilayer formed in a two step process. In the first step, a porous nonselective support membrane is formed. This is followed by the coating of an ultra-thin film (active layer) on the surface of the porous layer. Each of these individual layers can be optimized separately. The porous layer can be optimized separately for maximum strength and compression resistance while the active layer can be optimized separately for the desired combination of solvent flux and solute rejection characteristics. Although, composite membranes are more expensive to manufacture as compared to the asymmetric membranes, the cost is more than counterbalanced by the improved permeation characteristics of the TFC membranes.

2.3.1 Fabrication Procedures

Cadotte and Petersen (1981) list the following five major routes to obtain composite membranes:

1) casting the active layer separately followed by lamination on to a micro-porous support;

2) dip-coating a polymer solution on to a micro-porous support followed by drying in place;

3) dip-coating a solution of a reactive monomer or pre-polymer on to a micro-porous support followed by curing with heat or irradiation;

4) gas-phase deposition of the barrier layer from a glow discharge plasma;

5) interfacial polymerization of a reactive set of monomers on the surface of a micro-porous support.

2.3.2 Casting of the Micro-porous Support Used to Prepare TFC Membranes

The concept of composite RO membranes was first reported by Francis in 1966. An ultra-thin film of CA was float-cast on a water surface and then laminated on preformed micro-porous supports. Initial micro-porous supports were made from asymmetric CA by modification of the Loeb-Sourirajan procedure. Later work showed improved results with the use of cellulose ester microfiltration membranes as supports.

Initially, the major flux limiting concerns were related to the severe compaction under pressure of the cellulosic membranes. Rozelle *et al* (1968) synthesized and tested several non-cellulosic micro-porous support films based on polycarbonate, poly(phenylene oxide) and PSF. Of these, the micro-porous PSF films proved to have the best properties and have remained a mainstay in the field of composite membranes to this day.

The micro-porous PSF support membranes are made by the following procedure. A 15% solution of PSF solution in N,N-dimethylformamide is prepared and degassed, either by standing for a long period or by vacuum evacuation in a dessicator. The solution is cast on a clean glass plate at room temperature and spread by a doctor blade having a gap of 10 mils followed by quick immersion into water. Within a few minutes of immersion the PSF film detaches itself from the glass plate. The film is allowed to soak for several minutes and then subsequently rinsed with solvent-free water before it is used. The micro-porous PSF films have to be kept wet while simultaneously preventing the growth of micro-organisms on the film surface. This is due to the fact that PSF is hydrophobic and resists rewetting if allowed to dry.

Lau *et al* (1991) report polymer precipitation diagrams for PSF and poly(ether-sulfones) in various solvents. The addition of nonsolvents used in PSF solutions increases the sensitivity of the solution to water as a phase separation medium. The effect of several organic additives in PSF casting solutions have been reported by Hou *et al*

(1991). Based on a study of the cloud point data, rheological properties and the effect of these additives on the membrane pore size, they have proposed a mechanism for the action of organic additives in the PSF casting solutions. According to this mechanism, hydrogen bond interactions exist between additives and solvent in the PSF casting solution. Thus, the number of solvent molecules around the PSF is decreased and the extent of supermolecular structure of the polymer in solution is increased. Cabasso *et al* (1977) report the use of polyvinyl pyrrolidone (PVP) as an additive that acts as a viscosity promoting agent in the PSF casting solutions. Kesting *et al* (1990) have discovered that high viscosity solutions of PSF can be prepared by using 1:1 Lewis acid : base complexes as solvents.

2.3.3 Membranes Formed by Dip-coating

Various TFC membranes have been made either by dip-coating a polymer solution or by coating with reactive monomers. The earliest membranes formed by dip-coating were reported by Riley *et al* (1969). A mixed cellulose ester micro-porous support was initially coated with polyacrylic acid from its solution. This was followed by overcoating with a solution of CTA in chloroform and drying. Under RO testing conditions, the polyacrylic acid layer dissolved leaving behind the CTA layer. Reported salt rejections for this membrane were as high as 99%.

More recent composite RO membranes prepared by the dip-coating approach are discussed below:

1) Sulfonated polyfuran membranes : The NS-200 membrane comprises of a sulfonated polyfuran active layer formed on a micro-porous PSF support (Cadotte 1975). Synthetic

seawater tests on this membrane at 6.9 MPa produced salt rejections of 99.8% with fluxes of ~34 lmh. However, the long term stability of this membrane was a problem. Prolonged seawater tests on the membrane showed a significant decrease in salt rejection with time. The decreased rejection could be partially averted by periodically treating the membrane with a salt of a multivalent cation such as barium. Another problem was the swelling of the active layer; this was attributed to hydrolysis of the sulfate and sulfonate ester linkages in the sulfonated polyfuran matrix.

2) Sulfonated PSF membranes : Cadotte *et al* (1978) developed a composite sulfonated PSF membrane by dip-coating a PSF support in a water or water-alcohol solution of sulfonated PSF, followed by drying at 100 - 140°C. This caused the formation of sulfone crosslinks which served to immobilize the sulfonated PSF barrier layer. Alternatively, the addition of additives such as polyalcohols or polyphenols can produce sulfonate ester cross-links. Seawater salt rejections for these membranes did not exceed 80%. Albany International Corporation applied a similar process to form composite hollow fiber membranes that exhibited 98% salt rejection with a water flux of 1.7 lmh at 2.76 MPa with 3500 ppm brackish water containing 100 ppm chlorine at pH = 8 (Davis *et al* 1981). The performance of modules made with composite sulfonated PSF membranes have been reported by Allegrezza *et al* (1987). Salt passage of the membrane decreases with decreasing salinity, thereby showing a Donnan ion repulsion effect.

Ikeda *et al* (1984, 1985) report a TFC membrane that comprises a poly(ether-sulfone) active layer that is formed by the copolymerization of hydroquinone with 4,4'-bis-hydroxyphenylsulfone. Subsequently, all the hydroquinone moieties were sulfonated. The resulting membrane exhibited an ion exchange capacity which could be controlled by controlling the amount of hydroquinone incorporated into the poly(ether-sulfone).

3) Isocyanuric acid based TFC membranes : The PEC-1000 membrane is based on acid-catalyzed compositions of 1,3,5-tris (hydroxyethyl) isocyanuric acid (THEIC) (Kurihara *et al* 1982). If THEIC is condensed with reactants such as sorbitol or polyethylene glycol, this results in membranes having salt rejection values of 95 to 97% with very low water fluxes. However, dip-coating of the PSF support with an aqueous solution of one part THEIC, two parts furfuryl alcohol, two parts sulfuric acid and one part dodecyl sodium sulfate followed by curing at 150°C resulted in a membrane with a 10x increase in water flux. Typically, the PEC-1000 membrane exhibits TDS rejection of 99.9% and a water flux of 8.5 - 12.6 lmh when tested with 3.5% NaCl solution at 5.5 MPa (Kurihara *et al* 1980). This membrane is found to be stable over a broad pH range extending from 1 - 13. Another interesting property of this membrane was its high rejection (>95%) for organic solutes such as ε-caprolactam, dimethylsulfoxide and dimethylformamide (Niwa *et al* 1988). The commercial potential of this membrane appears to have been limited by its sensitivity to oxidants.

4) Poly(vinyl alcohol) (PVA) based TFC membranes : TFC membranes using PVA are useful due to its hydrophilic nature, as also its chemical and thermal stability. The unmodified membranes due to their high hydrophilicity are permeable to both water and salt (Jian and Ming 1987; Yang *et al* 1993). When used in RO, these membranes exhibit poor salt rejection (Katz *et al* 1981). Lang *et al* (1995) report the synthesis of TFC membranes prepared by coating porous PSF supports with a layer of PVA followed by crosslinking with an agent such as maleic acid in the presence of a catalyst. The resultant membrane exhibited increased salt rejection along with decreased water flux. She and

Shen (1987) report the synthesis of a crosslinked PVA based membrane that gave a salt rejection of 95% and a water flux of about 1.7 - 5.1 lmh when tested with 0.35% NaCl solution at 3.9 MPa. The membrane was formed by crosslinking PVA in the presence of sulfuric acid with a bicarboxylic acid such as oxalic acid followed by curing. Slightly better data was presented by Cadotte *et al* (1976) wherein a solution comprising of a 2:2:1 weight percent PVA : acrolein : sodium sulfite was refluxed in order to force addition of the hydroxyl groups across the active double bond of the acrolein. This was followed by the addition of sulfuric acid. The resultant solution was then coated on PSF , followed by curing at 135°C to form acetal linkages. These membranes gave salt rejection values of 96.5 - 96.7% with water fluxes of 30.6 - 35.7 lmh on synthetic seawater tests conducted at 10.3 MPa.

A composite RO membrane was prepared by casting a polymer solution containing both sulfonated PSF and PVA as an ultra-thin film on a micro-porous PSF support, evaporating the solvent and heat curing (Yang and Chu 1993). The salt rejection and water flux were found to increase with an increase in the ratio of sulfonated PSF to PVA. The reported salt rejections for these membranes are in the range 51 - 90% with water fluxes of 0.09 - 0.68 lmh at 8 MPa using a feed solution comprising of 3500 ppm NaCl.

2.3.4 Gas Phase Deposition of the Active Layer

Plasma polymerization involves fragmentation of the vaporized monomer by the energy of the gas plasma. A polymeric deposit is built-up from the deposition of the fragmented particles which condense on cooler surfaces. High plasma energy levels lead to higher fragmentation of the monomer, and consequently higher branching in the polymeric deposit. Plasma reactions involve not only polymerization but also depolymerization and modification of functional groups. Plasma polymerization has been reviewed by Yasuda (1977).

Buck and Davar (1970) report RO data on several monomer systems that were plasma polymerized. Composite membranes made from allylamine (Bell *et al* 1975; Hollahen and Wydeven 1977) gave salt rejections in the range of 98 - 99% with fluxes ranging from 6.8 - 13.6 lmh when tested at 4.1 MPa with a 0.1% NaCl solution. ESCA studies on the deposited barrier layer revealed the presence of nitrile and imine groups. Yasuda *et al* (1975) report plasma polymerized membranes with salt rejections as high as 99% and fluxes of 64 lmh at 10.3 MPa with 3.5% NaCl solution. A commercially successful membrane "Solrox" (Sumito Chemical Company) was developed by Sano *et al* (1980; 1981 and 1984). A micro-porous support film was cast from poly(acrylonitrile) followed by drying and exposure to helium or hydrogen gas plasma. The untreated poly(acrylonitrile) support film showed a water flux of 147 lmh at 0.96 MPa. Following plasma treatment the composite membrane exhibited a water flux of 18.7 lmh with a salt rejection of 98.3% when tested with 0.55% NaCl solution at 4.8 MPa. These membranes exhibited higher rejections towards organic solutes than the CA membrane. The "Solrox" membranes were however not chlorine tolerant.

2.3.5 Membranes Formed by Interfacial Polycondensation

The topic of interfacial polymerization has been discussed extensively by Morgan (1965). Interfacial polymerization generally occurs in the organic phase, in a narrow zone adjacent to the interface. The aqueous phase monomer (e.g. diamine) partitions into the organic phase wherein it meets a large excess of organic phase monomer (e.g. diacid chloride) and thereby gets acylated at both ends. The subsequent aqueous phase monomers which partition into the organic phase, encounter both the acylated oligomers as well as the organic phase monomer. The reaction then proceeds via irreversible coupling of the oligomers by the aqueous phase monomer. The composition and morphology of the interfacially formed polymer film depends on several variables (Petersen 1993) :

1) concentration of the reactants;

2) partition coefficients of the reactants;

3) reactivity ratios when blends of reactants are employed;

4) solubility of nascent polymer in the solvent phase as it is formed;

5) overall kinetics and diffusion rates of the reactants;

6) presence of by-products (such as hydrogen chloride in the case of the reaction of amine with an acyl chloride);

7) hydrolysis or other potentially competitive by-reactions;

8) crosslinking reactions; and

9) post-reactions or treatments of the resulting interfacial films.

Tsai and Lee (1987, 1988) report the influence of phase transfer agents on interfacial polycondensation. Though their work is based on stirred systems the conclusions also apply to the unstirred systems. For the interfacial polycondensation of bisphenol-A with isophthaloyl chloride, the transfer rate of bisphenolate and thus the polymerization rate was found to increase with increasing lipophilicity of the phase transfer agent in the order: tetrabutylammonium chloride (TBAC) > triethylbenzylammonium chloride (TEBAC) > tetratethylammonium chloride (TEAC). The phase transfer agents did not affect the equilibrium of bisphenolate between the organic phase and the aqueous phase. Also, a phase transfer agent of high lipophilicity (TEBAC) reduced the hydrolysis of the acid chloride.

Earlier work by Scala *et al* (1973) on interfacial membranes reported poor rejection values. Today, however, high flux and high rejection membranes are prepared routinely by this technique.

1) Polymeric amine based TFC membranes : A significant advance was made in the fabrication of TFC membranes by interfacial polycondensation with the development of the NS-100 membrane in 1970 (Rozelle 1977). This was the first successful non-cellulosic composite RO membrane. A PSF support was first coated with a polymeric amine (polyethylenimine) and then reacted with either toluene diisocyanate resulting in a polyurea or isophthaloyl chloride (IPC) resulting in a polyamide. This was followed by curing at 110°C. Synthetic seawater tests conducted on the polyurea membrane at 10.3 MPa gave a salt rejection value of 99% with water flux of 30 lmh. Though the polyamide version exhibited a higher flux as compared to the polyurea, it was found that the polyurea showed higher solute rejection and also better durability in long term tests. The NS-100 membrane showed higher rejection for organic compounds compared to other RO membranes at that time and could also be operated at temperatures in excess of 35°C. Though the membrane exhibited superior resistance to acids and alkalis, it was found to be very susceptible to halogen based disinfectants. Wrasildo (1976) claimed that this

susceptibility can be decreased by cyanoethylation of the primary amine groups in polyethylenimine.

The limitations of water flux and sensitivity to chlorine of the NS-100 membrane led to the development of polyepiamine based composites (Wrasildo 1977; Riley *et al* 1976). Riley *et al* (1977) developed poly(ether-amine) (also called polyepiamine) based composite membranes which exhibited increased flux and a slight increase in chlorine tolerance as compared to the NS-100 membrane. Interfacially prepared polyepiamine based composite membranes using IPC were designated as PA-300 which is a poly(ether-urea) while those made using toluene diisocyanate resulted in a poly(ether-amide) that was designated as RC-100. The PA-300 membrane exhibited salt rejections in excess of 99.4% with water fluxes of 34 - 42.5 lmh on simulated seawater tests conducted at 6.9 MPa. The membrane was stable over a broad pH range from 3 to 12. One of the first major installations in the world that involved the use of a composite RO membrane was the 3.2 x10^6 gallon per day desalination plant at Jeddah, Saudi Arabia which employed the PA-300 membrane in a spiral-wound element (Hickman *et al* 1979; Muirhead *et al* 1982). Due to insufficient stability towards long term seawater service, the PA-300 membrane was eventually replaced by the RC-100 version. The NS-100, PA-300 and the RC-100 membranes strongly absorb anionic surfactants resulting in a loss of flux. The lack of chlorine tolerance also necessitated strict chlorine monitoring and removal procedures.

2) Monomeric amine based TFC membranes : Kawaguchi *et al* (1980) described a new series of polymers based on poly(diallyl amine) as the aqueous phase monomer. The resulting polyamides were expected to exhibit improved chlorine tolerance as compared

to the NS-100, PA-300 and the RC-100 membranes. The absence of amidic hydrogen in the poly(diallyl amine) based polyamides was expected to improve the chlorine tolerance as there is no site for the initiation of chlorine attack. Chlorine resistance tests were conducted for a period of 40 to 80 hours with the addition of 5 ppm active chlorine to the feed in the pH range 6 to 6.5. The chlorine test results were found to be superior to that for the NS-100 membrane. It was also observed that the polyurea polymer obtained from diallyl amine gave a better salt rejection than the polyamide obtained from the same.

Cadotte *et al* (1976, 1978) reported that the interfacial reaction of piperazine with IPC resulted in a membrane with salt rejections as high as 98% in tests on synthetic seawater at 10.3 MPa. Improved membrane performances were obtained by optimizing the concentration of reactants, use of acid acceptors and surfactants. The piperazine based polyamides having no amidic hydrogen, were expected to resist chlorine oxidation. These membranes were found to be more chlorine tolerant than the NS-100 membrane but they were not fully chlorine resistant to the degree that they could be used with continuous chlorination of feed water.

This piperazine based membrane was modified to various extents in order to study changes in flux or salt rejection. A portion of the IPC was replaced with TMC. Varying the diacyl to triacyl chloride ratios from 100:0 to 0:100 caused a decrease in NaCl rejection but magnesium sulfate rejection remained steady at 99% or higher. The piperazine-TMC membrane was designated as the NS-300 membrane. The salt passage through this membrane is described as being anionically controlled. This suggests the membrane to be rich in carboxylic acid groups which may have resulted through partial hydrolysis of the acyl halide groups. Interfacial membranes were also prepared by replacement of piperazine with piperazine-terminated oligomers. Various oligomer compositions were made by the reaction of piperazine with one or more acyl halides (Cadotte *et al* 1979). These oligomers were then interfacially reacted with IPC in situ on PSF supports. The highest salt rejection value obtained was 99.2% but with a low water flux of 23.8 lmh on tests conducted with synthetic seawater at 10.3 MPa.

The basic chemistry of the NS-300 membrane was applied to several commercial nanofiltration membranes. The NF-40 membrane is one such example wherein the barrier layer comprises of an interfacial reaction product of piperazine with TMC. This is an anionically charged membrane and is designated as a nanofiltration membrane. This membrane exhibits a water flux of 42.5 lmh with 45% NaCl and 90% glucose rejections in tests that were conducted separately with 2000 ppm NaCl and 2000 ppm glucose solutions respectively at 1.6 MPa. The membrane shows a pH resistance range from 2 to 11. The water and salt transport properties through this membrane have been studied by Eriksson (1988). The barrier layer composition of the NF-40 membrane has been approved for repeated food contact (Petersen 1993).

Two composite membranes with significant chlorine resistance are the NTR-729HF and the NTR-739HF membranes (Kawada *et al* 1987). The chlorine resistance of these membranes is reported to be equal to or higher than that of the CA membrane. The infrared spectra of the active layer of these membranes are almost identical showing polyamide to be the major portion of the active layer (Petersen 1993). PVA is also present in both the barrier layers, more so in the NTR-729HF membrane. These membranes have been commercialized by Nitto Denko for use with low salinity brackish waters and are also particularly used in the preparation of ultrapure water for the semiconductor industry.

Kazuse *et al* (1984) describe the synthesis of a composite membrane comprising of PVA/poly(piperazineamide) wherein the membrane is irradiated in a post-treatment in order to increase the degree of crosslinking. The resultant membrane exhibited a water flux of 40.9 lmh and a 98.2% $MgSO_4$ rejection in tests conducted with a 500 ppm $MgSO_4$ solution at 0.98 MPa.

TFC membranes from poly-2-vinylimidazoline (PVI) have been reported by Hurndall *et al* (1992). These membranes are formed by coating a PSF support with an aqueous solution of PVI followed by subsequent contact with crosslinking agents such as 3-(chlorosulphonyl)benzoyl chloride, 3,5-di(chlorosulphonyl) benzoyl chloride or benzene-1,3-dicarboxylic acid dichloride. The best RO results were obtained from membranes made with sulphonyl chloride containing crosslinking agents. However, the membranes did not exhibit good chlorine resistance; this was attributed to the presence of the hydrolyzed form of the 2-imidazoline repeat unit in the PVI precursor.

3) *m*-Phenylene diamine (*m*-PDA) based TFC membranes : The FT-30 membrane, developed at FilmTec Corporation, comprises a crosslinked, fully aromatic polyamide active layer (Cadotte *et al* 1980) formed by the reaction of *m*-PDA in the aqueous phase with TMC in the organic phase (Cadotte 1981). The membrane is found to be insoluble in all solvents including concentrated sulfuric acid, thereby indicating a high degree of cross-linking. Based on ESCA studies, the free carboxylic acid groups accounted for only 9% of the total carbonyl groups present in the membrane (Koo *et al* 1986). Due to the presence of these free acid groups, the aromatic polyamide active layer is mildly negative in charge at neutral or alkaline pH levels. The membrane is also susceptible to

binding and fouling by cationic surfactants. The water and salt transport properties of the FT-30 membrane have been reviewed extensively (Eriksson 1988; Cadotte *et al* 1980; Larsen *et al* 1981; Petersen *et al* 1982; Redondo and Frank 1991). The membrane is stable over the pH range 3 - 11 and exhibits a salt rejection of 99% or greater in the pH range 5 - 11. Below pH = 5, the fall off in salt rejection was attributed to acid transport through the membrane. At pH = 12, the salt rejection falls below 98% due to membrane swelling. This membrane is found to have a 1000 ppm-hr level of chlorine tolerance. The rate of chlorine attack was found to be fastest under alkaline conditions while this rate was much slower in acidic conditions at pH = 1 and 5. Membrane failure at pH = 1 was due to embrittlement of the underlying PSF support.

A series of patents issued to Sundet (1985-88, 1991) cover fabrication of TFC membranes in which the active layer is based on aryl-alkyl polyamide as opposed to the fully aromatic structures in the FT-30 membrane. The active layer in this membrane comprises of the reaction product of *m*-PDA with cyclohexane-1,3,5-tricarbonyl chloride. A comparison was made of the membranes made by the reaction of 1,3-benzenediamine with cyclohexane-1,3,5-tricarbonyl chloride (HT), adamantane-2,6-dione-1,3,5,7-tetracarbonyl chloride (ADTC) and TMC. It was found that the HT or ADTC based membranes showed a higher flux but lower salt rejection value as compared to the TMC based membrane (Arthur 1989). The increased carboxylic acid content in the respective polyamides accounted for some, but not all of the increased water absorption.

Another type of membrane is made by reacting *m*-PDA interfacially with 1-isocyanato-3,5-benzenedicarbonyl chloride (Sundet 1991). This results in a active layer that contains both amide and urea linkages. The membrane gave a salt rejection of 99.3%

with a water flux of almost 42.5 lmh when tested with a 0.2% NaCl solution at 1.55 MPa.

UTC-80 developed at Toray Industries, is a crosslinked fully aromatic polyamide ultra-thin composite membrane that was developed for seawater desalination (Kurihara *et al* 1994). The chemistry of this membrane is believed to be similar to that of the *m*-PDA/TMC. The trihalomethane rejection of this membrane is much higher as compared to CA membrane. A spiral wound membrane element using this membrane known as SU-280 exhibits a high salt rejection of 99.75% with a water flux of 16 m^3/d at an operating pressure of 5.5 MPa for natural seawater fed at 25°C.

4) Diol based TFC membranes : A study by Kwak (1996) reports the effects of bisphenol monomer structure on the surface morphology and RO performance of TFC membranes composed of poly(phenylesters). The polarity of the connectors between two phenyl rings of bisphenols played an important role in determining the surface morphology and RO performance. Biphenol (BP), bisphenol-A (BPA), 4,4'-dihydroxydiphenyl ether (DHDPE) and bisphenol-S (BPS) were each interfacially reacted with TMC on a micro-porous PSF support and RO characteristics of the resultant membranes were studied. The solute rejection is found to decrease with increasing flux in the order BP/TMC < BPA/TMC ~ DHDPE/TMC < BPS/TMC indicating that solute separation is higher for the bisphenols containing no or non-polar connectors and vice versa for the water flux. All these poly(phenylester) membranes exhibited salt rejections below 60% on tests that were conducted at 2.9 MPa with a 2000 ppm NaCl solution. Atomic Force Microscopy (AFM) was used to study the membrane surface morphology. Non-polar bisphenol led to a membrane morphology of uniform, distinct nodular corrugation and a superior RO rejection but a relatively low flux. By contrast, the polar diol resulted in an irregular,

nodular membrane structure and a high flux.

Kim *et al* (1997) describe a polyester based TFC membrane wherein the PSF support is coated with either an aromatic polyester or a copolymer of an aromatic polyester and an aromatic polyamide. The PSF support when coated with an aqueous solution of 4,4'-dihydroxybiphenyl and subsequently contacted with a solution of TMC over a 30 min. period resulted in a PSF/crosslinked polyester membrane that gave a salt rejection of 90% with a water flux of 138 lmh. Alternatively, the PSF support was coated with a 1:1 mixed aqueous solution of 0.5% 4,4'-dihydroxybiphenyl and 0.25% of *m*-PDA and then contacted for a period of 30 min. with 0.5% TMC solution in *n*-hexane followed by curing at 60°C. The resulting membrane exhibited a salt rejection of 96.5% with a water flux of ~92 lmh. In both cases the RO tests were conducted at 0.34 MPa using a 5000 ppm synthetic brine solution.

2.4 SEPARATION PERFORMANCE OF NANOFILTRATION MEMBRANES

NF membranes find applications in water softening, desalting, food processing as well as waste water treatment. Some of the other commercial examples of NF membranes are the NF-40 (crosslinked polypiperazineamide), NF-50 and NF-70 (crosslinked fully aromatic polyamide); NF-40HF and XP-45 (crosslinked polypiperazineamide); NTR-7250 (active layer comprising of PVA and piperazine trimesamide); UTC-70, UTC-60, UTC-20HF, UTC-20HR (polypiperazineamide active layers, from Toray); Desal-5 (Desalination) that exhibits a performance similar to the NS-300 membrane and ESNA (Hydranautics). While the detailed chemistry and fabrication procedures are not available in the open literature, many of these membranes are based on the basic chemistry of the NS-300 membrane discussed in section 2.3.4. The separation performance of commercially available NF membranes are summarized below.

The NF-50 membrane exhibits 50% NaCl rejection with a water flux of 77.5 lmh on tests that were conducted at 0.74 MPa with a 500 ppm NaCl feed solution. Salt rejection of the NF-70 membrane is higher being about 85% with a water flux of 68 lmh under similar test conditions as for the NF-50 membrane. The NF-40HF and XP-45 (FilmTec) membranes are high flux, low pressure versions of the NF-40 membrane and exhibit salt rejections of 40% and 50% with water fluxes of 43 lmh and 36 lmh respectively on tests conducted with a 2000 ppm NaCl solution at 0.9 and 0.7 MPa in each case separately. The XP-45 membrane exhibits improved pH resistance and better solute rejection control (Cadotte *et al* 1988).

The UTC-20HR membrane exhibits 70% NaCl rejection with a water flux of 102 lmh on tests conducted at 1.5 MPa with a 1500 ppm NaCl feed solution. The UTC-20HF membrane is a high flux version of the UTC-20HR membrane exhibiting a water flux of 146 lmh with a salt rejection of 50% under the same test conditions as that reported for the UTC-20HR membrane. The salt rejections were found to be lower when the concentrations exceed 1500 ppm and higher when feed solution concentrations are lower. (Kurihara *et al* 1985). The salt rejection performance of the UTC-20 membranes is similar to that of NTR-7250 membrane. The salt rejection of the UTC-60 membrane is about 80% with a water flux that is similar to the UTC-20HF membrane. The chlorine tolerance of the UTC-60 membrane is suggested to be at the level of the CA membrane

(Kurihara and Himeshima 1991).

The Desal-5 membrane exhibits 47% NaCl rejection and has a water flux of 46 lmh when tested with a 1000 ppm NaCl solution at 1 MPa. The membrane, though, exhibits high rejections of 99% for lactose and sucrose and thus has found widespread application in cheese whey concentration (Comstock 1989).

The ESNA membranes, too, are ultra low pressure RO membranes that exhibit salt rejections of 85%. 4040-UHA-ESNA membrane exhibits a water flux of 6.4 m^3/d while high flux versions 8040 and 8540-UHY-ESNA exhibit fluxes of 30 and 34 m^3/d respectively.

The water and solute permeabilities of some of these commercial NF membranes are tabulated in Table 1 (see Appendix 1).

2.5 CHLORINE TOLERANCE

In this section the mechanism of chlorine attack on various types of polymeric membranes is discussed.

2.5.1 Chlorine Species in Water

The disinfection of water is carried out either by the addition of chlorine gas or sodium hypochlorite.

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

$$NaOCl + H_2O \rightleftharpoons HOCl + NaOH$$

The HOCl thus formed exhibits disinfection properties. Chlorine exists in water as one of the following three species : Cl_2 (low pH), HOCl (intermediate pH) and OCl^- (at pH>8). In the pH range 2 - 7.5, which encompasses the range of most water treatment, the dominant species is HOCl (see Fig. 2.1). A significant portion of the HOCl hydrolyzes above pH = 6 to form the hypochlorite ion OCl^- which is not an effective disinfectant (White 1978).

$$HOCl \rightleftharpoons H^+ + OCl^-$$

Frequently, membrane failure results from interaction of the membrane with disinfectants, such as HOCl, used for biofouling control (Ridgeway 1988). The chlorine resistance of polyamides depends not only on their chemical structures but also on the chlorination conditions such as pH and reaction time (Wu *et al* 1996). Decrease in intrinsic viscosity of the polymer, decreased salt rejections, and ultimately increased flux, are some of the distinctive features of a chlorine damaged membrane (Avlonitis *et al* 1992; Glater *et al* 1983). Since chlorine is a preferred disinfectant in water treatment systems (White 1972), cumbersome chlorine removal and its readdition are necessary with polyamide membranes (Glater *et al* 1983, 1981). Attempts at the fabrication of chlorine tolerant membranes with high flux and salt rejections have been discussed in several papers and patents (Cadotte 1981; Kawaguchi and Tamura 1984; Swedo and Zupancic 1989) and are summarized in the sections below. The major effort has been towards increasing the chlorine tolerance of polyamide based membranes.

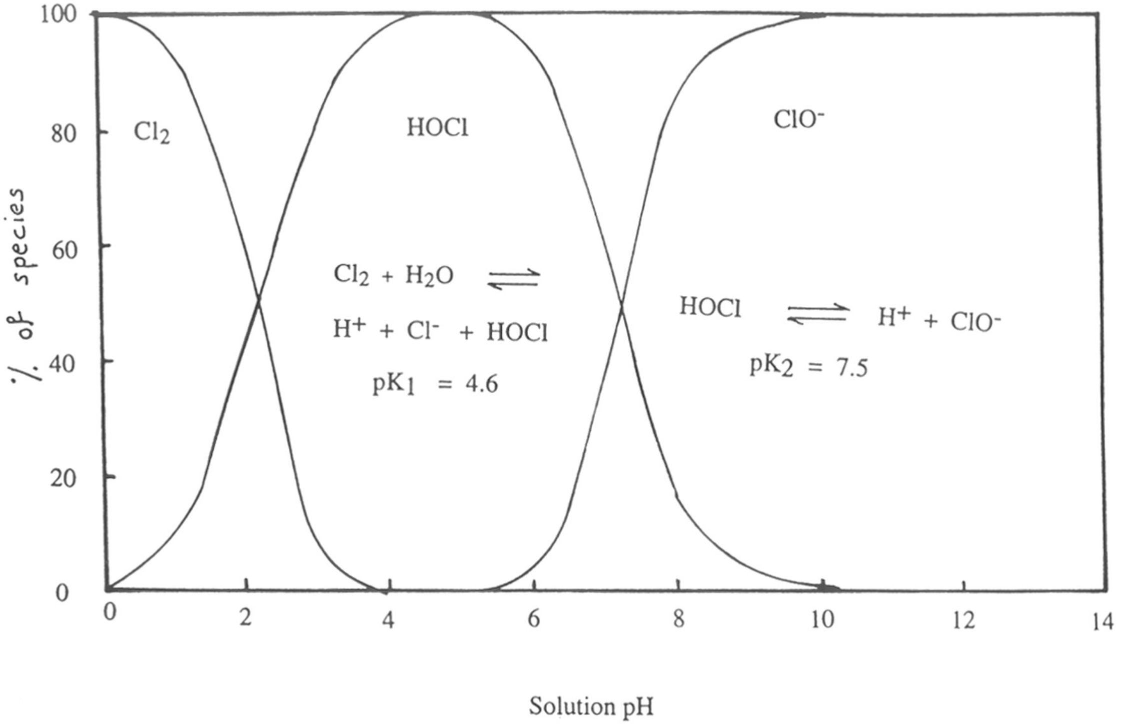


Figure 2.1 Equilibrium distribution of chlorine, hypochlorous acid and hypochlorite ion Vs solution pH at 25°C.

2.5.2 Mechanisms for Chlorination of Polyamides

Glater *et al* (1994) have reviewed mechanisms of polyamide membrane-chlorine interactions wherein it is concluded that chlorine sensitive features of membranes consist of nitrogen functional groups and aromatic rings and that secondary amide and urea linkages are the most vulnerable to chlorine attack.

The mechanism of this process is not clearly established but is considered to involve polymer chain deformation or amide bond cleavage. The mechanism of chlorination of aromatic polyamides involves (1) N-chlorination through chlorine attack on the amide nitrogen (2) aromatic ring chlorination through intermolecular rearrangement or direct substitution followed subsequently by structural degradation. In case of aromatic polyamides, initially chlorine attack leads to N-chloro derivatives. There exist two possible pathways towards ring chlorination i.e. (a) direct electrophilic aromatic substitution (Shafer 1970) and/or, (b) ring chlorination via Orton rearrangement following N-chlorination (Challis and Challis 1970; March 1992) (see Fig. 2.2).

Studies with model organic compounds have given valuable insights into the mechanism of chlorine attack on polyamides. These are summarized below.

In the reaction between acetanilide and chlorine, Orton *et al* (1928) have shown that the ratio of N- to C- chlorinated products thus obtained is time independent, thereby indicating that both N-chlorination and ring chlorination were simultaneous.

Direct chlorination of the aromatic ring has been favored by Glater and Zachariah (1985). This was based on bromination studies that were carried out on the model compound benzanilide. Benzanilide was chosen due to its structural similarity to the monomer units in the DuPont (Permasep) B-9 membrane. The bromination studies

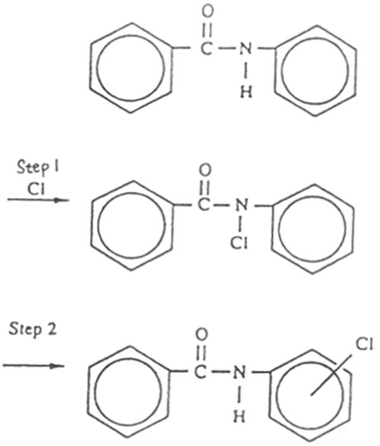


Figure 2.2 Proposed Orton rearrangement in the chlorination of benzanilide.

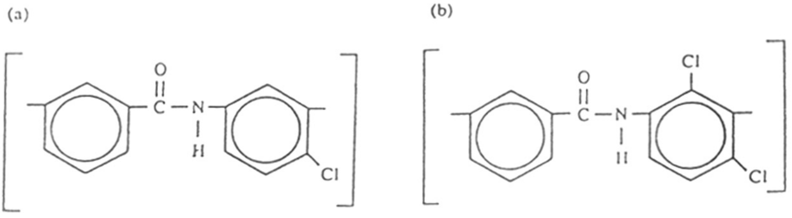


Figure 2.3 Chlorination pattern of a linear aromatic polyamide (poly-*m*-phenyleneisophthalamide) as reported by Kawaguchi and Tamura (1984) : (a) ring chlorination at para position and (b) ring chlorination at ortho and para positions.

showed that the reaction first took place at the para position of the ring adjacent to the N-H group. Further exposure resulted in the incorporation of a second bromine at the ortho position. On the other hand, aromatic rings attached to the carbonyl group were brominated at the meta position but at much slower rates. The study reports that this was expected since the N-H portion of the amide linkage is an ortho-para director while the C=O portion is a meta director (March 1992; Solomon 1992).

Experiments performed with poly(*m*-phenyleneisophthalamide) by Kawaguchi and Tamura (1984) showed initial chlorination at the para-position on the amine ring. The second chlorine atom then adds to the ortho position of this ring. In this case too, each para position is doubly activated by two -NH- groups. Though the ortho position is also doubly activated, it may be less vulnerable to chlorine attack due to steric hindrance. This chlorination pattern is shown in Fig. 2.3. These ^{1}H NMR studies are reported to be in good agreement with results observed by Geinger (1984) and the benzanilide results of Glater and Zachariah (1985).

A chlorine resistance study, carried out by Kawaguchi and Tamura (1984) on model compounds such as N-methylbenzanilide, N-phenylbenzanilide and benzanilide, confirmed ring chlorination via Orton rearrangement. While, benzanilide exhibited aromatic ring chlorination, the two tertiary amides did not undergo chlorination at all. It was therefore concluded that chlorination via the N-chlorination mechanism is a more feasible route for ring chlorination of polyamides obtained from aromatic primary diamines.

The study by Kawaguchi and Tamura (1984) also included the interaction of hypochlorous acid with various polyamides that contained different alkyl and aryl groups.

The modes of interaction were classified into three categories : 1) no reaction in the case of tertiary polyamides, 2) reversible chlorination at the amide nitrogen and 3) irreversible aromatic ring chlorination. Based on their experimental results it was shown that the aromatic primary diamines resulted in polyamides that were irreversibly chlorinated at the aromatic nucleus. Aliphatic primary diamines gave polyamides that resulted in N-chloro derivatives which could be easily dechlorinated. Polyamides based on secondary diamines were found to be inactive towards chlorine. It was therefore concluded that, based on chlorine susceptibility alone, the tertiary polyamides are the preferred candidates for chlorine resistant membranes followed by the aliphatic secondary polyamides.

Avlonitis *et al* (1992) have examined the effect of chlorine on asymmetric aromatic polyamide membranes, confirming the presence of ring chlorination. They concluded that aromatic chlorination is faster at pH = 4 than at pH = 9. Decreases in the melting point, tensile strength and intrinsic viscosity were related to increased chlorine exposure. A two-step chlorine degradation mechanism was suggested, wherein in the first step, aromatic chlorination transforms the crystalline regions in the polymer into amorphous states. In the second step, chlorine attacks the amide linkages in the amorphous regions resulting in chain cleavage which finally results in membrane failure.

Based on ESCA studies on chlorine damaged FT-30 membranes, Koo *et al* (1986) have proposed oxidative amide bond cleavage. A mechanism involving N-chlorination followed by a bond cleavage and oxidation of the benzene ring to substituted quinone derivatives was proposed.

Amide bond cleavage through chlorination could also occur by the Hoffman degradation route (Avlonitis *et al* 1992; Lee *et al* 1983). According to this mechanism, secondary N-chloroamides undergo hydrolysis in alkaline solutions yielding primary amines and carbon dioxide. Since Hoffman degradation occurs only in alkaline conditions, this mode of amide bond cleavage would not be encountered at conditions of usual feed water pH.

2.5.3 Effect of Polymer Structure on Chlorine Resistance

The correlation between chemical structure and chlorine resistance of polyamides have been studied by Wu *et al* (1996). Upon chlorination, polyamides that do not contain substituents on benzene ring of the amine were ring chlorinated. Poly(-1,3-phenylene terephthalamide) was found to undergo partial cleavage of the chain under basic conditions. Under acidic conditions, N-chlorination took place in polyamides which contained heterocyclic aromatic rings. Polyamides that contained substituents such as electron withdrawing or sterically hindering groups on the amine benzene ring showed no change on chlorination thereby indicating a high tolerance to oxidant chlorine.

Swedo and Zupancic (1989) also claimed that the chlorine tolerance of the aromatic polyamide membrane can be improved if the monomeric aromatic amine is 4-chloro or 5-chloro-1,3-diaminobenzene. However, the chloro group was found to exhibit a flux reducing effect as compared to the nonchlorinated aromatic diamine. Another example includes the nitration of polyamide membranes reported by Rajinder (1994). The acid medium nitration process appeared to cause morphological changes in the polymer, resulting in reduced membrane permeability and flux.

Asymmetric membranes from poly(piperazineamides) were first prepared by

Credali *et al* (1974) and reported to be chlorine resistant. Poly(piperazineamides) were considered to be extremely interesting membrane materials owing to their chemical structure which involves the absence of amidic hydrogen and also due to their considerable affinity towards water. As discussed in section 2.2.3, a variety of piperazineamide based composite membranes (Cadotte 1985) were studied and these did show some level of chlorine tolerance but were not commercialized owing to wide variations in water flux and salt rejection properties. Brackish water tests conducted on poly(piperazineamide) composite membranes made from a blend of IPC and TMC indicated that the membrane was not fully chlorine resistant (Petersen 1993). This was mainly attributed to the contamination of the system with iron deposits which could have catalytically promoted chlorine attack. Parrini (1983) has described the synthesis of a variety of poly(piperazineamide) based membranes. The polymers exhibited higher degrees of chlorine tolerance as compared to commercial CA membranes and this was attributed to the absence of amidic hydrogen.

Another class of polymers that lacked N-H groups in their backbone that were considered for development as RO membrane materials were the polyimides (Kesting 1985). These were therefore considered extensively for development as hyperfiltration membranes. However, these membranes were not found to exhibit adequate chlorine tolerance. This was thought to be a result of incomplete conversion of polyamic acid to polyimide or due to direct aromatic ring chlorination.

Other polymers that were considered for development as RO membranes were the benzimidazole and benzimidazolone polymers (Kesting 1985; Murakami and Igarashi 1981). These membranes exhibited high pH resistance (pH = 1 - 12), bacterial resistance and long term durability. The poly(benzimidazolone) membrane initially reported excellent chlorine stability which was unexpected owing to the presence of N-H group. Subsequent studies however failed to confirm the long-term resistance to low doses of chlorine.

NTR-7250 is a composite membrane comprising of poly(piperazineamide) as a major portion of the active layer but also showing the presence of PVA. The membrane contains fixed carboxyl groups in the active layer; therefore, the membrane reports higher selectivity towards inorganic salts as also a high rejection of divalent ions, especially divalent anions. The membrane is also reported to have a superior chlorine resistance compared to CA. It is reported (Kazuse *et al* 1984) that a composite membrane comprising of PVA/poly(piperazineamide) withstood a two week exposure to 100 ppm chlorine at pH = 1.

Lowell *et al* (1987) studied the chlorination susceptibility of various aromatic model compounds that contained amide, urea and ester linkages. These compounds were exposed to sodium hypochlorite solutions at pH = 4.5 and pH = 10. This experimental study confirmed that chlorine sensitivity is pH dependent. Ester linkages based on aromatic acids and aliphatic polyols were found to be chlorine resistant. In agreement with the results of Kawaguchi and Tamura (1984), model compounds that contained tertiary substituted nitrogen, exhibited the highest degree of chlorine tolerance. On the other hand, when the aromatic group was directly linked to the nitrogen in amides or urea, the chlorine sensitivity was enhanced. Ureas were found to be more chlorine sensitive than the amides. Most RO membranes generally comprise of nitrogen or oxygen functional groups which enhance the hydrophilicity of these membranes. The chlorine resistance of the membranes is expected to be enhanced if groups such as nitrogen functionalities which are chlorine sensitive could be excluded. The NS-200 and PEC-1000 (section 2.3.3) are two such membrane compositions that involved the use of furfuryl alcohol, a monomer containing oxygen functional groups. However, both these membranes exhibited high chlorine sensitivities which was mainly attributed to the unsaturated furfuryl alcohol and the nitrogen functionalities present in these membranes.

PSF based membranes such as sulfonated poly(ether-sulfone) or poly(sulfonamide) membranes show improved chlorine tolerance (Chan *et al* 1991; Gao *et al* 1991). Poly(sulfonamide) membranes have excellent heat stability, are stable to oxidation, hydration and microbial erosion. The membrane can be used for desalination of feed with high salinity. The improved chlorine resistance of this membrane is explained on the basis of deactivation of the secondary amide linkage through enhanced resonance stabilization. These studies however report only limited performance data.

2.6 POLYESTERAMIDE SYNTHESIS

A polyesteramide was first obtained by Carothers and Hill (1932) by heating together ε-aminocaproic acid, a dicarboxylic acid and a glycol. Polyesteramides have been synthesized by polycondensation of :

a) of dicarboxylic acids or their derivatives with aminoalcohols;

b) of diamines with glycols;

c) of aminoalcohols with aminoacids;

d) of aminoalcohols with hydroxycarboxylic acids;

e) of aminoalcohols with glycols;

f) of diamines with aminoalcohols;

g) of dicarboxylic acids or their esters, containing ester or amide groups in the molecule with glycols or aminoalcohols; and

h) of glycols containing ester or amide groups in the molecule with dicarboxylic acids or their chlorides, etc.

For example, Korshak and Vinogradova (1972) describe the low temperature polycondensation of polyesteramides based on polycyclic bisphenols by reacting a mixture of a diphenol and hexamethylene diamine with either sebacoyl chloride or terephthaloyl chloride.

Polyesteramides have been interfacially synthesized from the reactions between the following:

a) diacid chloride and a mixture of a diphenol and a diamine;

b) diacid chloride and an aminophenol;

c) diacid chloride containing an ester group and a diamine; and

d) diacid chloride and a diphenol containing an amide group.

Korshak *et al* (1962, 1963) have described the interfacial polymerization of various polyesteramides from diphenols and diamines by reaction with dichlorides of some aliphatic and aromatic dicarboxylic acids. The resultant polymers were reported to consist of soluble and insoluble parts. Evidence of copolymer formation was given by the deformation-temperature curves (Korshak *et al* 1962) and turbidimetric titration of the polymers obtained (Korshak *et al* 1963). In all cases, the polymers were found to be richer in nitrogen content than the theoretical value from initial stoichiometry. This indicates that the reactivity of the amine groups in interfacial condensation was higher than that of the phenolic hydroxyl groups. When the diamine was introduced a few minutes after the reaction of the diacid chloride and the diphenol had begun, it was observed that the value of nitrogen content in these polymers was quite close to the theoretical value.

Korshak *et al* (1962) have experimentally demonstrated the heterogeneity of copolymers formed from reacting a diacid chloride, diamine and diphenol. The heterogeneity is caused by the different rates of diffusion of the reactants into the reaction sphere and the difference in the reactivities of the diamine and the phenolate. The polyesteramides that were prepared by interfacial polycondensation were found to differ from those prepared by the melt technique in terms of melting points, thermochemical curves, relative amounts of soluble and insoluble fractions in a selected solvent and in the elemental compositions of these two fractions.

Polyesteramides from aminophenols and diacid chlorides by interfacial polycondensation were reported earlier by Panayotov (1977). In the reaction of the aminophenol with the acid chloride the more active amine group will react first. Thus, the structure -NHCORCONH- rather than -OCORCONH- or a mixture of both will be formed. The assumption by Morgan (1965) that these polymers are probably not of the random alternating type due to the differences in the reactivities of the amine groups versus the phenol groups was later supported by Preston (1970) who isolated the intermediate diphenolamides and verified that the structure formed is -NHCORCONH-.

Thus, it appears that the interfacial polycondensation of a mixture of diacid chlorides, diamines and diphenols results in copolymers that are probably composed of polyamide and polyester blocks. However, it is also possible to prepare random or alternating copolymers. Gonsalves and Chen (1994) have reported on the chain structure and hydrolysis of alternating polyesteramides which were synthesized and subjected to hydrolytic degradation. The first polyesteramide was prepared by a two-step polycondensation reaction from 1,6-hexanediol, adipoyl chloride and 1,6-hexanediamine and the second polyesteramide was prepared by anionic copolymerization of ε-caprolactam and ε-caprolactone. Increase in temperature and ester content was found to enhance the hydrolysis of these polyesteramides in buffer solutions. The hydrolysis was also catalyzed by both acid and base. Selective ester hydrolysis by base treatment showed that both the polyesteramides had random chain structures.

Akcatel and Jasse (1976) report the synthesis of aliphatic alternating polyesteramides. These were found to have a higher content of interchain hydrogen bonds than the corresponding random copolymers due to their high structural regularity. The random copolymers exhibited higher melting points and this was attributed to the heterogeneity of the amide group segments in the chain.

In certain instances the melting points of the polyesteramides prepared by the interfacial technique were higher than those prepared by the melt polymerization process (Korshak *et al* 1962, 1963). Polyesteramides that contained aliphatic chains with even number of carbon atoms were found to have higher melting points than those with odd number of carbon atoms (Panayotov 1977). Polymers obtained by interfacial polycondensation were usually colorless whereas those obtained by melt polycondensation were colored; this difference could be attributed to thermal degradation (Korshak *et al* 1963; Williams *et al* 1963).

Polyesteramides incorporating aromatic moieties have limited solubility in common organic solvents (Panayotov 1977). Polymers prepared from aminophenols and diacid chlorides are found to be soluble in a mixture of chloroform and methanol. Available literature data on the polyesteramides synthesized show these to be suitable for fibers, films and molded shapes.

Literature indicates two instances wherein membranes are formed with esteramide linkages. One of these is reported by Kim *et al* (1997) (see section 2.3.4) and the other refers to the synthesis of an asymmetric polyesteramide membrane that is useful in the fields of dialysis and ultrafiltration as reported by Francesco *et al* (1988). This membrane exhibits a water permeability of approximately 9 lmh and was prepared by spreading a solution of hexamethylenediamine-hexanediol-terephthalicacid copolymer on a flat support followed by dipping into a coagulation bath and washing in water. The membrane was then conditioned with a 70:30 water : glycerol mixture. Various diffusion coefficients of the membrane for NaCl, urea, uric acid, creatinine and vitamin B12 are reported.

CHAPTER 3

EXPERIMENTAL

This chapter describes the experimental techniques used in the synthesis and characterization of the various adducts and novel TFC membranes and their chlorine studies. The synthesis, characterization and methodology of the chlorine study used with the adducts is described first. This is followed by a description of TFC membrane fabrication, RO permeation and chlorine tolerance testing procedures. Lastly, the preparation and characterization of various polyester/polyamide homopolymers and polyesteramide polymers is described.

The standard equipment used in this study along with various model specifications are listed in Table 2 (Appendix 1).

The chemicals used in this study along with their grade and sources are listed in Table 3 (Appendix 1).

3.1 ADDUCT SYNTHESIS, CHARACTERIZATION AND CHLORINE STUDY

3.1.1 Synthesis of Adducts

3.1.1.1 Diamide synthesis

The reactant amines were purified before adduct synthesis. Model compounds containing diamide linkages were prepared by benzoylation of *o*-, *m*- or *p*-PDA's using benzoyl chloride. *o*-PDA was purified by recrystallization from water, *m*-PDA was used as such and *p*-PDA from ethanol. Benzoyl chloride was used directly. TEA was stored over KOH for 24 hours prior to use.

A typical procedure for benzoylation consisted of dissolving 0.01 mole of the diamine in a mixture of 50 ml chloroform and 0.02 mole of TEA followed by the addition of 0.022 moles of benzoyl chloride under stirring over a period of ten minutes. The reaction mixture was further stirred for one hour. The resultant residues were collected on a Buchner funnel and washed with 0.005N HCl and 0.005N NaOH solutions respectively followed by several neutral water washes. The product diamide adducts so obtained were purified by recrystallization from benzyl alcohol, followed by methanol washes.

3.1.1.2 Diester synthesis

HQ and Res were used as received while Bis-A was purified by recrystallization from toluene.

3.1.1.2.1 Diester from hydroquinone

0.01 mole of HQ was dissolved in 65 ml of a mixture of dioxane and chloroform (1:2 v/v) with the addition of 0.03 moles of TEA. Benzoylation was carried out as described in the previous section using 0.026 moles of benzoyl chloride. The residue obtained was given the same washing treatment as described previously and purification was carried out by dissolution in chloroform followed by the addition of petroleum ether until turbidity was attained. The solution was reheated and cooled to obtain the product.

3.1.1.2.2 Diester from resorcinol

0.01 moles of resorcinol was dissolved in 70 ml of a mixture of dioxane and chloroform (1:2 v/v) with the addition of 0.03 moles of TEA. This was followed by benzoylation using 0.027 moles of benzoyl chloride. The adduct was then extracted in. ethyl acetate and washed with 0.005N HCl and 0.005N NaOH solutions respectively followed by neutral water washes. Ethyl acetate was distilled out to obtain the product which was further purified by recrystallization from petroleum ether.

3.1.1.2.3 Diester from bisphenol-A

0.002 moles of Bis-A was dissolved in 225 ml of chloroform containing 0.008 moles of TEA. Benzoylation was carried out using 0.0082 moles of benzoyl chloride. The clear solution obtained was poured into petroleum ether and the product was recovered by filtration. The precipitate was given similar washing treatments as described previously. Purification was carried out by recrystallization from acetone.

3.1.1.3 Esteramide synthesis

Both *m*- and *p*-AP's were purified by recrystallization from water.

3.1.1.3.1 Esteramide from m-aminophenol

0.01 moles of *m*-AP was dissolved in 45 ml of chloroform containing 0.024 moles of TEA. Benzoylation was carried out using 0.022 moles of benzoyl chloride. The resultant solution was concentrated and washed with 0.005N HCl and 0.005N NaOH solutions respectively followed by neutral water washes. The solution was then cooled to a temperature of 4°C and the white solid obtained was used as such.

3.1.1.3.2 Esteramide from p-aminophenol

0.01 moles of *p*-AP was dissolved in a 65 ml mixture of dioxane and chloroform (1:2 v/v) with the rest of the procedure remaining the same as in the case of *m*-AP. The resultant solution obtained was given the same washings as described in the previous cases. Finally the solid product obtained during the course of washing was purified by recrystallization from a mixture of chloroform : dioxane (1:4 v/v).

All the adducts described above were dried at 100 - 110°C before further use. All the adduct structures were confirmed from proton NMR spectra.

3.1.2 Chlorination of Adducts

All the diamides, diesters and esteramides synthesized as described above were first ground to a fine powder (talcum powder) form and then exposed to three levels of chlorine treatments. The first two levels involved single day exposures at chlorine concentrations of 10,000 ppm (A) and 35,000 ppm (B) respectively while the third level involved exposure upto seven days at chlorine concentration of 35,000 ppm (C). Table 4 (Appendix 1) lists these various levels of chlorine treatments that were carried out.

The chlorination procedure involved addition of required amount of NaOCl solution of known concentration (4 - 6%) at a specific pH = 6 - 6.5 to the respective adducts followed by dilution where necessary. The chlorine concentration was determined using a chloroscope kit. The chlorine estimation procedure involved taking 5 ml of solution, appropriately diluted, into a test tube. Three drops of orthotolidine reagent was added to this solution and the color developed was matched with the colors indicated for the various ppm concentrations on the chloroscope kit and then corrected for the dilution factor. Orthotolidine is an aromatic compound that is oxidized in acid solution by chlorine, chloramines and other oxidants to produce a yellow colored complex.

The chlorine solution containing the powdered adducts was stirred on a magnetic stirrer for the required period of time. As a control, these adducts were simultaneously stirred in distilled water during the same time. At the end of the exposure time, the chlorine and water treated adducts were washed several times with distilled water until the conductivity of the washings matched that for the distilled water. The chlorine treated and water treated adducts were then dried at 100 - 110 $^{\circ}$C for a week.

3.1.3 Material Characterization of Adducts

All the adducts synthesized along with the chlorine treated samples were characterized using spectral techniques such as IR, ^{1}H NMR and melting point measurements :

i) IR spectroscopy : The IR spectra were scanned on all the adduct samples (prepared as described in section 3.1.1) that were previously subjected to drying using the nujol mull technique. The IR spectra was used to confirm the presence of amide, ester and esteramide linkages in the various adducts that were so synthesized.

ii) Melting point : The melting point of all the untreated, chlorine treated (treatments A, B and C) and water treated adduct samples were recorded on a standard melting point apparatus with an accuracy of ±0.5 - 1°C.

iii) NMR spectroscopy : The structures of all the adducts (untreated, chlorine treated and water treated) were determined by ^{1}H NMR using either a 200 or 300 MHz NMR spectrometer. The diamides were dissolved in DMSO-d6, the esteramides in deuterated acetone and the diesters in deuterated chloroform. The COSY (COrrelated SpectroscopY) spectra of the esteramide adduct obtained from *p*-AP subjected to treatment C was obtained using the MSL 300 MHz spectrometer. The 2D-contour plot reveals the spin-spin coupling relationships in a molecule.

3.2 TFC MEMBRANE STUDY

3.2.1 Fabrication and Characterization of the Micro-porous (PSF) Support

3.2.1.1 Fabrication

A micro-porous PSF support was prepared by casting a 17.3% solution of PSF (UDEL P-3500) in DMF onto a polyester fabric passing through a casting blade with a knife gap of 8 to 10 mils. After an air gap of 7 sec. this was immersed into a tank containing water (15°C). This was followed by washing of the membrane at 50°C. The resulting PSF membrane was rinsed in water overnight. This membrane was then used as the micro-porous support for all further studies in the preparation of TFC membranes.

3.2.1.2 Characterization

The resultant PSF membrane was characterized for BSA rejection using 0.2% (w/w) BSA solution in 0.2M phosphate buffer at pH = 7.5. The BSA transmission through the PSF membrane was measured using a stirred cell (13.4 cm^2 area, 600 rpm) assembly operated at a pressure of 0.7 kg/cm^2 at ambient temperature. The permeate and retentate samples were collected. The protein concentration in the feed and permeate were determined spectrophotometrically by UV absorbance measurements at 280 and 260 nm using the following equation :

Protein conc. (mg/ml) = (1.55 x Abs.280nm) - (0.74 x Abs. 260nm)

The BSA rejections were thus calculated as $R = 1 - C_p/C_r$.

The PSF prepared as described in section 3.2.1.1 gave about 70 - 80% BSA rejection with a water flux of 30 - 40 lpm under the conditions described above.

3.2.2 Fabrication of TFC Membranes

For all the TFC membranes prepared, the micro-porous PSF support prepared as described above was cut into 6" x 4" pieces and taped onto a glass plate from two sides. This support was kept soaked in water until the interfacial coating procedure. In all cases the interfacial coating was done as follows :

The aqueous and organic phases were poured into separate dip tanks of 250 ml capacity. The glass plate with the micro-porous PSF support taped on two sides was first dipped in the aqueous phase for a specified time. The plate was then removed and placed vertically for a fixed air drying period. Following the drying, the PSF support was taped on the remaining two sides. This was followed by dipping the air-dried, amine-coated PSF support in the organic phase for varying time periods. The TFC membranes so formed were cured for specific times at set curing temperatures. The aqueous phase dip times, air drying period and the organic phase dip times for the various systems at various compositions are given in Tables 9 -14 (Appendix 2).

In all the studies a phase transfer catalyst was included in the aqueous phase. This is in accordance with the studies reported by Tsai and Lee (1987,1988). Although these studies have concentrated on stirred systems the chemistry is the same as in the present TFC membrane study. However, the concentrations used in this study are in excess of that mentioned by Tsai and Lee. Since the present study involved lower solution concentrations and smaller reaction times the amount of phase transfer catalyst used was the same as that used in high speed stirred interfacial reactions that involve short reaction times of 5 - 10 minutes (Morgan 1965).

In all cases the *m*-PDA concentration in the solutions was confirmed by comparison with a previously obtained calibration plot of UV absorbance versus concentration of standard solutions. The sample absorbance was measured at 289 nm.

3.2.2.1 Reference standard polyamide TFC membrane

Table 9 lists the standard polyamide membranes that are formed from the reaction of TMC with *m*-PDA. A 3% (w/w) aqueous solution comprising of *m*-PDA dissolved in water was prepared. The solution was treated with activated charcoal (1 gm/25 gm charcoal) followed by filtration and addition of NaOH to adjust the pH to 9. Finally the solution concentration was confirmed as described at the end of section 3.2.2 followed by dilution to 2.5% (w/w).

The organic phase in all cases comprised of 0.15% (w/v) of TMC dissolved in hexane.

3.2.2.2 TFC polyesteramide membranes prepared from the reaction of TMC with varying compositions of m-AP : m-PDA

Table 10a lists polyesteramide membranes prepared from the reaction of only *m*-AP with TMC. The aqueous solution in this case comprised of 2.5% (w/w) of *m*-AP dissolved in water. Additionally, 1:0.0125 moles of NaOH : BTEAC with respect to one mole of *m*-AP was added to this solution. Subsequent Tables 10b-h list polyesteramide membranes prepared from varying compositions of *m*-AP : *m*-PDA. In all instances, the aqueous solutions comprised of 2.5% (w/w) of mole ratios 90:10, 80:20, 70:30, 50:50 and 30:70 of *m*-AP : *m*-PDA. Additionally, 1:0.0125 moles of NaOH : BTEAC with respect to one mole of *m*-AP was added to all these solutions. As listed in Tables 10d, 10f and 10h, the aqueous solutions in these cases corresponding to 80:20, 70:30 and 50:50 *m*-AP : *m*-PDA compositions also comprised of 0.5% of the surfactant SLS.

The organic phase in all cases comprised of 0.15% (w/v) of TMC dissolved in hexane.

3.2.2.3 TFC polyesteramide membranes prepared from the reaction of TMC with varying compositions of Bis-A : m-PDA

Table 11a-d list polyesteramide membranes prepared from varying compositions of Bis-A : *m*-PDA. In all cases, aqueous solutions comprising of 2.5% (w/w) of mole ratios 80:20, 70:30, 50:50 and 30:70 of Bis-A : *m*-PDA was prepared. Additionally, the aqueous solutions also comprised of 2:0.025 moles of NaOH : TBABr with respect to one mole of Bis-A; except in case of the 70:30 and 80:20 Bis-A : *m*-PDA compositions where the Bis-A : NaOH mole ratio used was 1:2.74.

The organic phase in all cases comprised of dissolving 0.15% (w/v) of TMC dissolved in hexane.

3.2.2.4 TFC polyesteramide membranes prepared from the reaction of TMC with varying compositions of HQ : m-PDA

Table 12a-d list polyesteramide membranes prepared from the reaction of varying compositions of HQ : *m*-PDA. In all cases, aqueous solutions comprising of 2.5% (w/w) of mole ratios 80:20, 70:30, 50:50 and 30:70 of HQ : *m*-PDA was prepared. In addition, 2:0.025 moles of NaOH : TBABr with respect to one mole of HQ was also added to the aqueous solutions.

The organic phase in all cases comprised of dissolving 0.15% (w/v) of TMC dissolved in hexane.

3.2.2.5 TFC polyamide prepared from the reaction of 1,5-naphthalene diamine with mixed acid chlorides and TMC

Tables 13a and 13b list polyamide membranes prepared from the reaction of 1,5-naphthalene diamine with mixed acid chlorides TPC + IPC and TMC + IPC. A 0.2% (w/w) solution of 1,5-naphthalene diamine in 50:50 methanol : water (w/w) was prepared by dissolving the diamine in methanol first.

The organic phase comprised of 1% and 0.15% (w/w) of 50:50 mole proportions of TPC : IPC or TMC : IPC in these cases.

Tables 13c-g list membranes formed by using only TMC in varying proportions (0.15 - 0.35% w/v) as the acid chloride in the organic phase. In Tables 13d and 13f, the organic phase solvent was cyclohexane, while in all other cases hexane was used. The aqueous phase comprised of either 0.18% or 0.2% of 1,5-naphthalene diamine dissolved in a 50:50 methanol : water mixture.

3.2.2.6 TFC polyamide prepared from the reaction of TMC with 2,6-diaminopyridine

Tables 14a-l list the various membranes formed from the reaction of 2,6-diaminopyridine with TMC. The aqueous phase comprised of dissolving 2,6-diaminopyridine in water at various concentrations (2.5 - 7%) as mentioned in the tables. As indicated in Tables 14d, 14e and 14g, the aqueous phase in addition to the diamine also contained the surfactant SLS. The critical micellar value (CMC) of SLS is 8×10^{-3} molar. The specific concentrations (always less than the CMC) used are indicated in these tables.

The organic phase comprised of varying concentrations (0.2 - 0.7%) of TMC (w/v) dissolved in hexane.

3.2.3 Reverse Osmosis Testing Procedure

The experimental set up for the RO unit is shown in Fig. 3.1. The unit comprised of four cells (corresponding to areas of 27.5 cm^2, 21.7 cm^2, 23.8 cm^2 and 23.8 cm^2 respectively) with channel heights of 3 mm in each case. The membrane coupons were rectangular of approximate dimensions of 1" x 3". The four cells were connected in series. A feed tank of 2 lit. capacity was used as a reservoir for feed recirculation. A positive displacement volumetric pump (Vellorie, India) giving 50 lph at a pressure of 2.76 MPa was used. The feed solution comprised of 2000 ppm salt or a mixture of 2000 ppm salt with 5% sucrose dissolved in distilled water. The feed was pumped into the cells at the pressures indicated in the various tables. The resultant permeate samples were collected and these along with the feed solutions were tested for their conductivities in order to determine the salt rejection values. The conductivity values were converted to ppm values using an empirical equation obtained by calibration of standard samples :

$$\log(\text{NaCl ppm}) = [\log(\text{conductivity of permeate, mmhos}) \times 1.0585 + 2.76]$$

The salt rejection was calculated using equation 1.1. The water flux through each membrane, measured with a timer and 10 ml graduated cylinder, was normalized by the cell area. The water and solute permeabilities were calculated using equations 1.2 and 1.4 respectively.

3.2.4 Chlorine Tolerance Testing of Selected TFC Membranes

The chlorination study was carried out by adding NaOCl to the feed (NaCl) solution and measuring the increase in salt transmission through the membrane as a result

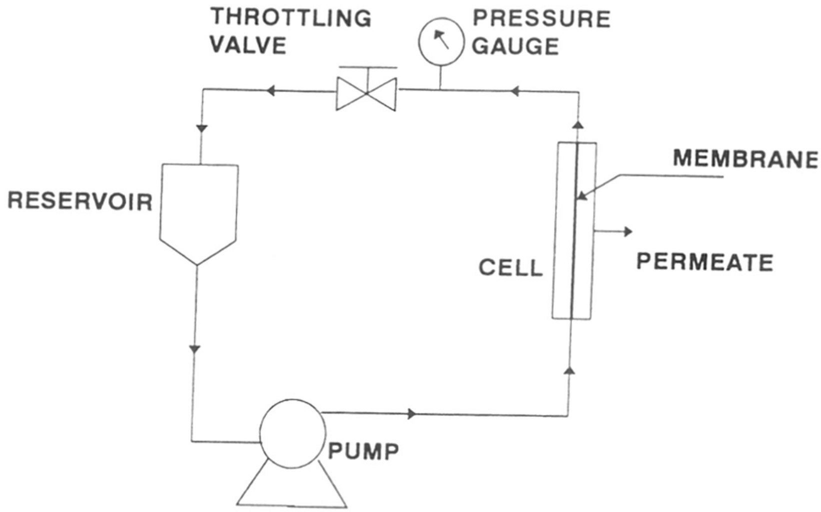


Figure 3.1 Schematic of the reverse osmosis testing unit.

of chlorine exposure time. Initially, the salt rejections and water fluxes through the membranes were measured using a feed solution comprising of 2000 ppm salt dissolved in water. The solute transmission T_o ($=C_p/C_f$) in the absence of chlorine was determined.

A required amount of NaOCl solution of known chlorine concentration (4 - 6%) was added to the feed, so that the residual chlorine concentration of the feed solution was about 200 ppm. This was immediately followed by the addition of HCl so that the pH was stabilized in the range of 6 - 6.5. The chlorine concentration was monitored every 20 minutes using the chloroscope kit (as described in section 3.1.2). The feed solution was diluted 100x prior to the addition of the orthotolidine reagent to 5 ml of this solution in order to estimate chlorine concentration. Any decrease in chlorine concentration of the feed was immediately stabilized with the addition of fresh NaOCl solution followed by the addition of HCl to stabilize the pH to 6 - 6.5. Generally, the chlorine concentration could be maintained within ±20 ppm of the target value of 200 ppm. In all the chlorine studies, one of the cells always contained the standard polyamide membrane (see section 3.2.2.1) used as reference while the other three cells contained the novel polyesteramide membranes. The feed and permeate samples were collected at regular intervals of 20 - 30 minutes and analyzed for their conductivities in order to calculate the value of T (solute transmisson = C_p/C_f after chlorine addition). At these time intervals, the corresponding water permeability (equation 1.2) through the membranes was also monitored.

The NaOCl concentration range was usually 4 - 6% with the rest of the solution thus being NaOH. As a result, it was observed that on addition of NaOCl solution followed by HCl addition to stabilize the pH to 6 - 6.5, the conductivity of the feed solution increased by about 2 - 3x. This increase in conductivity is therefore attributed to

NaCl that is formed in the neutralization reaction between the acid and base. Therefore, in the chlorine study all rejections have been calculated based on the conductivity values directly without conversion to ppm values unlike as was done for the RO studies.

3.3 POLYMER SAMPLE PREPARATION AND CHARACTERIZATION

3.3.1 Polymer preparation

The reactivities of the aminophenols and the diols are lower than that of the diamines (Korshak *et al* 1962,1963 and Morgan 1965). It was thus essential to quantify the percent ester incorporated in the polyesteramide as this proportion could be quite different from the aqueous phase reaction mixture ratio. Since ATR-IR spectra of the TFC membranes did not yield any appreciable difference between the signal to noise ratios, FTIR studies were conducted on a Nicolet FTIR instrument using the KBr pellet technique. Various polyesteramide, polyester and polyamide polymers were synthesized under controlled conditions in order to develop a procedure for estimation of the percent ester incorporation in the polyesteramides. This was done in two parts as discussed below :

3.3.1.1 Homopolymer synthesis

Homopolymers of polyamide, polyesteramide and polyester polymers were prepared by the unstirred interfacial polycondensation technique. An organic solution comprising of 0.15% (w/v) of TMC in hexane was prepared and reacted with the following aqueous phase solutions:

A : A 2.5% solution of *m*-PDA in water was prepared as described in section 3.2.2.1.

B : A 2.5% (w/w) solution of *m*-AP in water was prepared. Final solution composition comprised of 1:1:0.0125 moles of *m*-AP : NaOH : BTEAC.

C : A 2.5% (w/w) solution of Bis-A in water was prepared. Final solution composition comprised of 1:2:0.025 moles of Bis-A : NaOH : TBABr.

D : A 2.5% (w/w) solution of HQ in water was prepared. Final solution composition comprised of 1:2:0.025 moles of HQ : NaOH : TBABr.

The aqueous layer in each case was added to a petrie dish of size 8". This was followed by the addition of the organic solution above the aqueous layer using a 15 ml dropper until the organic layer completely covered the aqueous layer. The resultant film formed at the interface of the two layers was withdrawn and immediately transferred into a solution of dilute HCl. This procedure was repeated 8 - 10 times in order to obtain an adequate amount (sufficient for FTIR studies) of polymer sample. The resultant polymers were then washed several times with dilute NaOH solution followed by water washes until neutral pH is attained. Finally the polymers were vacuum dried at 60°C for a week.

The reaction of TMC with solution A yielded a polyamide, that with solution B yielded a polyesteramide while those with solutions C and D yielded the respective polyesters.

3.3.1.2 Polyesteramides by reaction with mixed aqueous phases

The second part involved the preparation of polyesteramide polymers by unstirred interfacial reaction between solutions of 50:50 mole ratios of *m*-AP : *m*-PDA, Bis-A : *m*-PDA and HQ : *m*-PDA each separately in contact with the same TMC solution as described in section 3.3.1.1. This was done using the following aqueous phases :

E : A 2.5% solution comprising of 50:50 mole proportion of *m*-AP : *m*-PDA was prepared. Solution composition comprised of 1:1:0.0125 moles of *m*-AP : NaOH : BTEAC.

F : A 2.5% solution comprising of 50:50 mole proportion of Bis-A : *m*-PDA was prepared. Solution composition comprised of 1:2:0.025 moles of Bis-A : NaOH : TBABr.

G : A 2.5% solution comprising of 50:50 mole proportion of HQ : *m*-PDA was prepared. Solution composition comprised of 1:2:0.025 moles of HQ : NaOH : TBABr.

The same petrie dish procedure as described in section 3.3.1.1 was used followed by similar washing and drying conditions for all the polyesteramide polymers.

3.3.2 Polymer Characterization

The polymer samples were characterized by FTIR study. The main purpose of this study was to evaluate the percent ester composition in the polyesteramide polymers prepared from solutions of 50:50 mole proportions as described above. For this, initially physical mixtures were prepared as follows :

i) Physical mixture-A : 0.57 mg of polyesteramide from *m*-AP and TMC (obtained from the reaction of TMC with solution B) + 0.41 mg of polyamide from *m*-PDA and TMC (obtained from the reaction of TMC with solution A);

ii) Physical mixture-B : 0.45 mg of polyester from Bis-A and TMC (obtained from the reaction of TMC with solution C) + 0.45 mg of polyamide from *m*-PDA and TMC (obtained from the reaction of TMC with solution A).

iii) Physical mixture-C : 0.58 mg of polyester from HQ and TMC (obtained from the reaction of TMC with solution D) + 0.45 mg of polyamide from *m*-PDA and TMC (obtained from the reaction of TMC with solution A).

The ester signal in the region between 1720 - 1765 cm^{-1} was used to quantify the percent ester composition in the physical mixtures as well as the polyesteramide polymers. A standard deconvolution software package (Full Optimization Curve Analysis Software, FOCAS) was used to quantify the peak for the ester signal in relation to the amide signal. The ester signals at 1720 - 1745 cm^{-1} along with the amide (I) signals at 1640 - 1680 cm^{-1} in both the physical mixtures as well as the polyesteramide polymers were deconvoluted in order to obtain the area under the signals and these results are tabulated in Table 15 (Appendix 2).

The polymer obtained from HQ was dark colored, and in addition, this polymer could not be ground properly to yield a uniform dispersion in the KBr pellet. These factors have hindered a proper FTIR study on this particular system.

CHAPTER 4

CHLORINE RESISTANCE STUDIES OF DIAMIDE, DIESTER AND ESTERAMIDE ADDUCTS : RESULTS AND DISCUSSION

In this chapter, the results of the adduct study are presented and discussed. As described in chapter three, various diamide, diester and esteramide adducts were synthesized and then exposed to chlorine treatments at pH = 6 - 6.5 of varying severity (treatment severity A < B < C). The adducts were characterized before and after chlorine exposure by IR, melting point and proton NMR techniques. The results cast light on the effect of substitution pattern on chlorine resistance and the susceptibility of ester and esteramide linkages in comparison to amide functionalities.

4.1 IR CHARACTERIZATION

The appropriate assignments of the absorption frequencies for the various adducts have been summarized in Tables 1 - 3 (Appendix 2). IR spectroscopy was used as a tool for the confirmation of amide, ester and esteramide groups in the various adducts so synthesized. The IR spectra can be seen in the figures as summarized below :

a) diamides are shown in Figs. 4.1a-c,

b) diesters are shown in Figs. 4.2a-c

c) esteramides are shown in Figs. 4.3a and 4.3b.

The identification of the various absorption frequencies has been done on the basis of references by Silverstein *et al*, 1974; Skoog and West, 1971 and Khanna and Pearce, 1981.

All the adducts synthesized show the expected characteristic absorption frequencies :

(a) All the diamides, diesters and esteramides exhibit absorption bands between 500 cm^{-1}

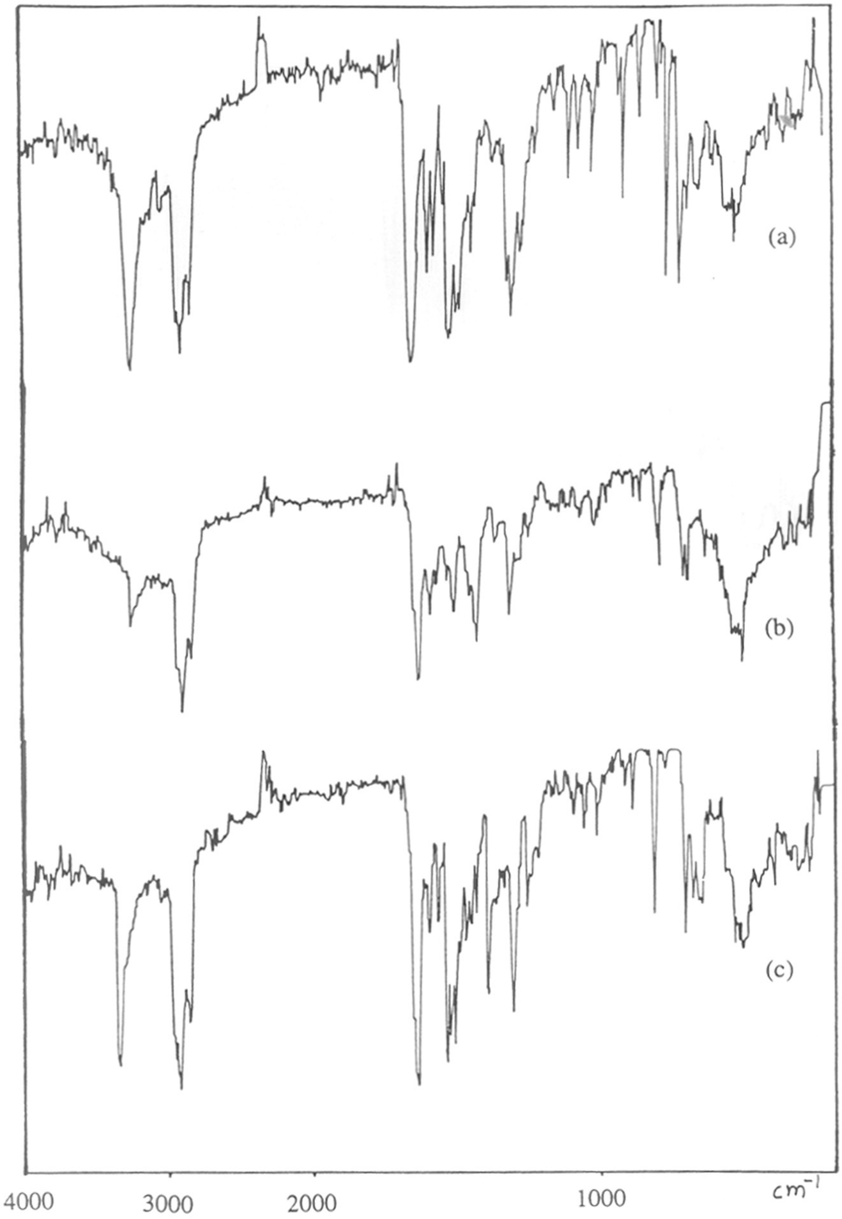


Fig. 4.1 : IR spectra of the untreated diamides (a) diamide obtained from *o*-PDA, (b) diamide obtained from *m*-PDA and (c) diamide obtained from *p*-PDA.

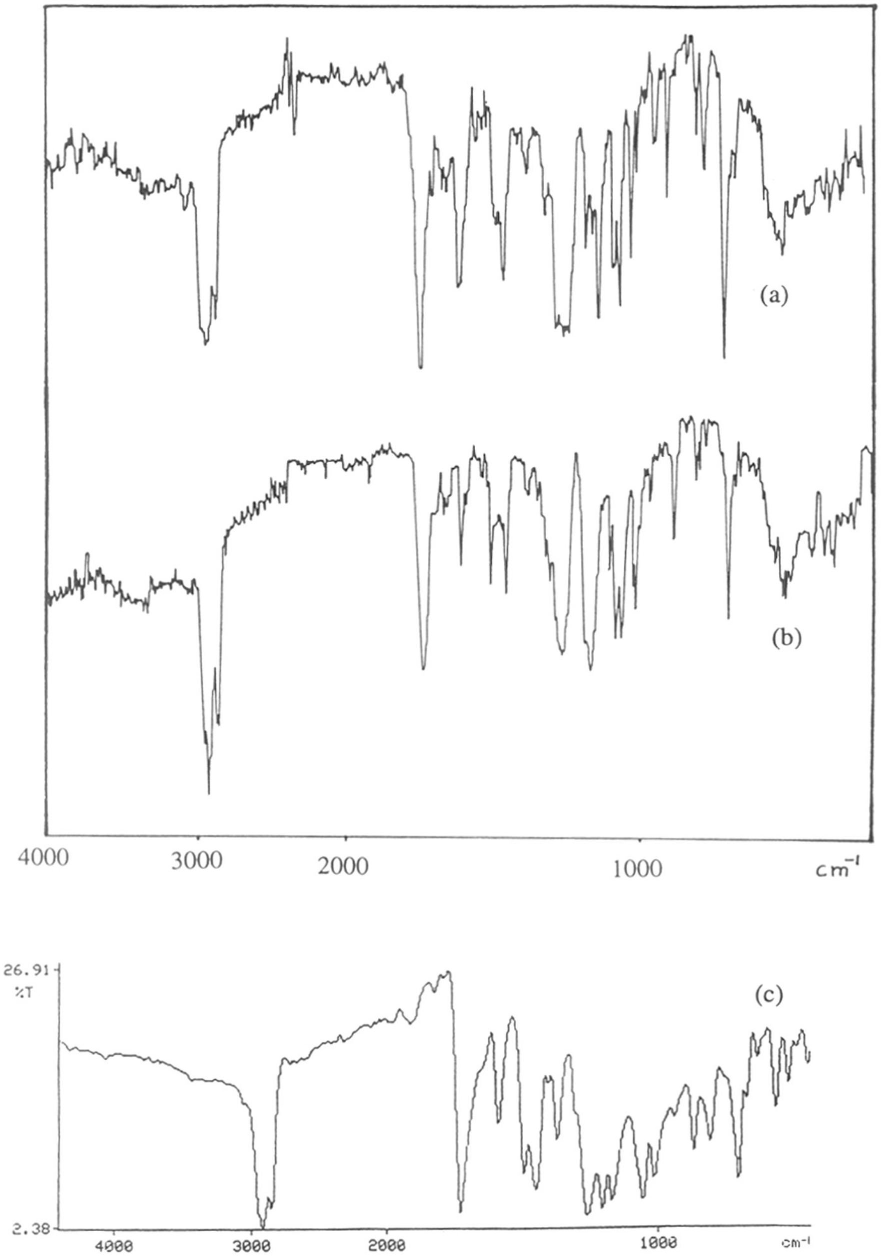


Fig. 4.2 : IR spectra of the untreated diesters (a) diester obtained from Res, (b) diester obtained from HQ and (c) diester obtained from Bis-A.

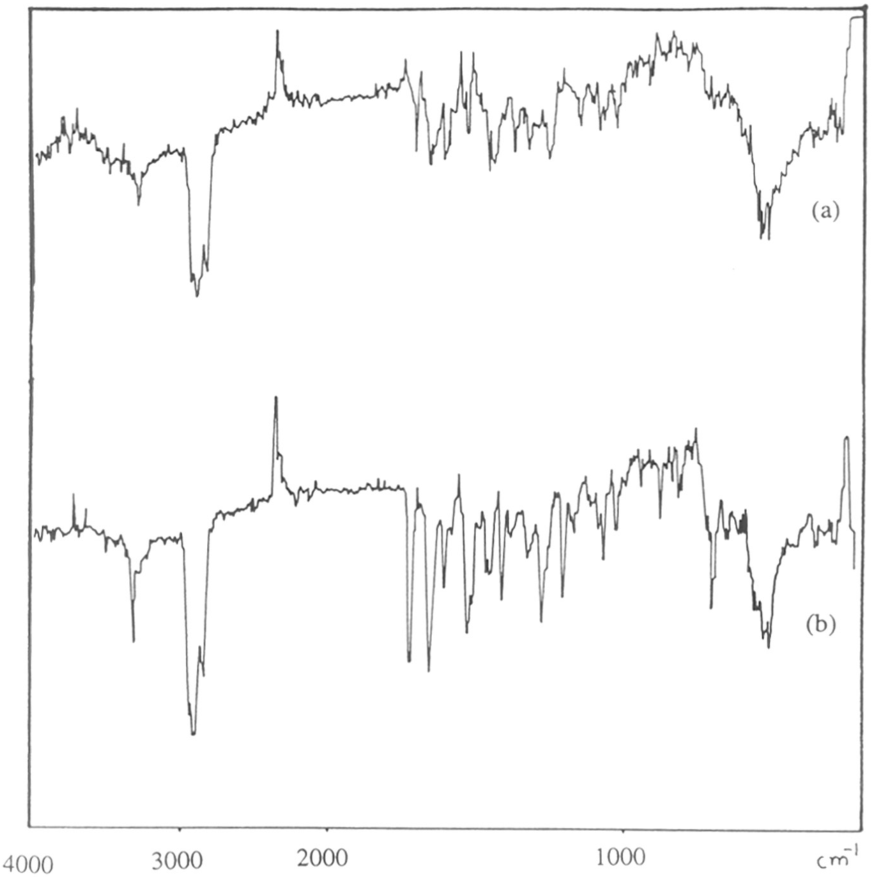


Fig. 4.3 : IR spectra of the untreated esteramides (a) esteramide obtained from *m*-AP and (b) esteramide obtained from *p*-AP.

and 810 cm^{-1} which are attributed to in-plane and out-of-plane ring deformations of the phenyl rings and out-of -plane bending of the C-H bonds of substituted benzenes.

(b) The diamides and the esteramides exhibit a single strong band between 3150 - 3350 cm^{-1} that is characteristic of N-H stretch. They also show a strong absorption band in the region between 1525 - 1560 cm^{-1} which is indicative of the Amide(II) band that arises due to the interaction of N-H bending and C-H stretching. The strong band in the region between 1630 - 1680 cm^{-1} is a result of the Amide(I) band arising due to C=O stretching and is characteristically seen in the diamides and the esteramides.

(c) The diesters in addition to the esteramides exhibit a strong band at 1700 - 1735 cm^{-1} arising due to the C=O stretch in esters. The C-O-C antisymmetric stretch in esters that occurs between 1170 - 1280 cm^{-1} is also seen as a strong band in both the esteramides and the diesters.

Thus, the IR spectra is clearly indicative of the presence of amide, ester and esteramide linkages in the various adducts so synthesized. However, IR was not suitably sensitive to detect changes in the chlorine treated samples.

4.2 MELTING POINT STUDY

The melting point for the untreated, water treated and the various chlorine treated adducts are presented in Table 4 (Appendix 2). The results for the three classes of adducts, viz. diamides, diesters and esteramides, are discussed below.

4.2.1 Diamides

The diamide obtained from the benzoylation of *o*-PDA did not show any change in the melting point which remained almost constant at 286 - 289°C for treatments A, B and C as well as for the untreated adduct.

The diamide obtained from the benzoylation of *m*-PDA did not show any change in the melting point which remained almost constant at 228 - 232°C on treatments A and B as compared to the untreated adduct whereas treatment C resulted in an increase in the melting point to a value of 250 - 252°C.

The diamide obtained from the benzoylation of *p*-PDA too did not show any change in the melting point which was around 303 - 306°C for treatments A and B as compared to the untreated adduct whereas a decrease in melting point to a value of 248 - 251°C is observed for treatment C.

The constant melting point for the diamide formed from *o*-PDA even at the most severe chlorination conditions indicates that this particular adduct is not easily chlorinated. The diamides formed from *m*-PDA and *p*-PDA showed no change in the melting points for treatments A and B as compared to the untreated adducts; however, both were affected with treatment C. Chlorination typically would be expected to result in a lower melting point because of decreased H-bonding. Avlonitis *et al* (1992) examined the effect of chlorine on a polyamide membrane and have reported a decrease in melting point with increased chlorine exposure. The diamide formed from *p*-PDA subjected to treatment C has shown a decrease in melting point as compared to the untreated adduct. Surprisingly, an increase in melting point is noted for the diamide formed from *m*-PDA subjected to treatment C. This is the only case wherein an increase in melting point is noted.

4.2.2 Diesters

None of the diesters showed any change in the melting points for treatments A, B and C as compared to the untreated adducts in each case. The diester obtained from the benzoylation of Res showed a melting point of 110 - 112°C for all the treatments A, B and C as well as for the untreated adduct. The untreated diester obtained from the benzoylation of HQ showed a melting point of 195 - 199°C which remained unchanged for all the treatments A, B and C. The diester obtained from the benzoylation of Bis-A showed a melting point of 152 - 154°C for all the treatments A, B and C as well as for the untreated adduct. This would indicate that the diesters are resistant to chlorination.

4.2.3 Esteramides

The esteramide obtained from the benzoylation of *m*-AP showed no change in the melting point for treatment A as compared to the untreated adduct. The melting point remained steady at 146 - 149°C. Treatment B did result in a decrease in melting point to a value of 117 - 120°C while treatment C caused the melting point to further decrease to a value of 105 - 107°C.

The untreated esteramide obtained from the benzoylation of *p*-AP showed a melting point of 225 - 228°C while treatment A on this esteramide resulted in a decrease in melting point to 220 - 222°C. Treatment B resulted in a further decrease of the melting point to 209 - 211°C and finally treatment C resulted in a still further decrease to a value of 127 -134°C.

The esteramide formed from *m*-AP did not show any change in melting point for treatment A as compared to the untreated adduct; however, the samples subjected to treatments B and C showed a dramatic lowering of melting points. By comparison the esteramide formed from *p*-AP shows a small decrease in melting point for treatments A, B while treatment C resulted in a dramatic reduction in melting point.

4.3 NMR STUDY

The description of the proton signals for all the adduct structures are listed in Tables 5 - 8 (Appendix 2). The NMR spectra are shown in Figs. 4.4 - 4.15 and provide more detailed information about the chlorination susceptibility of the various adducts than either of the previous methods. No change in the NMR spectra of the water treated samples in case of any of the adducts was recorded as compared to the untreated adducts. This is also supported by the melting point study (see Table 4 - Appendix 2). As an example see Fig. 4.13. The NMR characterization results for each adduct are discussed below.

4.3.1 Diamide Formed from *o*-PDA

The proton NMR spectra for treatments A, B and C were similar to that for the untreated adduct thereby indicating the absence of chlorination in each instance (Figs. 4.4a - 4.4d). This is in accordance with the melting point study wherein no change is noted for any of the treatments. Thus, it appears that the diamide formed from *o*-PDA is quite resistant to chlorination under the conditions of chlorination employed in this study.

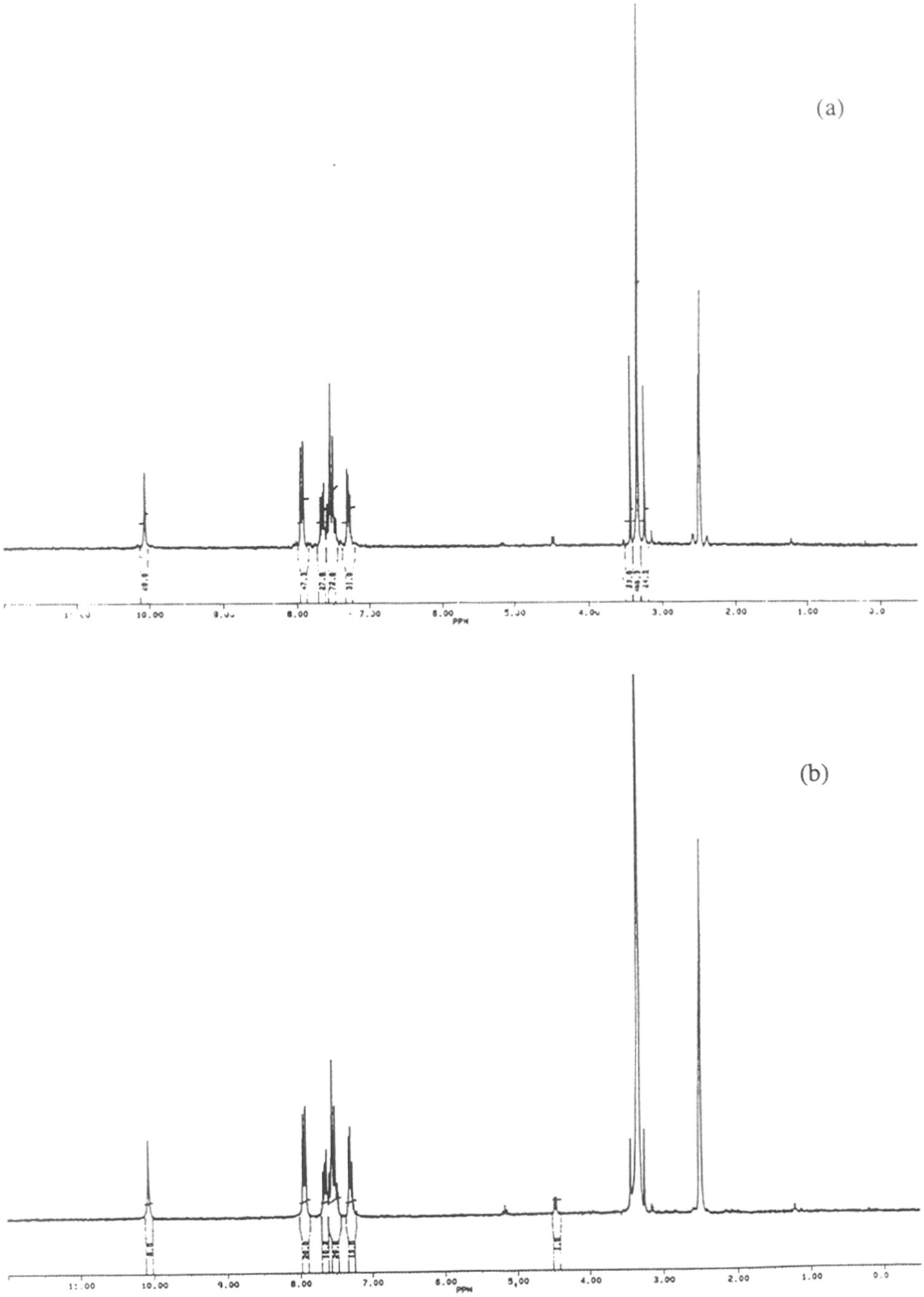


Fig. 4.4 : ^{1}H NMR spectra of the diamide obtained from *o*-PDA (a) after treatment A and (b) after treatment B.

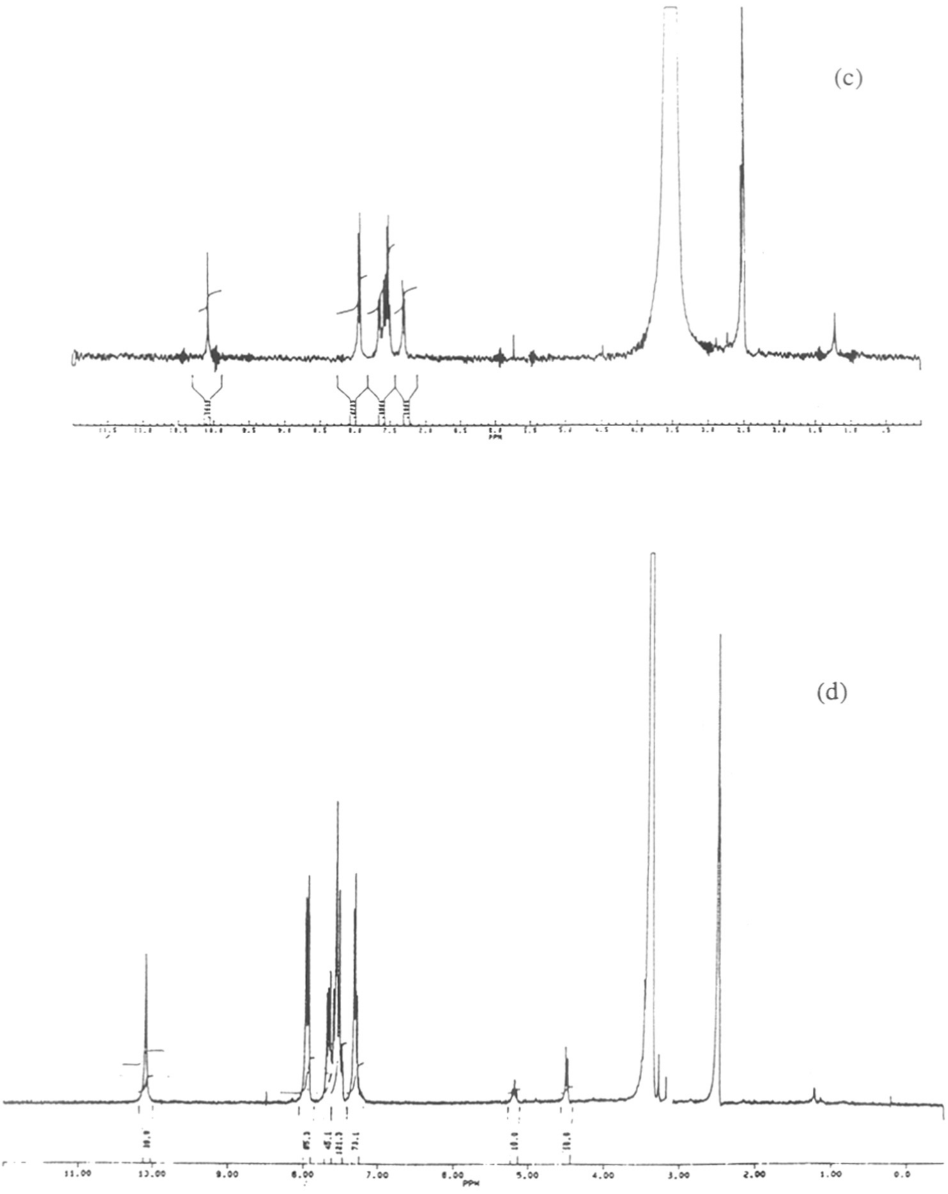


Fig. 4.4 : ^{1}H NMR spectra of the diamide obtained from *o*-PDA (c) after treatment C and (d) untreated.

4.3.2 Diamide Formed from *m*-PDA

As seen from the spectra shown in Figs. 4.5a, 4.5b, and 4.5d for treatments A, B and the untreated adduct, it is clearly observed that the signal positions for treatments A and B match that of the untreated adduct. The amide signal observed at ~10.3δ in Figs. 4.5a, 4.5b and 4.5d also does not show any change.

The absence of any change in the NMR spectra for treatments A and B in comparison to the untreated adduct is consistent with the melting point study which also showed no change for the samples subjected to these treatments. Thus, we can conclude that no chlorination was observed for the diamide formed from *m*-PDA exposed to the two lowest severity conditions.

In comparison, significant changes are seen for treatment C (see Fig. 4.5c). The signals at ~8.35δ and ~7.3δ disappear after treatment C. The ratio of the signal intensities at ~7.6δ (8 protons in the untreated sample) and ~8.0δ (4 protons in the untreated sample) was ~2.0 in the untreated adduct, whereas this has reduced to a value of ~1.3 in the sample subjected to treatment C. The amide signal is also seen to be affected. A weak amide signal is observed at ~10.7δ in addition to a stronger amide signal at ~10.45δ.

The disappearance of the signal at ~8.35δ can be attributed to chlorination at this aromatic ring site, which in turn can lead to a down-field shift for the proton signal for the proton at ~7.3δ. These observations are thus consistent with ring chlorination. The nature of the spectrum seems to suggest the predominance of a trichloro-substituted product as this is the only possibility which can give rise to minimum number of proton NMR signals as is seen in Fig. 4.5c. The formation of a trichloro-substituted product could also explain the increase in melting point observed for this sample subjected to

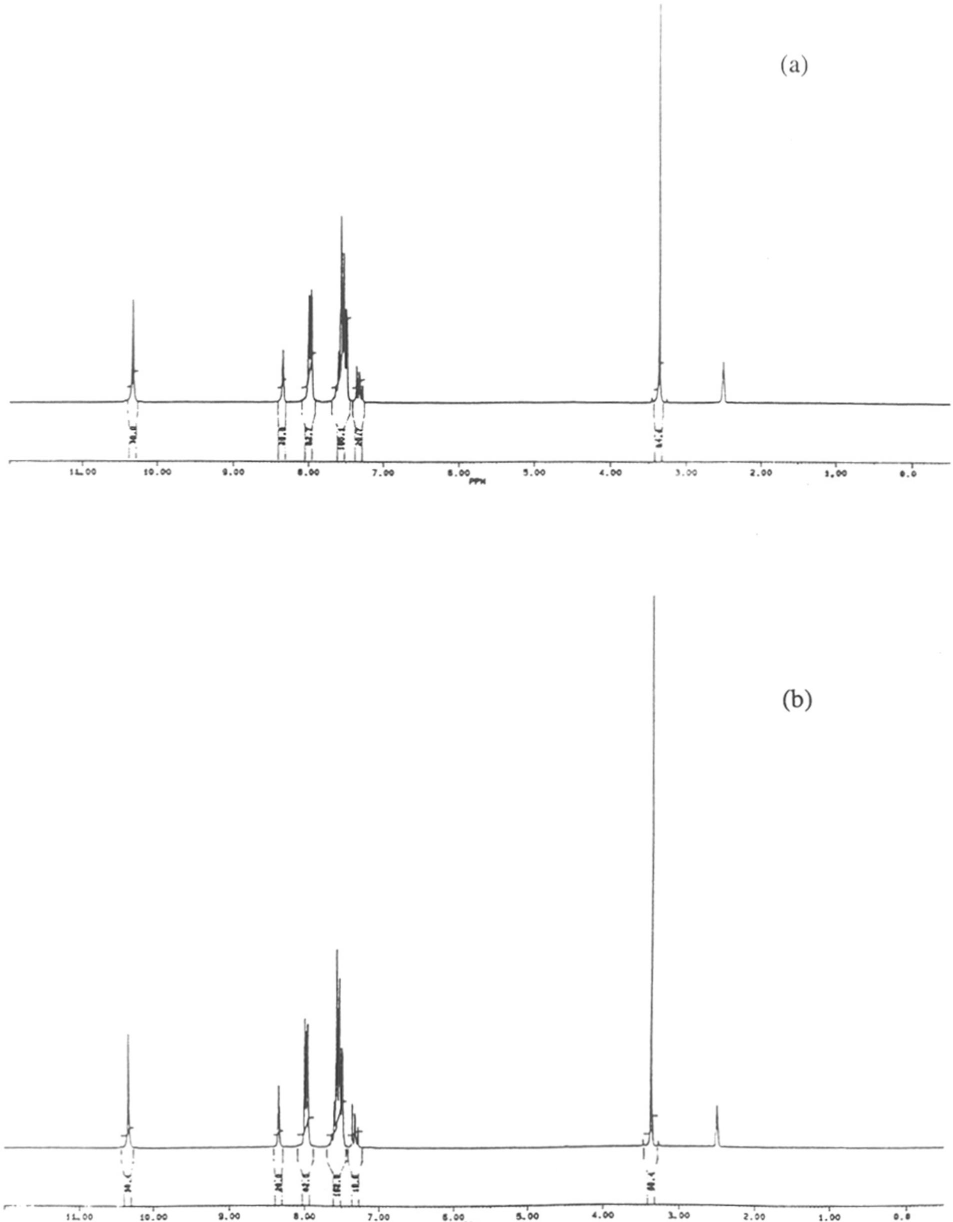


Fig. 4.5 : ^{1}H NMR spectra of the diamide obtained from *m*-PDA (a) after treatment A and (b) after treatment B.

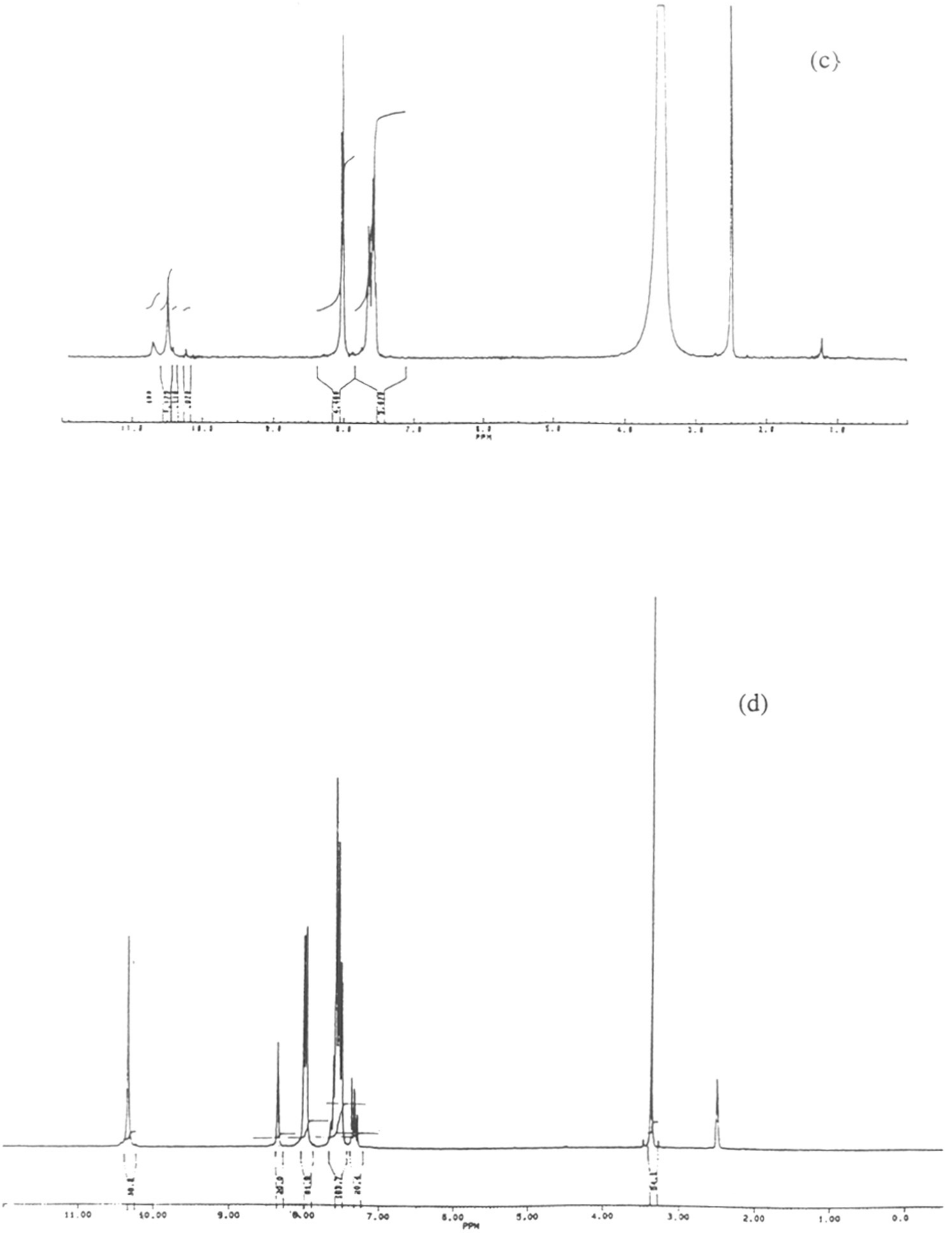


Fig. 4.5 : ^{1}H NMR spectra of the diamide obtained from *m*-PDA (c) after treatment C and (d) untreated.

treatment C.

The weak amide signal at ~10.7δ can be considered to be arising from a monochloro- or dichloro-derivative. The evidences from the NMR spectrum are not conclusive enough to differentiate them. The decrease in the ratio of the signal intensities at ~7.6δ and ~8.0δ also indicate the effect of ring chlorination. Thus, it appears that treatment C of the adduct has resulted in the trichloro-derivative as the major product along with smaller fractions of either monochloro- or dichloro- derivatives.

4.3.3 Diamide Formed from *p*-PDA

The NMR spectra depicted in Figs. 4.6a and 4.6b for treatments A and B respectively were similar to that shown in Fig. 4.6d for the untreated adduct. The amide signal is observed at ~10.25δ in the untreated adduct as well as in the samples subjected to treatments A and B. Thus, this adduct too shows no effect of chlorination on treatments A and B. The melting point study had also shown no change in the melting point for the samples subjected to treatments A and B as compared with the untreated adduct.

As observed from the spectra shown in Fig. 4.6c for the adduct subjected to treatment C, the amide region of the treated sample showed three distinct signals out of which the major one at ~10.26δ closely corresponds to the amide signal in the untreated adduct. The signals in the aromatic region (7.2δ - 8.5δ) also showed many additional signals apart from the signals observed in this region for the untreated adduct. One of the signals is a singlet observed at ~7.85δ.

Though it was difficult to identify the nature of chlorination explicitly, some

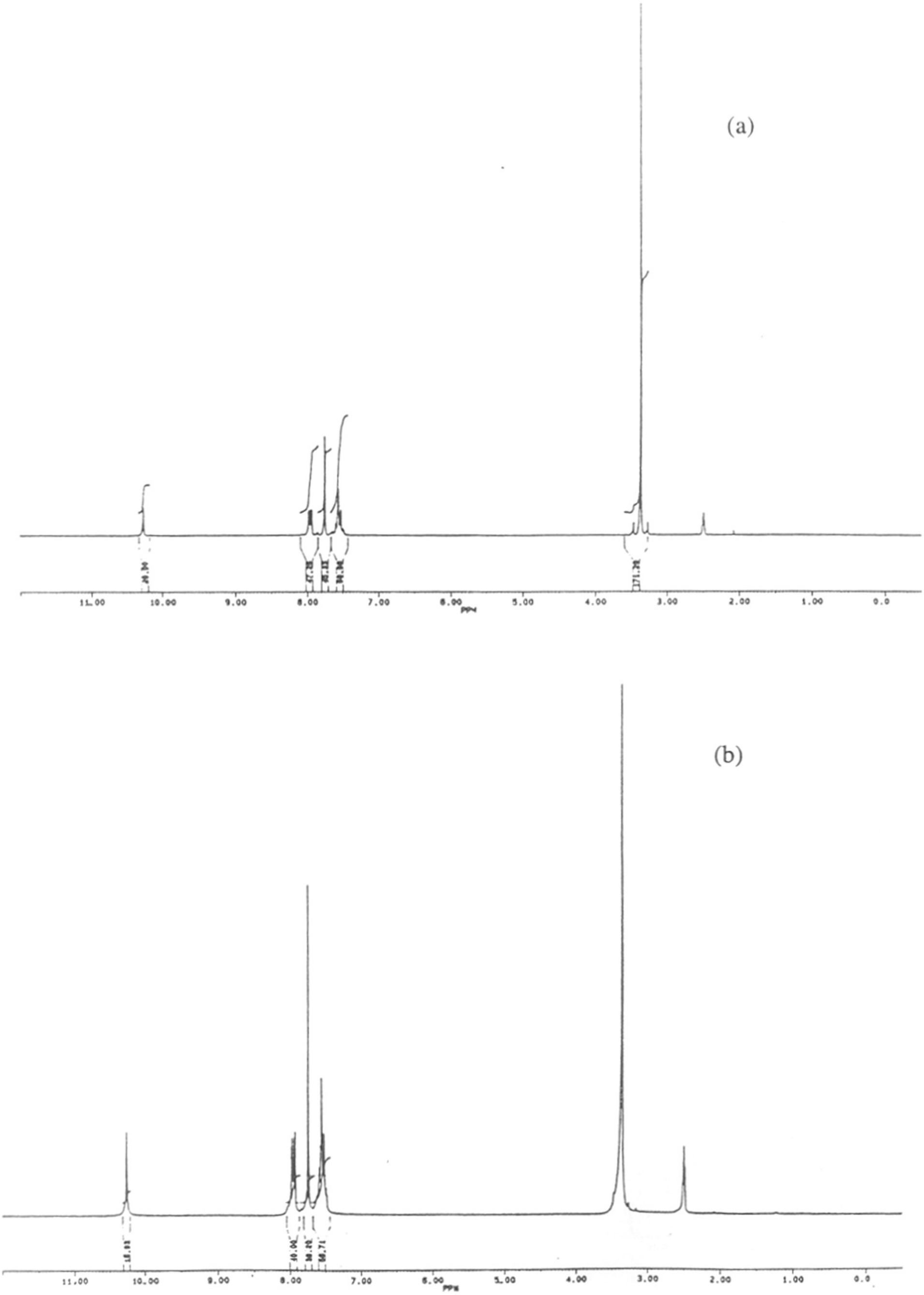


Fig. 4.6 : ^{1}H NMR spectra of the diamide obtained from *p*-PDA (a) after treatment A and (b) after treatment B.

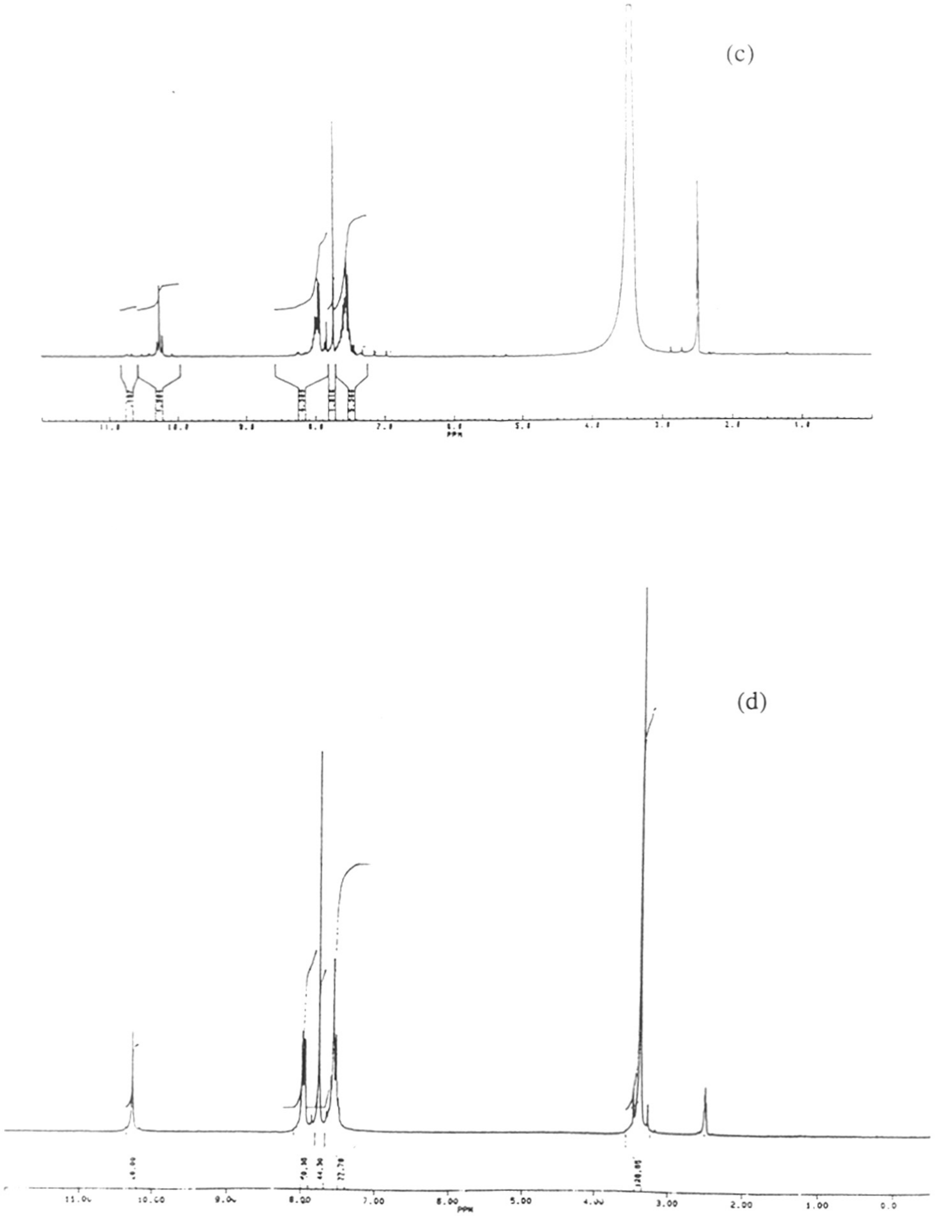


Fig. 4.6 : ^{1}H NMR spectra of the diamide obtained from *p*-PDA (c) after treatment C and (d) untreated.

qualitative informations can be arrived at from the proton spectra. The extent of ring chlorination is less since the major contribution to the signal comes from the non-chlorinated part. The other signals are arising due to monochloro- and dichloro-derivatives. The singlet at ~7.85δ most likely arises due to a dichloro-derivative. Also, from melting point study we have observed a decrease in the melting point for this sample subjected to treatment C. Thus, treatment C of the diamide formed from *p*-PDA results in a major portion of unchlorinated adduct i.e. the starting compound along with some monochloro- and dichloro-derivatives.

4.3.4 Diesters

The NMR spectra for the diester samples subjected to treatments A, B and C in comparison to the untreated sample (D) are shown in the figures as indicated below:

a) Figs. (4.7a-d) : Diester obtained from Res

b) Figs. (4.8a-d) : Diester obtained from HQ

c) Figs. (4.9a-d) : Diester obtained from Bis-A

None of the diester based adducts have shown any change for the treatments A, B and C as compared to the untreated adducts. Thus, the diester based adducts have shown the maximum degree of chlorine tolerance under the conditions of chlorination in this study. This is also supported by the melting point study wherein no change in the melting points for any of the treatments in comparison with the untreated adduct was observed.

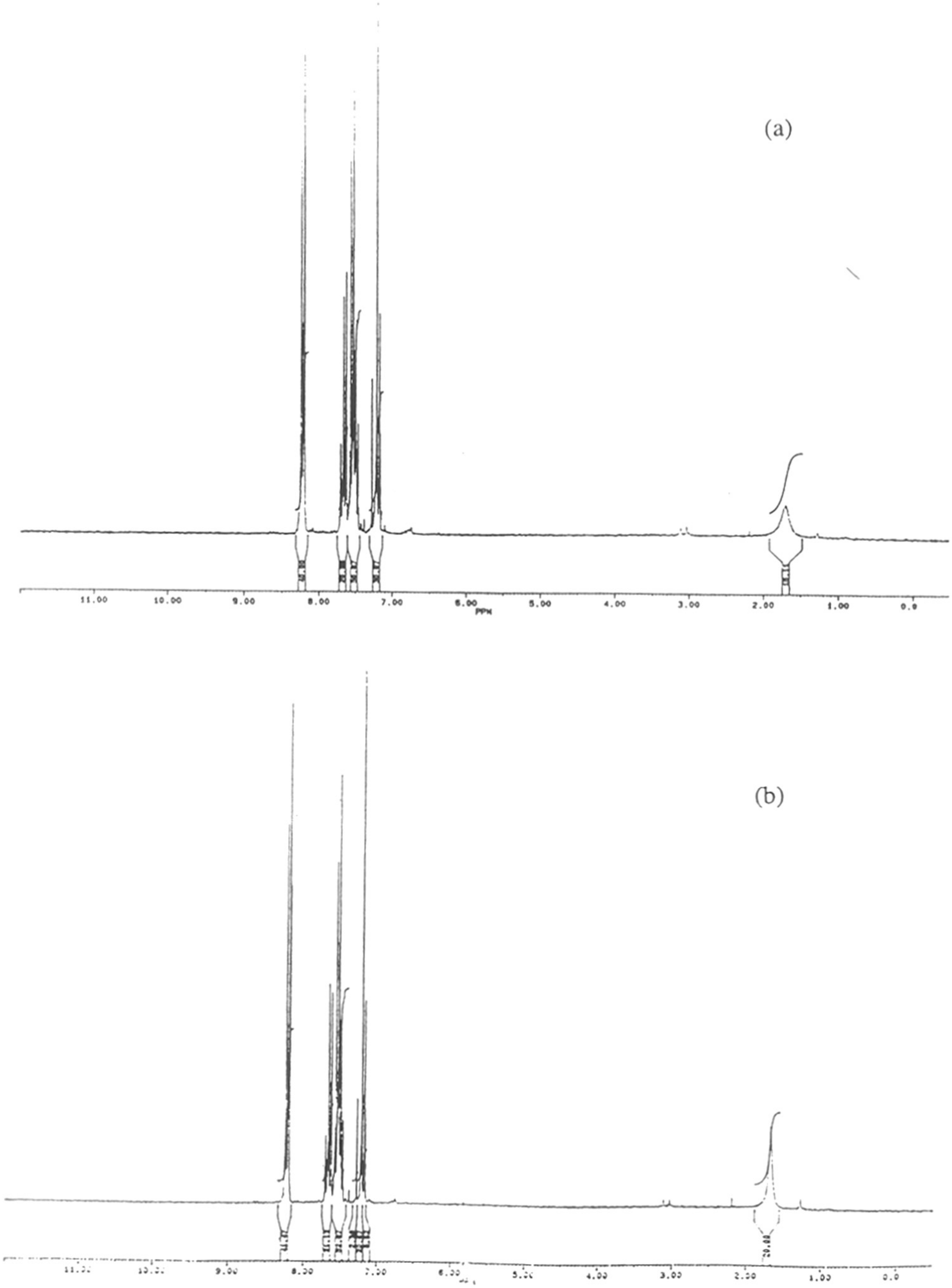
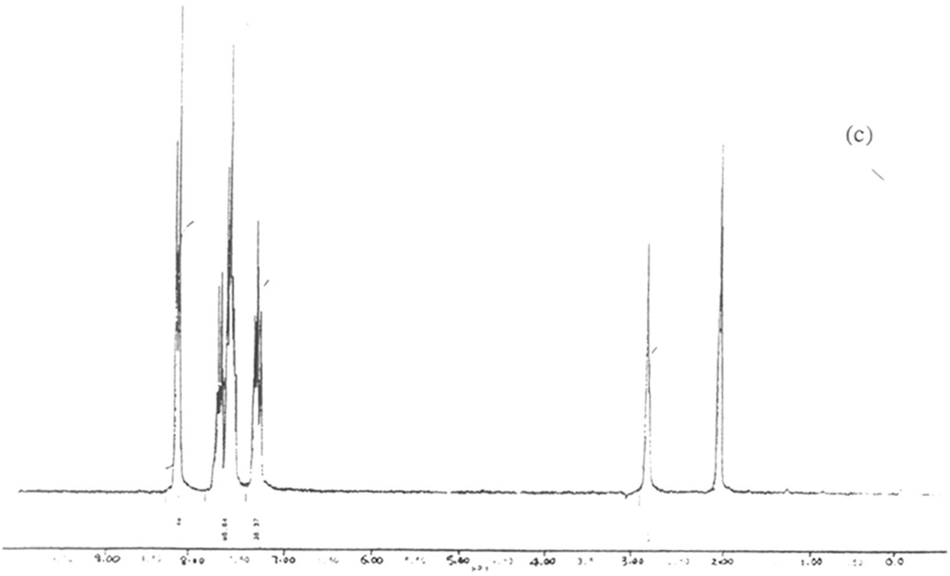


Fig. 4.7 : ^{1}H NMR spectra of the diester obtained from Res (a) after treatment A and (b) after treatment B.



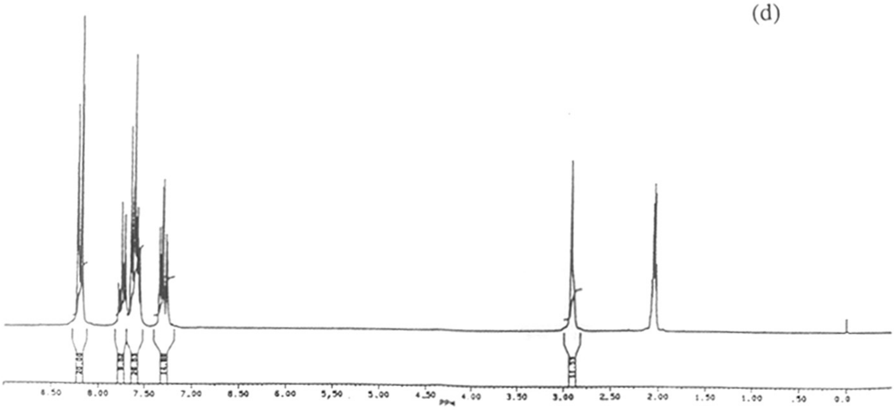


Fig. 4.7 : ^{1}H NMR spectra of the diester obtained from Res (c) after treatment C and (d) untreated.

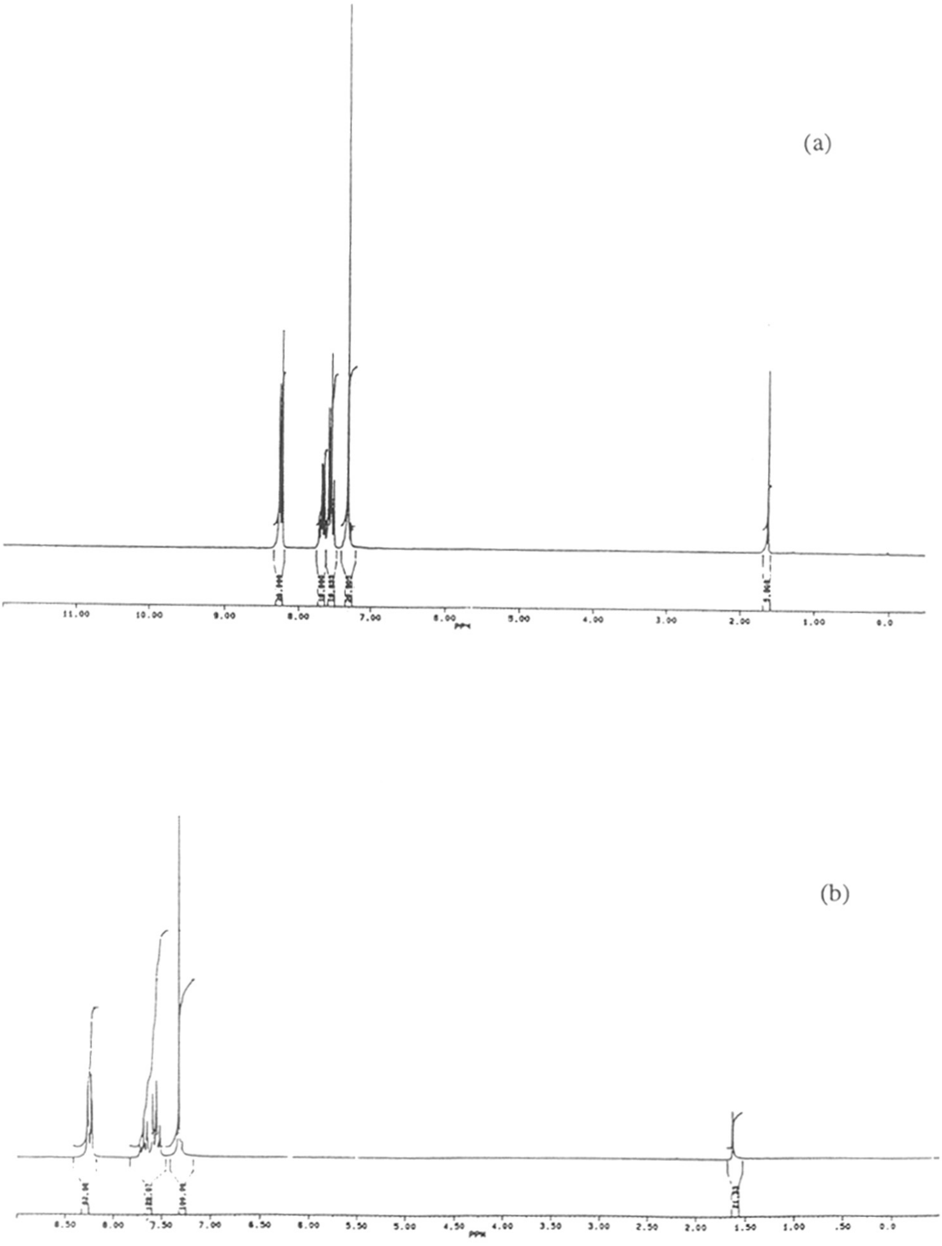


Fig. 4.8 : ^{1}H NMR spectra of the diester obtained from HQ (a) after treatment A and (b) after treatment B.

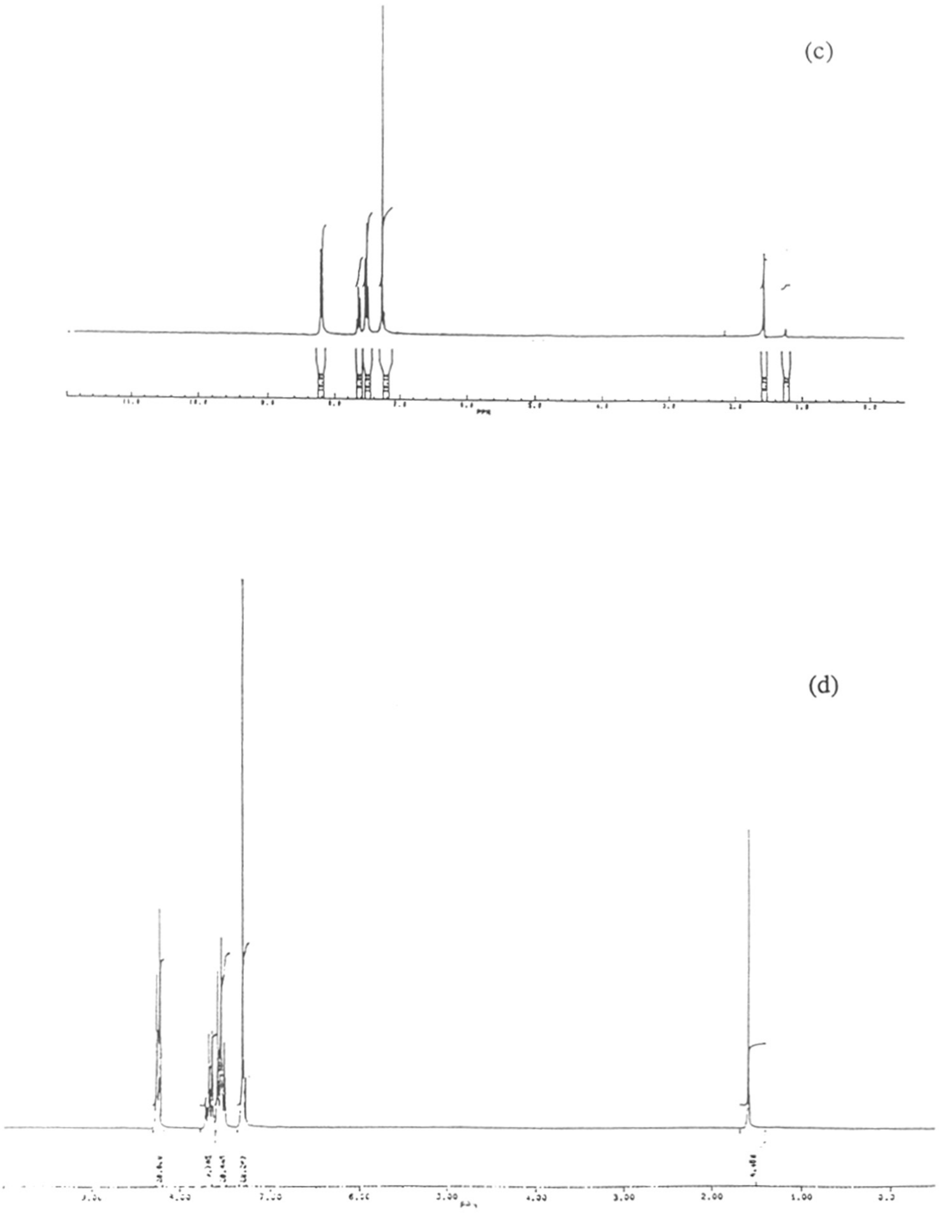


Fig. 4.8 : ^{1}H NMR spectra of the diester obtained from HQ (c) after treatment C and (d) untreated.

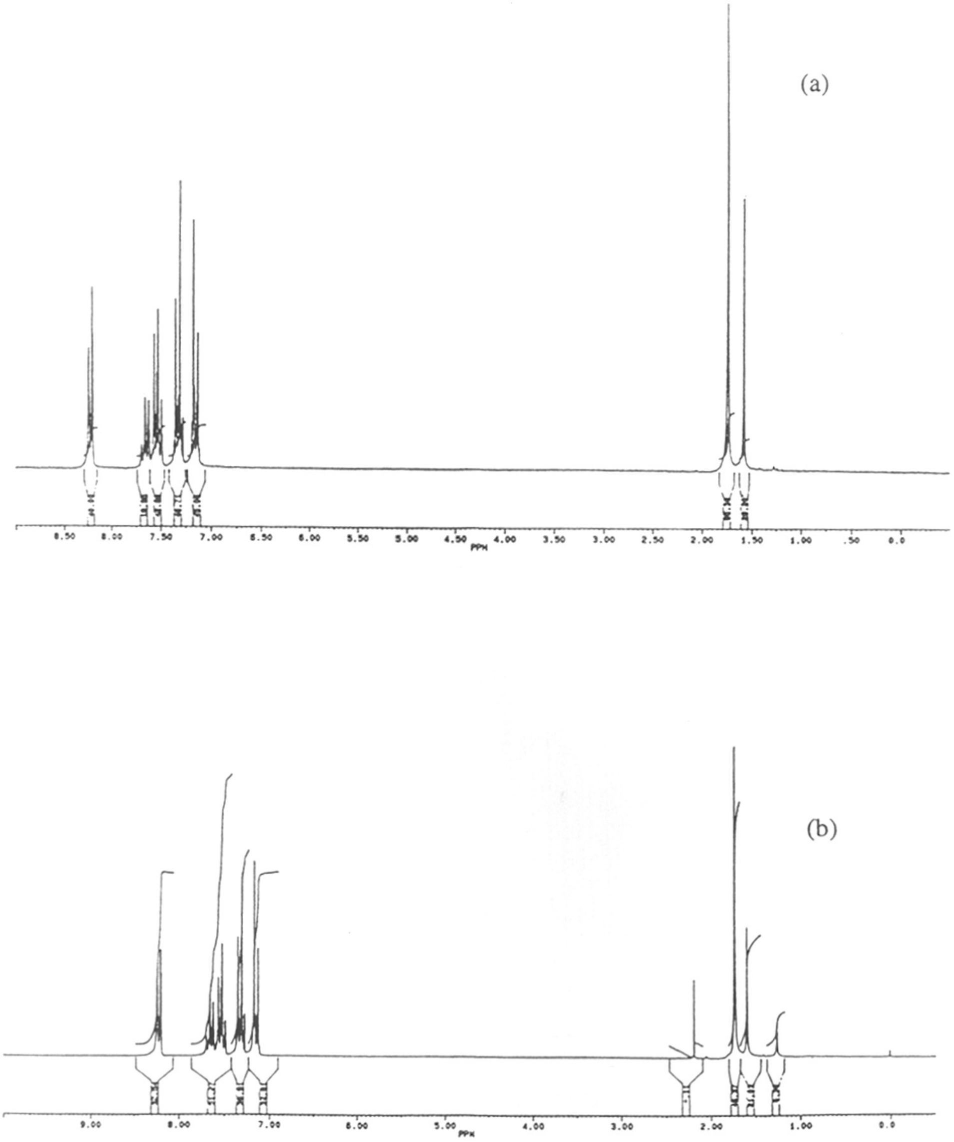


Fig. 4.9 : ^{1}H NMR spectra of the diester obtained from Bis-A (a) after treatment A and (b) after treatment B.

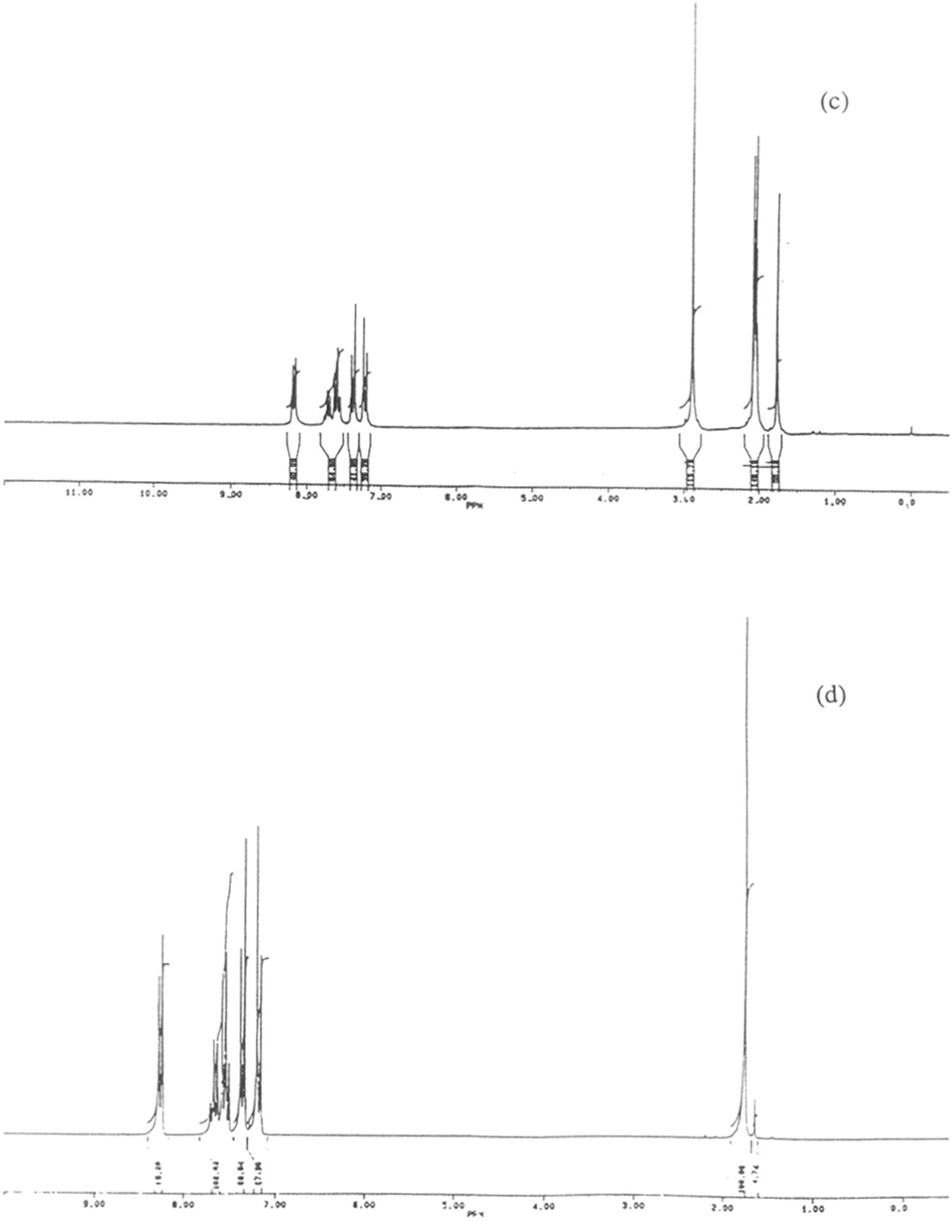


Fig. 4.9 : ^{1}H NMR spectra of the diester obtained from Bis-A (c) after treatment C and (d) untreated.

4.3.5 Esteramide Formed from *m*-AP

The NMR spectra shown in Figs. 4.10d and 4.10a for the untreated as well as the sample subjected to treatment A are similar. The amide signal is observed at ~9.75δ. In accordance with the NMR results, the melting point for treatment A also did not show any change.

The sample subjected to treatment B (Fig. 4.10b) showed the emergence of new signals while the sample subjected to treatment C (Fig. 4.10c) was affected to the extent that the presence of the starting material was absent. This increase in chlorination levels with treatments B and C is shown by the progressive development of new sets of signals especially at ~8.36δ, ~8.27δ, ~7.8δ. These spectra show the presence of three singlets at ~8.4δ, ~7.8δ and ~7.6δ respectively which were previously not observed in Figs. 4.10d and 4.10a. In addition, the spectra depicted in Fig. 4.10c shows the disappearance of signals at ~7.05δ and ~7.95δ (triplet), apart from many other minor changes. The -NH- signal in case of the sample subjected to treatment C could not be located properly in this spectra due to the exchange between the water present in acetone-d6, which was used as the solvent for recording the NMR spectrum. The water peak was too broad to be detected at the normal amplification employed.

The presence of two singlets at ~8.4δ and ~7.6δ is one of the interesting features of the proton spectrum of the samples subjected to treatment C. Such a possibility can exist only when chlorination takes place at the positions ortho and para to the amide function as is shown in Structure 4.1a. This seems to be the major product. The other minor signals are arising mostly due to the monochloro- and other dichloro-derivatives which are very difficult to identify from this proton spectrum alone. The presence of yet

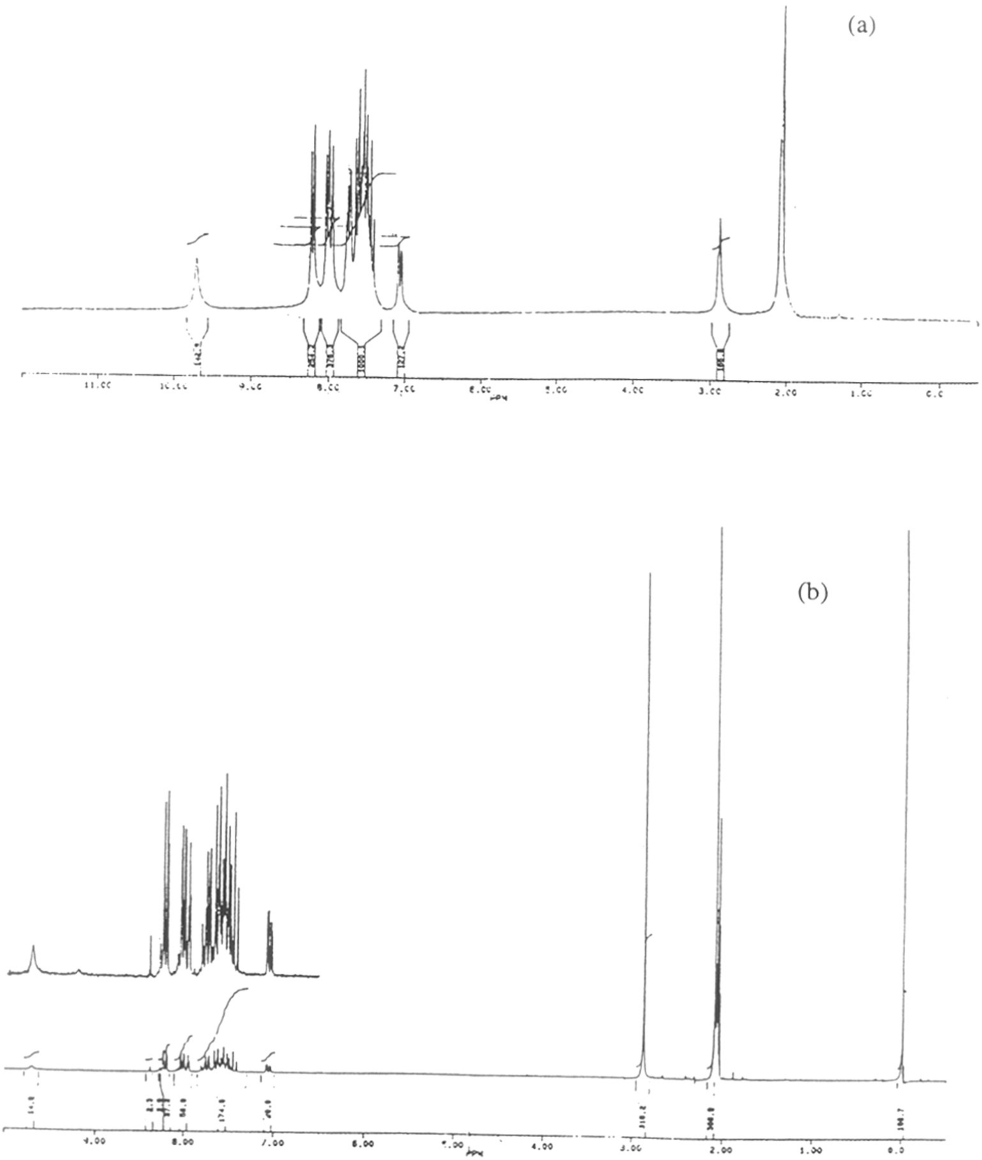


Fig. 4.10 : ^{1}H NMR spectra of the esteramide obtained from *m*-AP (a) after treatment A and (b) after treatment B.

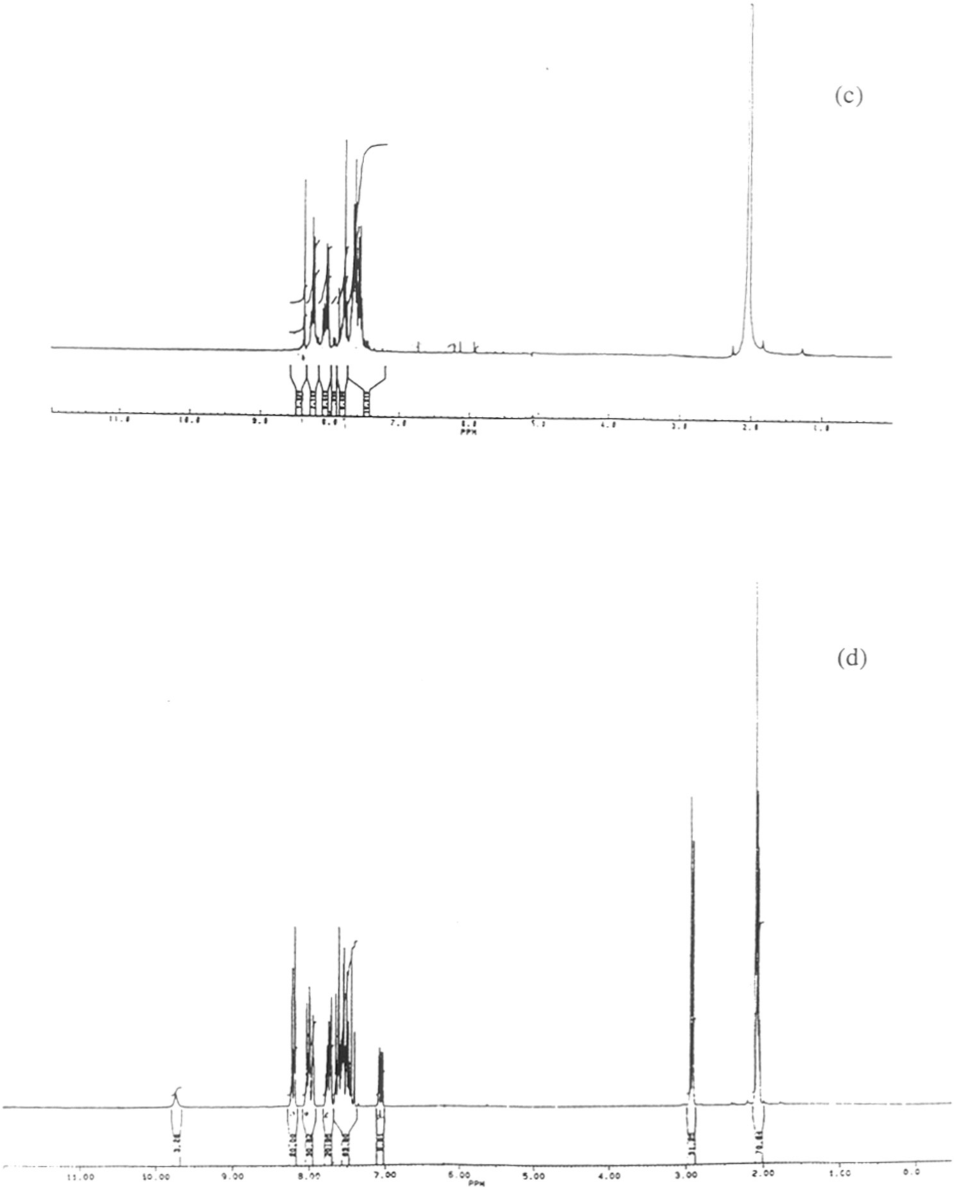
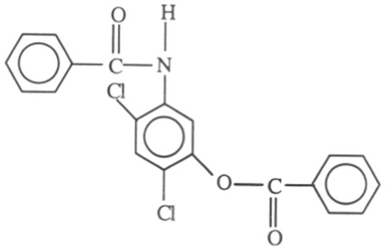
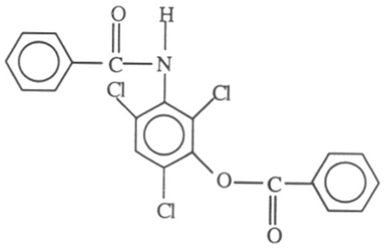


Fig. 4.10 : ^{1}H NMR spectra of the esteramide obtained from *m*-AP (c) after treatment C and (d) untreated.



Structure 4.1a : Dichlorinated adduct



Structure 4.1b : Trichlorinated adduct

another singlet at ~7.87δ is most likely arising from a trichloro-derivative as shown in Structure 4.1b. We thus conclude that treatments B and C have resulted in a dichloro-derivative as one of the major products along with some trichloro-derivative. The other minor signals could be arising from other monochloro- and dichloro-derivatives.

4.3.6 Esteramide Formed from *p*-AP

The proton NMR spectrum for the untreated adduct is shown in Fig. 4.11d in which the amide signal is observed at ~9.7δ. The expanded aromatic region for the untreated sample and the samples subjected to treatments A, B and C are also represented in Fig. 4.12. The spectrum shown in Fig. 4.11a for the sample subjected to treatment A shows the emergence of a minor signal in the amide -NH- (~9δ - 10δ) as well as the aromatic region at ~7.36δ and ~8.1δ. These minor signals in sample exposed to treatment A increase in intensity as seen in Figs. 4.11b and 4.11c respectively for the samples subjected to treatments B and C respectively. The signal due to the parent compound has completely disappeared as observed in Fig. 4.11c. Similar changes are also noticed in the amide i.e. -NH- region. The spectrum shown Fig. 4.11c for the sample subjected to treatment C showed two amide protons at ~9.18δ and ~9.53δ which are different from the parent compound (seen at ~9.7δ in Fig. 4.11d). The other noticeable features are the disappearance of the signal at 7.95δ, appearance of a doublet of doublet at ~7.38δ and the build up of a sharp signal at ~7.65δ.

The changes observed in the aromatic proton signals clearly show that the system is undergoing ring chlorination. Similarly, changes are also noticed in the -NH- region. The complex nature of the proton NMR spectrum of the chlorine treated sample suggests

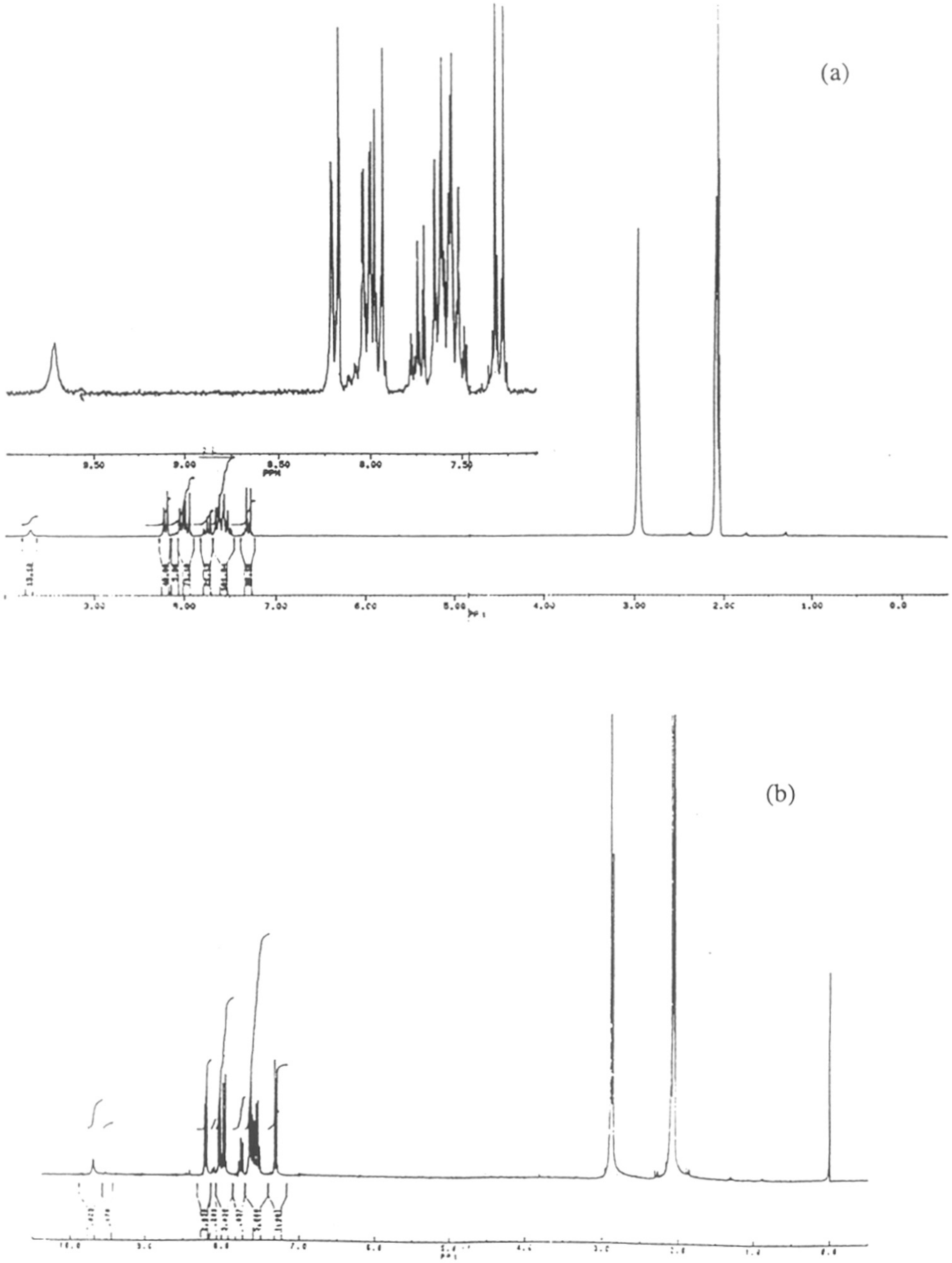


Fig. 4.11 : ^{1}H NMR spectra of the esteramide obtained from *p*-AP (a) after treatment A and (b) after treatment B.

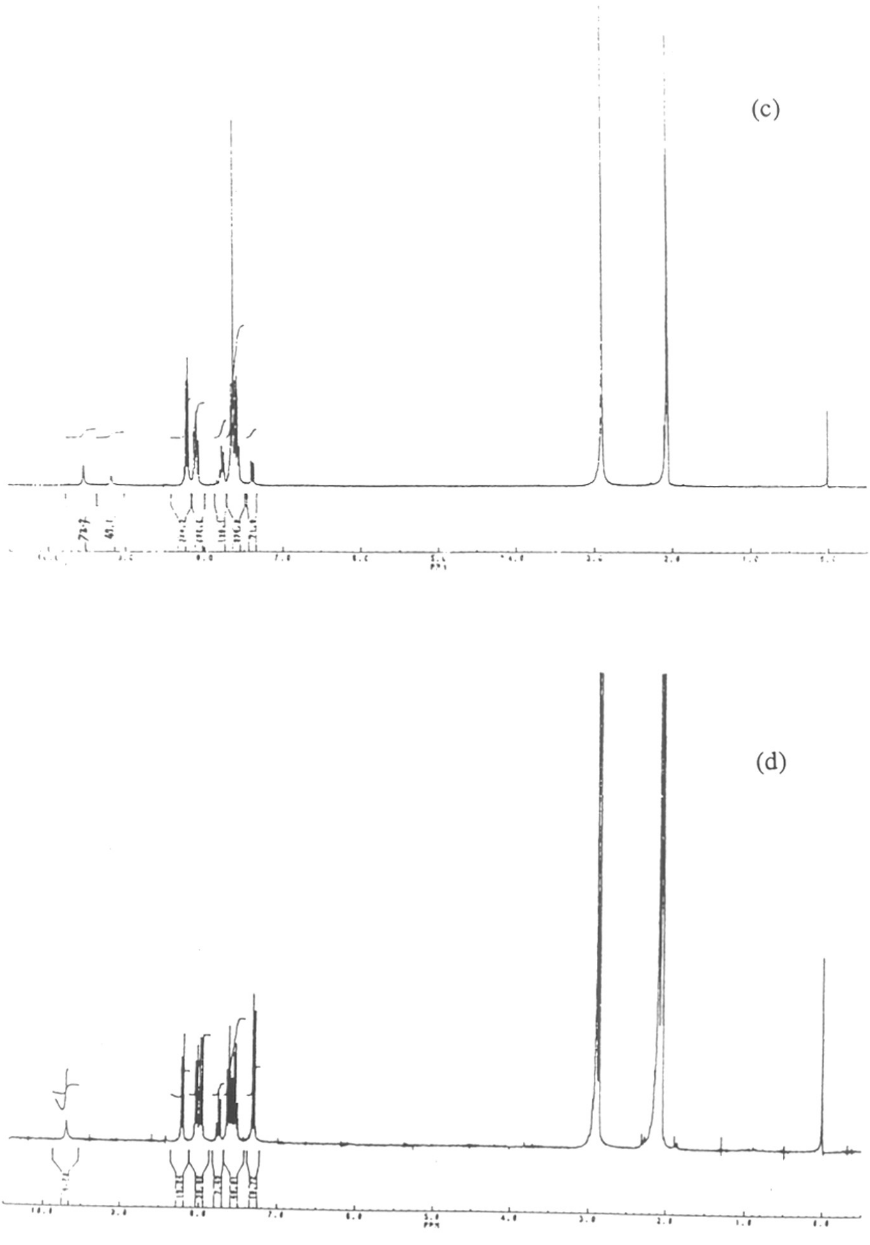


Fig. 4.11 : ^{1}H NMR spectra of the esteramide obtained from *p*-AP (c) after treatment C and (d) untreated.

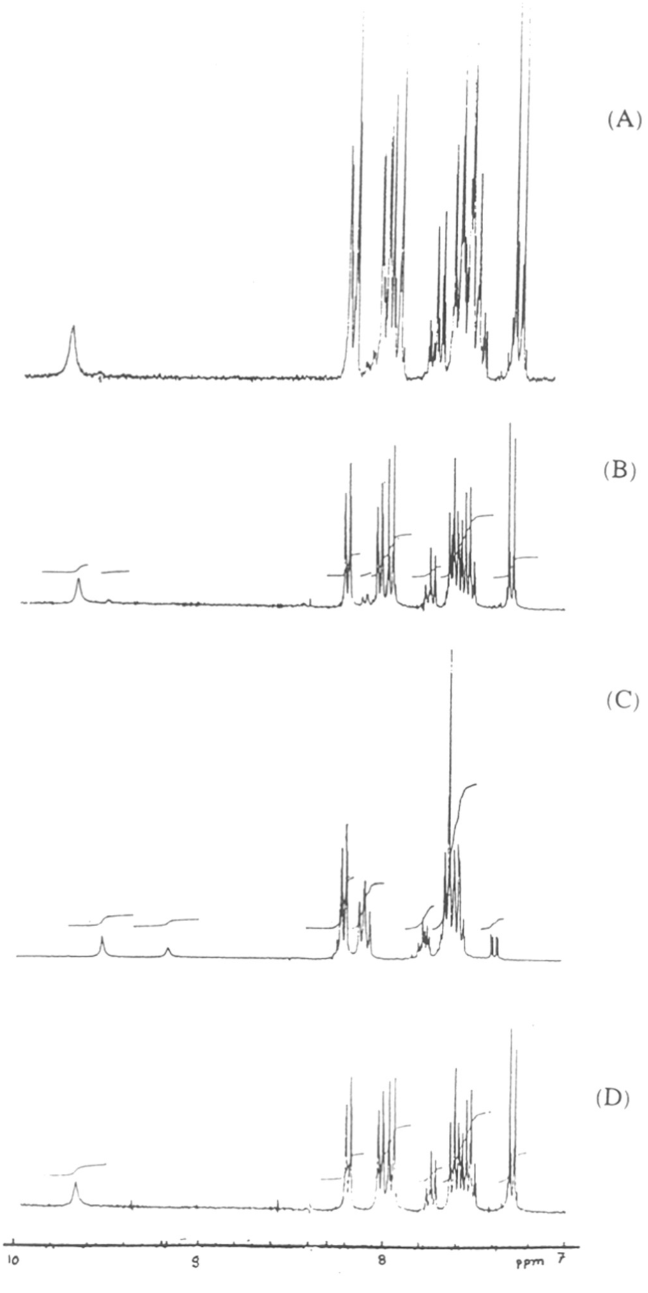


Fig. 4.12 : ^{1}H NMR spectra of the expanded aromatic region (7 -10δ) corresponding to the various treatment levels for the esteramide obtained from *p*-AP.

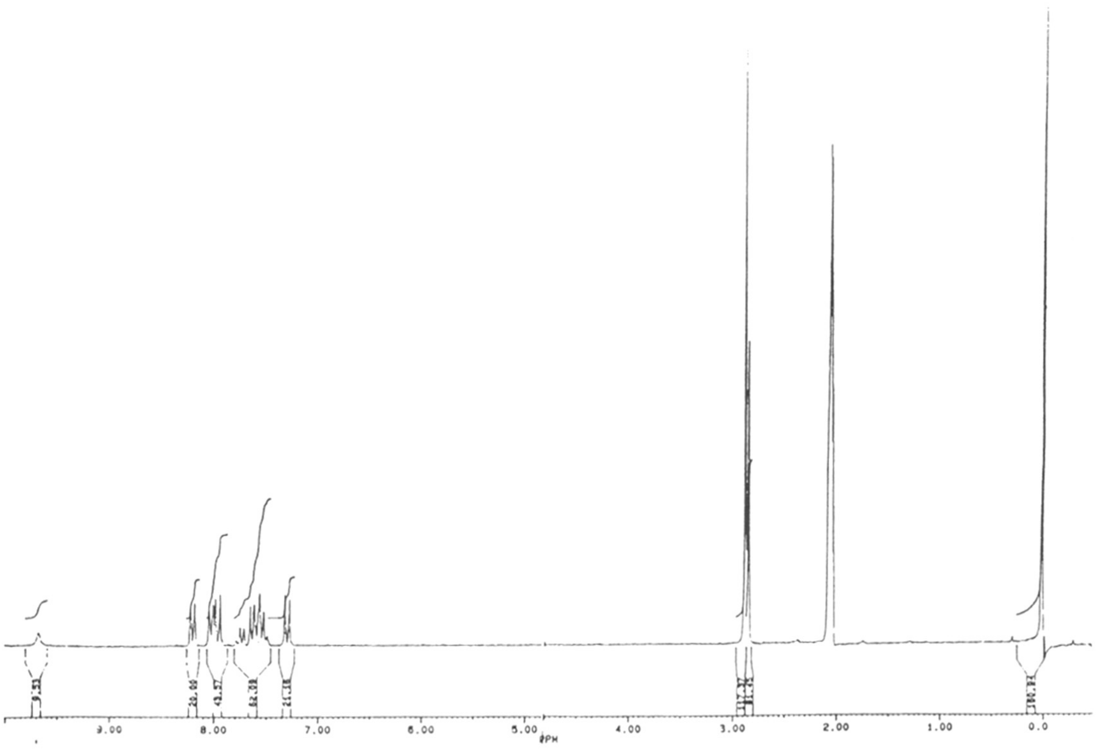


Fig. 4.13 : ^{1}H NMR spectra of the esteramide obtained from *p*-AP after water treatment.

the formation of more than one product. Moreover, the appearance of two amide proton signals (Fig. 4.11c) seem to suggest the presence of at least two chlorinated compounds which vary in proportion. Since the assignments of the proton spectrum was not straight forward, a 2D COSY study was carried out on the untreated sample and the sample subjected to treatment C. The 2D COSY spectra are presented in Figs. 4.14 (for untreated adduct) and 4.15 (for the sample subjected to treatment C). The description of the proton signals for the sample subjected to treatment C is presented in Table 8 (Appendix 2).

From the 2D COSY spectrum for the untreated adduct, shown in Fig. 4.14, it is evident that the signal at ~8.2δ (H_a) shows correlations with those at 7.75δ (H_c) and at 7.6δ (H_d). This refers to the coupling between the benzoyl ring protons at the ester group. Further the signal at 8.0δ (H_b) shows correlations with those at 7.6δ (H_d) and at 7.3δ (H_e). This indicates coupling between the H_b and H_d protons in the benzoyl ring at the amide group and that between the H_b and H_e protons on the amine phenyl ring in the adduct (see Table 7 - Appendix 2 for the untreated esteramide formed from *p*-AP).

The 2D COSY spectrum for the sample subjected to treatment C shown in Fig. 4.15 showed unambiguous assignments of the complex partners. The proton coupling is discussed below with reference to proposed chlorinated structures shown in Table 8 (Appendix 2) :

(i) The doublet of doublet at ~7.38δ (H_e) showed correlations to signals at ~7.6δ (H_d) and ~8.2δ (H_a). This clearly suggests that the signal is arising from an ortho and meta coupling and such a possibility arises only in the monochlorinated compound (see Table 8 - Appendix 2 - for monochlorinated structure).

(ii) The sharp signal at ~7.64δ (H_d) did not show any coupling to other protons. Hence,

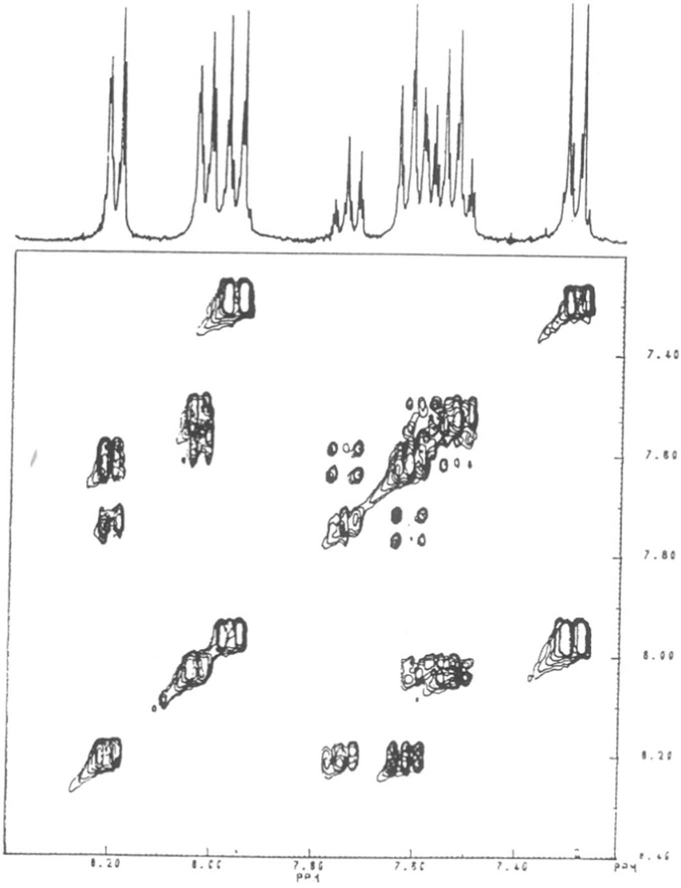


Fig. 4.14 : COSY spectra of the esteramide obtained from *p*-AP (untreated).

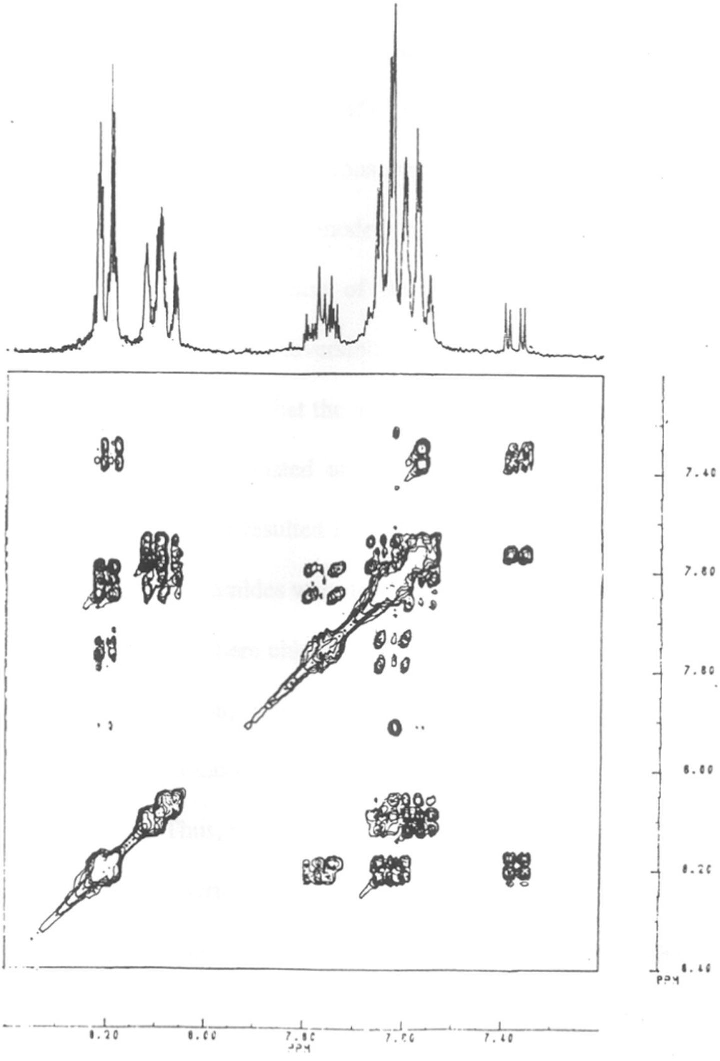


Fig. 4.15 : COSY spectra of the esteramide obtained from *p*-AP after subjection to treatment C.

this can be assigned to the ring protons of the dichloro-derivative (see Table 8 - Appendix 2 - for dichlorinated structure) in which both the protons are likely to be equivalent.

(iii) Ring chlorination also affects the chemical shift of the benzoyl ring protons. These changes are especially seen on the ortho protons on the benzoyl ring attached to the amide part. These protons appear at the signal ~8.1δ (H_b). The protons at signal ~8.1δ (H_b) showed correlations with that at ~7.6δ (H_d). This indicates a coupling between the protons in the benzoyl ring at the amide group.

(iv) The signal at 8.2δ (H_a) shows correlations with those at 7.75δ (H_c)and at 7.6δ (H_d). This is consistent with the coupling between the benzoyl ring protons at the ester group.

Considering the coupling assignments, the product formed in case of the sample subjected to treatment C can be identified as a mixture of the monochloro- and the dichloro-derivatives. An approximate estimation of their relative composition can be obtained from the integration of the amide peaks. This estimation shows that the esteramide formed from *p*-AP exposed to treatment C consists of ~40% dichloro-derivative and ~60% monochloro-derivative.

4.4 DIAMIDE CHLORINATION : MECHANISM AND EFFECT OF SUBSTITUTION PATTERN

As discussed in chapter two section 2.5.2, ring chlorination can take place through either direct chlorination or by ring chlorination via Orton rearrangement. The dominance of the second possibility has been suggested by Kawaguchi and Tamura (1984) who performed chlorine resistance tests on three model compounds : N-methylbenzanilide, N-phenylbenzanilide and benzanilide. Only benzanilide could be chlorinated at the aromatic nucleus whereas the amides from secondary amines gave no reaction product. These reactions strongly support Orton's theory thereby suggesting that direct chlorination at the aromatic nucleus is much less feasible and via N-chlorination scheme seems to be more practical. This is further supported by the study by Kawaguchi and Tamura (1984) which also included the interaction of hypochlorous acid with various polyamides that contained different alkyl and aryl groups. The modes of interaction were classified into three categories : 1) no reaction in the case of tertiary polyamides, 2) reversible chlorination at the amide nitrogen and 3) irreversible aromatic ring chlorination. Based on their experimental results it was shown that the aromatic primary diamines resulted in polyamides that were irreversibly chlorinated at the aromatic nucleus. The aliphatic primary diamines gave polyamides that resulted in N-chloro derivatives which could be easily dechlorinated. The tertiary polyamides were found to be inactive towards chlorine.

In all instances in this study where chlorination is detected by a macroscopic test such as melting point determination, ring chlorination is also detected by NMR spectroscopy. The ring chlorination has consistently occurred at the positions either *o*- or *p*- or both to the amide function. Thus, in this study too, the overall results are consistent with N-chlorination followed by Orton rearrangement, even though N-chloro amide formation could not be specifically detected by the NMR studies. This may be due to the fact that the N-chloro amides have limited stability. Thus, the results indicate a reaction mechanism that involves N-chlorination which is followed by molecular rearrangement via Orton rearrangement to yield a irreversibly chlorinated ring.

The chlorine resistance of a particular class of adducts is thus greatly influenced by the substitution pattern. The fact that the diamide obtained from *o*-PDA could not be chlorinated even on treatment C may be due to steric hindrance at the -NH- position or possible hydrogen bonding between the amide proton and carbonyl group. This effect is consistent with the above postulated reaction mechanism. Since N-chlorination is difficult for the diamide formed from *o*-PDA, no aromatic ring chlorination is observed. The adduct obtained from *o*-PDA was as resistant to chlorination as the diesters.

The diamide formed from *p*-PDA showed less extent of chlorination than that formed from *m*-PDA. Neither of the diamides obtained from *m*- or *p*-PDA showed any changes at the lower chlorine severity conditions (treatments A and B). With treatment C, the diamide obtained from *m*-PDA was chlorinated completely with no trace of the starting compound, while that formed from *p*-PDA showed a major portion of adduct that remained unchlorinated along with smaller fractions of monochloro- or dichloro-derivatives. This could be explained on the basis that in the diamide formed from *m*-PDA each ortho and para position is doubly activated by both the -NH- groups. It is known that the -NH- group is a ring activating ortho-para director (March 1992). This may be the reason for the formation of a trichlorinated product as a major product in this case. By contrast, in case of the diamide formed from *p*-PDA, each position is only singly activated by the -NH- group. This would then explain the lower extent of chlorination for the diamide formed from *p*-PDA as compared to that formed from *m*-PDA. In conclusion, the diamides have shown the following increasing order of chlorine reactivity :

diamide formed from *o*-PDA < diamide formed from *p*-PDA < diamide formed from *m*-PDA diamide.

The above remarks regarding the ortho-para directing nature of the -NH- functionality and the steric hindrance at the ortho position, which thereby affects the chorine sensitivity of the adducts formed from *o*-PDA, *m*-PDA and *p*-PDA are in good agreement with ^{1}H NMR studies performed by Kawaguchi and Tamura (1984) with poly(*m*-phenyleneisophthalamide). Initially, chlorination took place at the para-position on the activated ring. The second chlorine atom was then added to the ortho position of this ring. This result could be explained by the fact that each para position in this case is doubly activated by two -NH- groups. Though the ortho position is also doubly activated it may be less vulnerable to chlorine attack due to steric hindrance. No chlorination was observed on the ring attached directly to the -C=O group.

4.5 COMPARISON OF THE SUSCEPTIBILITY OF ESTER AND AMIDE FUNCTIONALITIES TO CHLORINATION

In the present study, no chlorination is observed on the rings attached directly to the -C=O group in case of any of the adducts. None of the diester based adducts could be chlorinated even at the more severe chlorination conditions (treatment C). All the diesters showed similarly high levels of chlorine tolerance. Thus it was not possible to differentiate between the substitution pattern (comparison of diesters formed using HQ and Res) or the effect of the bridge aliphatic carbon in the case of Bis-A.

While, the diesters showed the highest level of chlorine tolerance, the esteramides showed a relatively lower degree of chlorine tolerance. In fact, the esteramides showed an even lower degree of chlorine tolerance than the diamides. Upon chlorination both the esteramides underwent ring chlorination. Both NMR and melting point data showed that the esteramide obtained from *p*-AP was affected even at the mildest chlorination conditions (treatment A) where no change was observed with the esteramide formed from *m*-AP. Both the esteramides are susceptible when exposed to more severe chlorination; the extent of chlorination is more with the esteramide formed from *m*-AP than that formed from *p*-AP. In case of the esteramide obtained from *m*-AP the formation of a dichloro- and a trichloro-derivative is attributed to the two ortho and one para position that are activated by the -NH- group. Thus, the chances of formation of mixed chlorinated products is increased. In case of the esteramide obtained from *p*-AP, only the two positions ortho to the -NH- group are activated. This leads to the formation of only monochloro- or dichloro-derivatives. From the NMR and COSY data presented for the esteramide obtained from *p*-AP subjected to treatment C, we have confirmed the presence of mixed monochloro- and dichloro-derivatives.

As mentioned above, while both diamides (except for that formed from *o*-PDA) and esteramides are susceptible to chlorination, all the diesters resisted chlorination even on most severe conditions (treatment C). The lack of chlorine attack in the case of the diesters and the susceptibility in case of esteramides also supports the reaction mechanism in which chlorine attack in the case of diamides takes place via the N-chlorination scheme proposed by Orton.

While, the diesters showed the highest level of chlorine tolerance, the esteramides showed an even lower degree of chlorine tolerance than the diamides. Both *p*- and *m*-AP based adducts showed more chlorine sensitivity than the corresponding diamides. It thus appears that if both ester and amide functions are present on the same ring, the activating ortho-para directing effect of the -NH- group predominates.

CHAPTER 5

TFC MEMBRANE STUDY : RESULTS AND DISCUSSION

This chapter discusses the performance of various polyesteramide and polyamide TFC membranes which were synthesized and characterized as described in chapter 3. All membranes were tested for RO performance using either salt or mixed NaCl/sucrose solutions. In most cases, the tests were conducted at 2.76 MPa using a feed solution comprising of 2000 ppm NaCl in addition to 5% sucrose. In cases where the sucrose rejections are not reported, the feed solution comprised of only 2000 ppm NaCl. The results are discussed in terms of the water and solute permeabilities as defined in equations. 1.2 and 1.4 (see chapter one). The results obtained with selected membranes in a chlorine tolerance study using 200 ppm chlorine concentration at pH = 6 - 6.5 are also discussed.

In this chapter, the RO performance results with the various polyesteramide and novel polyamide TFC membranes are first compared with that of the standard polyamide membrane based on *m*-PDA/TMC. The chlorine tolerance of selected polyesteramide membranes are then compared using the standard polyamide membrane as the reference.

5.1 STANDARD POLYAMIDE MEMBRANE : TFC MEMBRANES FORMED FROM THE REACTION OF TMC WITH *m*-PDA

The fabrication parameters and RO performance data for membranes obtained by the reaction of *m*-PDA with the acid chloride TMC are listed in Table 9 (Appendix 2). The aqueous dip times are maintained at one minute while the dip times in the organic phase were maintained at 30 sec.. The polyamide membranes so synthesized exhibited salt permeability coefficient values ranging from 0.07 - 0.3 x 10^{-6} m/s corresponding to salt rejections varying from 98 - 91%. The water permeability coefficient for these membranes ranged from a high of 3.7 x 10^{-6} to a low of 1.4 x 10^{-6} m/s-MPa corresponding to water fluxes in the range of 34 - 12 lmh at 2.76 MPa for 2000 ppm NaCl. The scatter in the data is indicative of defects in individual samples arising from either the PSF membrane casting or TFC hand coating procedures. In agreement with literature data, the target performance of these membranes can be taken as having a water permeability of 3 x 10^{-6} m/s-MPa and salt permeability of 0.1 m/s. The sucrose permeability is negligible. These membranes are used as a reference to compare the performances of the new polyesteramide and novel polyamide TFC membranes.

In case of membranes with nanofiltration potential, a reference comparison can be made with reported data for commercial nanofiltration membranes e.g. ESNA (Hydranautics), NF-40 and NF-70 membranes (FilmTec) (see section 2.4). These membranes are known to be anionically charged and hence it is primarily the anion repulsion that determines salt rejection. The water and salt permeability coefficient values for some of these commercial NF membranes have been tabulated in Table 1 (Appendix 1).

5.2 POLYESTERAMIDE TFC MEMBRANES

5.2.1 Polyesteramide TFC Membranes Based on *m*-AP and *m*-AP : *m*-PDA

TFC membranes formed from the reaction of TMC with varying compositions of *m*-AP : *m*-PDA are discussed in this section. The fabrication parameters and RO performance data for TFC membranes prepared in this section are listed in Table 10a-i

(Appendix 2).

5.2.1.1 TFC membranes formed from the reaction of TMC with *m*-AP alone

Table 10a lists the membranes formed from the reaction of TMC with *m*-AP alone. The membranes prepared in this way gave high fluxes and poor salt as well as sucrose rejections. Varying the dip time did not improve the membrane performance.

5.2.1.2 TFC membranes formed from the reaction of TMC with 90:10 *m*-AP : *m*-PDA

Table 10b lists the fabrication parameters and RO performance data for TFC membranes prepared from a 90:10 *m*-AP : *m*-PDA composition using TMC as the acid chloride. The water and salt permeability coefficients for this system are high. The water permeability coefficients were in the range of 10 - 12 x 10^{-6} m/s-MPa while the salt permeability coefficients are also high, ranging from 10 - 34 x 10^{-6} m/s. In comparison, the sucrose permeability coefficients were lower by an order of magnitude (~1.8 - 2.8 x 10^{-6} m/s), thus indicating that this membrane could be used to separate organics from monovalent salts. Increasing the dip time decreased the permeabilities of both solutes while the water permeability was relatively unaffected. Increasing the curing temperature resulted in poorer membrane separation properties.

5.2.1.3 TFC membranes formed from the reaction of TMC with 80:20 *m*-AP : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes obtained from a 80:20 *m*-AP : *m*-PDA composition are listed in Table 10c. This system exhibited overall lower permeabilities for water as well as both salt and sucrose. The difference in permeability coefficients for sucrose over salt is also considerably reduced compared to the 90:10 *m*-AP : *m*-PDA system. The lowest solute permeabilities for this system were obtained at a 30 sec. dip time in the organic phase.

A surfactant such as SLS was tried in order to determine whether the salt rejections for this system could be improved further. The resultant membranes are listed in Table 10d. SLS addition resulted in drastically decreased permeabilities. Though the salt and sucrose permeabilities are now comparable to the standard polyamide membrane, the water permeability is less by 10x. Increasing the curing temperature from 45°C to 69°C as well as increasing the dip time in the organic phase yielded membranes with poorer salt rejections.

5.2.1.4 TFC membranes formed from the reaction of TMC with 70:30 *m*-AP : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from a 70:30 *m*-AP : *m*-PDA composition are listed in Table 10e. This system yielded membranes with generally high permeabilities. The best results were obtained for the membrane formed with a 60 sec. dip time in the organic phase which exhibited the lowest salt and sucrose permeability coefficient values of 0.6×10^{-6} m/s and zero respectively, (corresponding to rejections of 91.4% for salt and 100% for sucrose) combined with a water permeability of 3.1×10^{-6} m/s-MPa (corresponding to a water flux of 25.5 lmh). Both lower as well as higher dip times than 60 sec. gave membranes with poorer separation characteristics.

From Table 10f it is observed that addition of SLS to this system causes all the permeability coefficients to decrease by 2x. Thus, there is no significant effect on the separation ability of the membrane to compensate for the loss in water flux.

5.2.1.5 TFC membranes formed from the reaction of TMC with 50:50 *m*-AP : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from a 50:50 *m*-AP : *m*-PDA composition are listed in Table 10g. It appears that at various fabrication conditions, this system can yield TFC membranes with similar solute permeabilities as the standard polyamide membrane but with 1/3 of its water permeability. The salt permeability coefficient values for this particular system range from 0.04 - 0.6 x 10^{-6} m/s with negligible permeability for sucrose. In certain instances, much higher salt permeabilities are reported and these result probably from minor defects in the support membrane structure. For example, a 10 sec. dip time in the organic phase resulted in a membrane with a salt permeability of 0.13 x 10^{-6} m/s and sucrose permeability coefficient values of zero corresponding to 93 - 94% salt rejection values and 100% sucrose rejection respectively. The water permeability coefficient values for this membrane ranged from 0.7 - 0.9 x 10^{-6} m/s-MPa corresponding to a water flux of 6 - 7 lmh. Similar data could be obtained at other dip times as well. This membrane can be made with lower overall permeabilities; however, this does not improve the separation ability significantly.

The data for membranes obtained with the addition of SLS to this system are listed in Table 10h. These membranes were tested only with NaCl solutions. At low dip times (15 - 30 sec.), the addition of SLS results in membranes with higher water and salt permeabilities. Thus, while the water permeability approaches that of the standard polyamide membrane, the salt permeability is 2 - 3x higher. At higher dip times (45 - 60 sec.), the membrane permeabilities resemble the previous results shown in Table 10g.

5.2.1.6 TFC membranes formed from the reaction of TMC with 30:70 *m*-AP : *m*-PDA

Data for membranes formed from the reaction of TMC with 30:70 *m*-AP : *m*-PDA are listed in Table 10i. All these membranes exhibited low salt permeabilities. The salt permeabilities and rejections compare favorably with the standard polyamide membrane; however, the water permeability is 2 - 3x lower. Both water and salt permeabilities show an overall decreasing trend with increasing dip times.

5.2.2 Polyesteramide TFC Membranes Based on Bis-A : *m*-PDA

Tables 11a-d (Appendix 2) list data for the membranes formed from the reaction of TMC with varying compositions of Bis-A : *m*-PDA. Membranes formed from the reaction of Bis-A alone with TMC as well as those formed from 90:10 Bis-A : *m*-PDA gave negligible salt and sucrose rejections. These are therefore not listed here.

5.2.2.1 TFC membranes formed from the reaction of TMC with 80:20 Bis-A : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from a 80:20 Bis-A : *m*-PDA compositions are listed in Table 11a. The water permeability of these membranes is similar to the standard polyamide membrane; however, the salt permeability is an order of magnitude higher. The decreasing passage of sucrose with increasing dip times may indicate the decreasing number of defects in the TFC membrane as a result of increasing the dip time. At high dip time of 60 sec., the membrane exhibited salt and water permeabilities of 0.6 x 10^{-6} m/s and 2.3 x 10^{-6} m/s-MPa respectively combined with zero sucrose permeability. This formulation thus shows slight promise as a "loose" RO or NF membrane.

5.2.2.2 TFC membranes formed from the reaction of TMC with 70:30 Bis-A : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes obtained from a 70:30 Bis-A : *m*-PDA composition are listed in Table 11b. All these membranes reject sucrose completely. These membranes can be prepared to have similar permeabilities as the 80:20 Bis-A : *m*-PDA formulations listed in Table 11a. The membrane formed from a 15 sec. dip time in the organic phase exhibited salt and sucrose permeabilities of 0.2×10^{-6} m/s and zero corresponding to salt and sucrose rejections of 96% and 100% respectively. The water permeability of this membrane is 2.4×10^{-6} m/s-MPa corresponding to a water flux of 19.9 lmh. The effect of dip time is not as noticeable for this system as with the 80: 20 Bis-A : *m*-PDA composition; however, it appears that the 30 and 45 sec. dip times gave lower permeabilities than either the 15 or 60 sec. dip times in the organic phase.

5.2.2.3 TFC membranes formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from a 50:50 Bis-A : *m*-PDA composition have been listed in Table 11c. The data shows some scatter, which is attributable to membrane defects. On the whole, the RO characteristics are similar to those for the systems with higher Bis-A compositions i.e. sucrose is rejected completely and water permeabilities are similar to the standard polyamide membrane. The salt permeability and rejection also appear similar to the previous Bis-A systems discussed above. Because of the scatter in the data, no conclusions regarding dip times appears possible; however, it does not appear to be a major variable.

5.2.2.4 TFC membranes formed from the reaction of TMC with 30:70 Bis-A : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from a 30:70 Bis-A : *m*-PDA composition have been listed in Table 11d. Again, these membranes show RO characteristics similar to the other Bis-A compositions i.e. zero permeability for sucrose combined with relatively high permeabilities for both water and salt. The membrane formed from a 45 sec. dip time in the organic phase is particularly interesting as it showed the highest salt as well as water permeabilities of 1.5 x 10^{-6} m/s and 4.2 x 10^{-6} m/s-MPa respectively.

5.2.3 Polyesteramide TFC Membranes Based on HQ : *m*-PDA

The results for TFC membranes obtained from reacting TMC with varying compositions of HQ : *m*-PDA have been listed in Tables 12a-d (Appendix 2). Membranes obtained from the reaction of HQ alone with TMC and 90:10 HQ : *m*-PDA gave negligible salt and sucrose rejections and hence have not been listed here.

5.2.3.1 TFC membranes formed from the reaction of TMC with 80:20 HQ : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from an 80:20 HQ : *m*-PDA composition are listed in Table 12a. As was the case for the polyesteramide membranes based on Bis-A, all these membranes also show complete rejection of sucrose. The salt permeabilities for the membranes formed from 15 and 30 sec. dip times in the organic phase ranged from 0.4 - 0.5 x 10^{-6} m/s with high water permeabilities ranging from 2.7 - 2.3 x 10^{-6} m/s-MPa. While the membranes prepared at 45 sec. dip time show slightly higher salt permeability, the water permeability of all these membranes is comparable. A further increase in the dip time to 60 sec. resulted in the tightest membrane which exhibit the lowest salt permeability (~0.2 x 10^{-6} m/s) and highest rejection (95%) for this system, combined with a water permeability of 1.7 - 1.9 x 10^{-6} m/s-MPa, corresponding to a water flux of 14 - 15 lmh.

5.2.3.2 TFC membranes formed from the reaction of TMC with 70:30 HQ : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes obtained from a 70:30 HQ : *m*-PDA composition have been listed in Table 12b. With the exception of the membranes fabricated with 30 sec. dip time in the organic phase, all other membranes exhibited salt permeability coefficient values ranging from 0.1 - 0.2 x 10^{-6} m/s corresponding to salt rejection values of 95 - 96%. The water permeabilities for these membrane are also comparable to that of the standard polyamide membrane. All the membranes tested exhibited 100% sucrose rejections. While the salt rejection is slightly higher and the water permeability is slightly lower than that achievable with the best samples of the standard polyamide membrane, this promising data indicates that this system is worthy of further attention.

5.2.3.3 TFC membranes formed from the reaction of TMC with 50:50 HQ : *m*-PDA

The fabrication parameters and RO performance data for TFC membranes formed from 50:50 HQ : *m*-PDA composition are listed in Table 12c. The RO characteristics of this composition are similar to those obtained with the 70:30 HQ : *m*-PDA composition. Again, similar to previous cases, the highest salt permeabilities were obtained at intermediate dip times, while the dip times of 15 and 60 sec. in the organic phase gave the highest salt rejections. The salt permeability of this membrane can be comparable to that of the standard polyamide membrane while the water permeability is 70% of the best values for the standard. In all cases, the membrane rejects sucrose completely.

5.2.3.4 TFC membranes formed from the reaction of TMC with 25:75 HQ : *m*-PDA

The data for membranes formed from a 25:75 HQ : *m*-PDA composition are listed in Table 12d. These membranes were tested only with salt solutions. These membranes all have salt permeabilities less than 0.1 x 10^{-6} m/s while the water permeability is 1/3 that of the standard polyamide membrane. As the dip time in the organic phase is increased, the salt permeability decreases and rejection increases up to 98%. The water permeability is not significantly affected by the increasing dip time.

5.3 NOVEL POLYAMIDE TFC MEMBRANES

Membranes based on 1,5-naphthalene diamine and 2,6-diaminopyridine are discussed in this section.

5.3.1 Polyamide TFC Membranes Based on 1,5-Naphthalene Diamine

The fabrication parameters and RO performance data for TFC membranes based on 1,5-naphthalene diamine as the aqueous phase monomer are listed in Tables 13a-g (Appendix 2). Since 1,5-naphthalene diamine has only a limited solubility in water, the aqueous medium used for the reaction comprised of 50:50 water : methanol mixture. The TFC membranes were formed from the reaction of various acid chloride mixtures (IPC, TPC and TMC) with 1,5-naphthalene diamine.

5.3.1.1 TFC membranes formed from the reaction of mixed acid chlorides with 1,5-naphthalene diamine

Initial trials using only IPC or TPC as the acid chloride yielded membranes with negligible salt or sucrose rejections. The results of these trials are not listed here.

Table 13a lists trials based on the reaction of 1,5-naphthalene diamine with a mixture of diacid chlorides (TPC + IPC). These membranes gave both poor solute rejections as well as low water permeabilities.

Changing the acid chloride mixture to TMC + IPC yielded membranes with slightly improved solute rejections (see Table 13b). However, these improvements were not enough; when combined with the low water permeabilities, it was decided not to pursue the use of diacid mixtures as the reacting species in organic phase. Further trials on this system thus involved the use of only TMC as the acid chloride.

5.3.1.2 TFC membranes formed from the reaction of TMC with 1,5-naphthalene diamine

The data for membranes formed using 0.2% TMC as the acid chloride and 0.18% concentration of diamine are listed in Table 13c. The dip time in the aqueous phase was maintained at 3 minutes while the dip time in the organic phase was varied. Though the salt permeability was significantly lower for these membranes, the sucrose permeability did not decrease as much as expected. Thus, even the membrane formed from a 60 sec. dip time in the organic phase which had a salt rejection value of 73% and a very low water permeability (0.3×10^{-6} m/s) still showed a sucrose rejection of only 89%. Thus, it appears that these TFC membranes, though relatively thick or poorly permeable to water, have a significant number of defects which allow larger organics to penetrate through.

The fabrication procedure was varied in order to hopefully decrease the postulated defects. Table 13d lists data for membranes formed by decreasing the TMC concentration slightly to about 0.15% while changing the organic solvent from hexane to cyclohexane. The diamine concentration was also slightly increased to 0.2% and the curing temperature was elevated to 90°C. This approach gave very low water permeabilities while decreasing solute permeabilities further. Even though the salt rejection could be increased to 85%, the sucrose rejection was only ~98%.

Various other fabrication variables were studied unsuccessfully in order to improve the membrane performance :

Table 13e lists data for membranes formed by maintaining both the diamine and the acid chloride concentration at 0.2%. The organic phase solvent was switched back to hexane. Slightly better results were obtained in the case when the aqueous dip times were maintained at 3 minutes instead of 2 minutes

Table 13f lists data for membranes formed by maintaining both the diamine and the acid chloride concentration at 0.2% while changing the organic phase solvent from hexane to cyclohexane. The solute rejections are worse with this change as compared to the case (Table 13e) when the organic solvent was hexane.

Table 13g lists data for membranes formed by increasing the acid chloride concentration to 0.35% while maintaining the diamine concentration at 0.2%. This increase in the acid chloride concentration also did not improve the solute rejections for this system.

5.3.2 Polyamide TFC Membranes Based on 2,6-Diaminopyridine

Data for membranes formed from the reaction of TMC with 2,6-diaminopyridine have been listed in Table 14a-l (Appendix 2).

Table 14a lists the membranes formed when diaminopyridine and TMC concentrations were maintained at 2.5% and 0.2% respectively. It was observed that reasonably good TFC membranes could be made with this system as compared to that with 1,5 naphthalene diamine; however, the performance was significantly below that of the standard polyamide membrane. The best results were obtained when the aqueous dip time was at 4 minutes as against 2 and 6 minutes. The membranes formed from a 4 minute dip time in the aqueous phase followed by a 45 sec. dip time in the organic phase gave salt and sucrose permeabilities of 0.3 x 10^{-6} m/s and 0.06 x 10^{-6} m/s respectively, corresponding to rejections of 85% and 97%. The water permeability for this membrane was 0.8 x 10^{-6} m/s-MPa corresponding to a water flux of 6.9 lmh.

The aqueous phase dip times were maintained at 4 minutes for all the other diaminopyridine systems discussed below.

Table 14b lists data for the case where the diaminopyridine and the TMC concentrations were both increased to 3% and 0.35% respectively. These membranes show both high water 1.5 - 2.9 x 10^{-6} m/s-MPa and salt permeability of 1.1 - 3.3 x 10^{-6} m/s. Though the sucrose rejection never reached 100%; this membrane also shows good potential for separating organics from NaCl as there is considerable difference in the permeabilities of these two solutes

Table 14c lists membranes formed from a 3% solution of diaminopyridine and a slightly increased concentration (0.4%) solution of TMC. As compared to the data in

Table 5.6b, this system shows that both water and salt permeabilities have been reduced by approximately 2x with marginal improvement in sucrose rejection.

The surfactant SLS was added to the diaminopyridine solution at a level corresponding to 18% of its critical micellar concentration (CMC). The data for membranes obtained thus have been listed in Table 14d. The addition of the SLS tended to decrease all solute and water permeabilities further. However, a second set of data, presented in Table 14e, in which the SLS concentration was varied from 10% to 90% of its CMC value contradicts this conclusion. These membranes exhibit both low water flux as well as poor solute rejections.

Table 14f shows the results for membranes made when the TMC concentration was further increased to 0.5% while maintaining the diaminopyridine concentration at 3%. At these conditions, complete sucrose rejection can be achieved with moderate salt permeability (0.5 - 0.8 x 10^{-6} m/s). However, the water permeability (1.5 - 1.7 x 10^{-6} m/s-MPa) is only 1/2 of the value for the standard polyamide membrane; hence, the performance is not adequate for use as a NF membrane. The effect of adding the surfactant SLS to about 18% of its CMC value to the diaminopyridine solution is shown in Table 14g SLS addition again gave very scattered results in terms of the solute rejection. There was a reduction in the water permeability.

The effect of increasing TMC concentration in hexane, at a fixed diaminopyridine concentration of 3%, can be seen by comparing the data presented in Tables 14c (0.4% TMC), 14f (0.5% TMC), 14h (0.6% TMC), and 14i (0.7% TMC). At the higher TMC concentrations, there is a clear trend towards higher permeabilities with increasing organic phase dip times. There is also an overall trend towards higher solute and water permeabilities with increasing TMC concentrations. However, the ratio of salt to sucrose permeabilities (2 - 5) is not sufficiently high.

The effect of increasing diaminopyridine concentration to 5% is shown in Table 14j (TMC concentration at 0.25%) and Table 14k (0.35% TMC). All the membranes shown in Table 14j exhibit high solute and water permeabilities. The salt permeability for these membranes is almost 10x the value for sucrose. Similar performance characteristics can be seen for one of the membranes shown in Table 14k (at 60 sec. dip time). Increasing dip times in the organic phase results in increasing solute permeabilities.

A further increase in the diaminopyridine concentration to 7% while lowering the TMC concentration to 0.25% resulted in poor membranes with low water permeability as well as poor solute rejection (see Table 14l).

5.4 FTIR SPECTRA OF THE STANDARD POLYAMIDE, POLYESTERAMIDE POLYMERS AND THE PHYSICAL MIXTURES

As discussed in section 2.6, the unequal reactivities of the diamine and diol monomers implies that the final TFC membrane polymer composition need not be the same as the reaction mixture. In order to quantify this effect, various polyesteramide and polyamide samples were prepared by interfacial polycondensation and analyzed spectroscopically (see section 3.3 for experimental details). Since the ATR-IR spectra of the TFC membranes did not yield adequate signal to noise ratios, the following discussion refers only to the results of the FTIR study. The FTIR spectra of the polyamide polymer prepared from the reaction of TMC with *m*-PDA is shown in Fig. 5.1.

The spectra for the polyesteramide polymers obtained from the reaction of TMC with 50:50 *m*-AP : *m*-PDA, 50:50 Bis-A : *m*-PDA and 50:50 HQ : *m*-PDA each separately (i.e. the same compositions selected for the chlorine tolerance studies, section 5.5) along with the corresponding physical mixtures prepared as described in sections 3.3.1.2 and 3.3.2 are shown in Figs. 5.2a,b; 5.4a,b and 5.6a,b respectively.

A definitive ester signal appears in the range of 1720 - 1765 cm^{-1}. This ester signal at 1720 - 1765 cm^{-1} can be used to quantify the percent ester linkages in the polymer as this signal is absent in the FTIR spectra of the polyamide obtained from the reaction of TMC with *m*-PDA (see Fig. 5.1). This signal can be distinctly observed in case of the polyesteramide obtained from Bis-A and appears as a shoulder of the amide (I) band at 1640 - 1680 cm^{-1} in case of the polyesteramides obtained from 50:50 HQ : *m*-PDA and *m*-AP : *m*-PDA based systems. A standard deconvolution software known as FOCAS (Full Optimization Curve Analysis Software) was used to quantify the peak for the ester signal in relation to the amide signal. The ester signals along with the amide (I) signals at 1640 - 1680 cm^{-1} in the polyesteramide polymers and the physical mixtures were deconvoluted in order to obtain the area under the signals. The deconvoluted signals for the polyesteramide polymers and the corresponding physical mixtures are depicted in Figs. 5.3a,b; 5.5a,b and 5.7a,b.

Table 15 (Appendix 2) lists the percent ester and amide compositions estimated from the ratios of the deconvoluted areas of the ester and amide signals. In each case, the percent amide or ester was calculated by dividing the area corresponding to the particular signal by the total area corresponding to both signals.

The analysis of the physical mixtures validates the method for percent ester

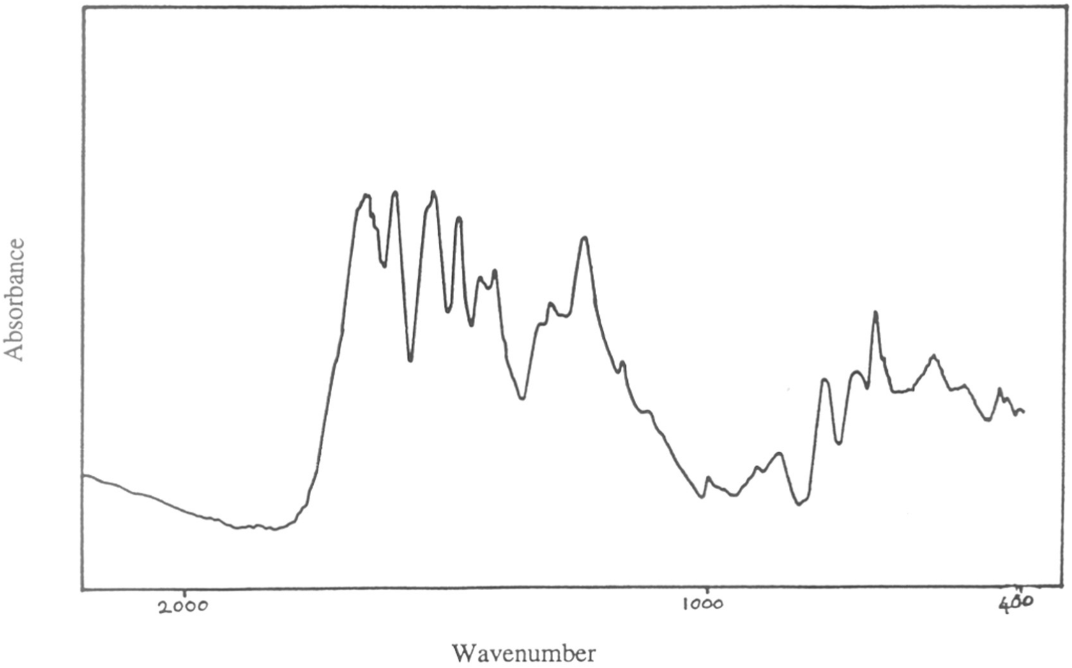


Fig. 5.1 : FTIR spectra of the polyamide obtained from the reaction of TMC with *m*-PDA.

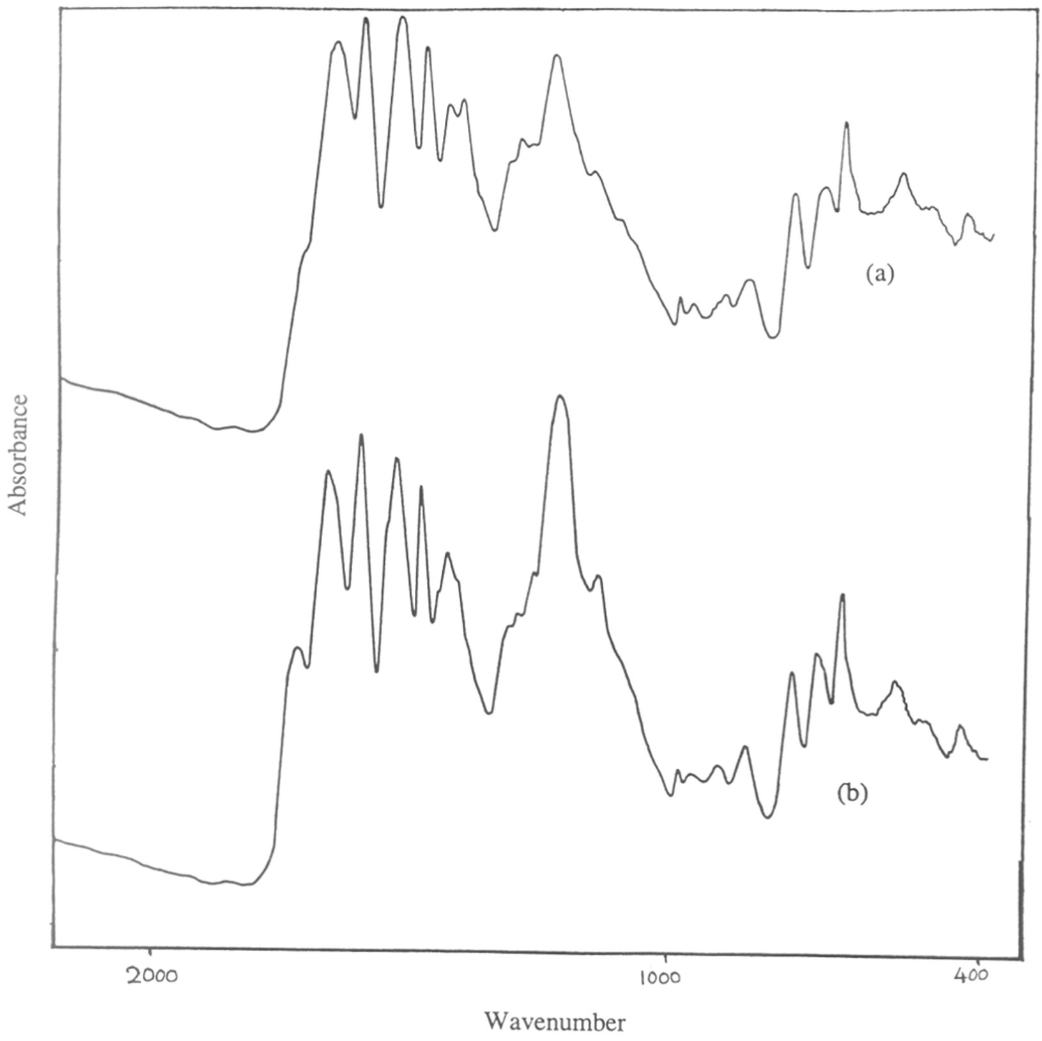


Fig. 5.2 : FTIR spectra of (a) polyesteramide obtained from the reaction of TMC with 50:50 *m*-AP : *m*-PDA and (b) physical mixture of polyesteramide obtained from the reaction of TMC with *m*-AP and polyamide obtained from the reaction of TMC with *m*-PDA.

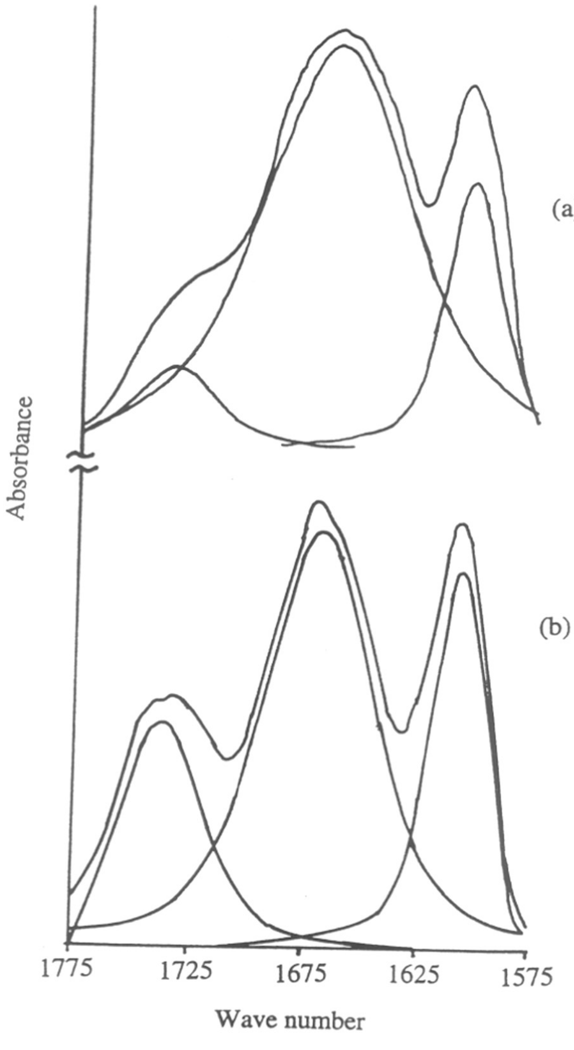


Fig. 5.3 : Deconvoluted FTIR spectra of (a) polyesteramide obtained from the reaction of TMC with 50:50 *m*-AP : *m*-PDA and (b) physical mixture of polyesteramide obtained from the reaction of TMC with *m*-AP and polyamide obtained from the reaction of TMC with *m*-PDA.

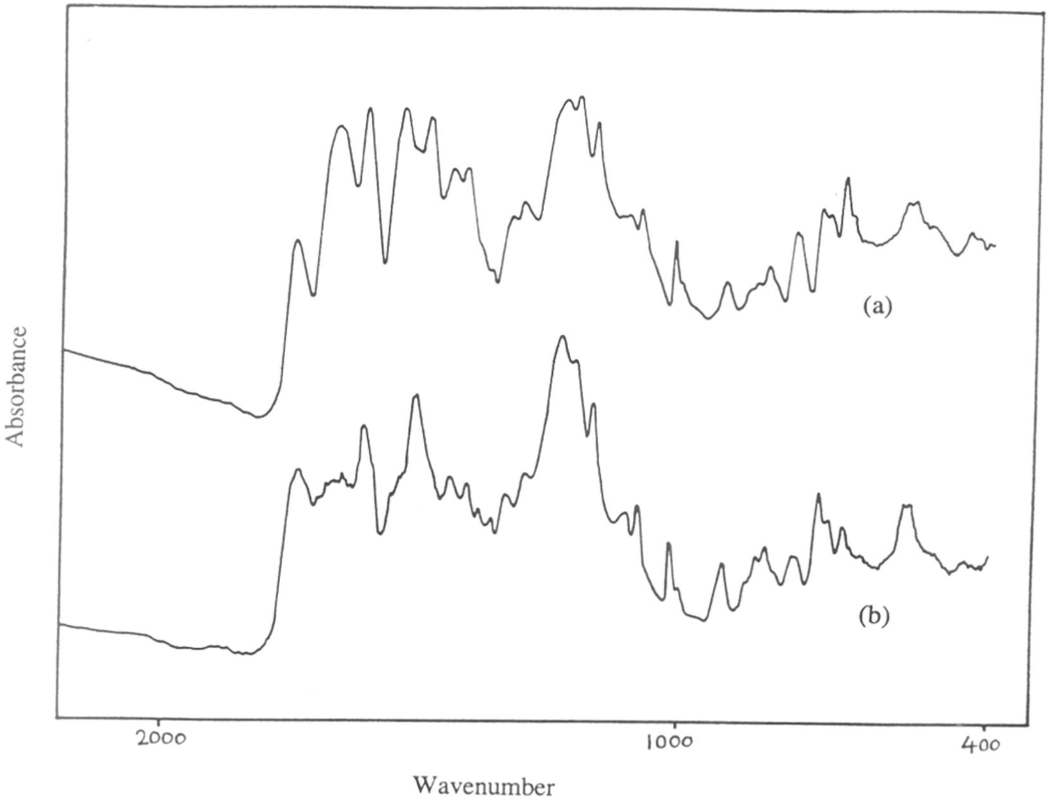


Fig. 5.4 : FTIR spectra of (a) polyesteramide obtained from the reaction of TMC with 50:50 Bis-A : *m*-PDA and (b) physical mixture of polyester obtained from the reaction of TMC with Bis-A and polyamide obtained from the reaction of TMC with *m*-PDA.

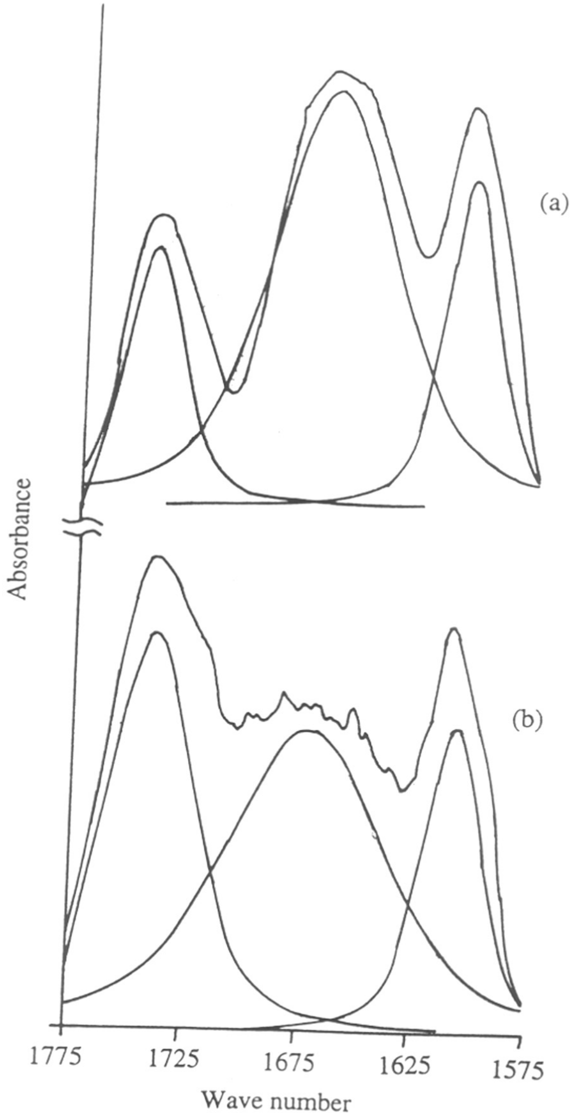


Fig. 5.5 : Deconvoluted FTIR spectra of (a) polyesteramide obtained from the reaction of TMC with 50:50 Bis-A : *m*-PDA and (b) physical mixture of polyester obtained from the reaction of TMC with Bis-A and polyamide obtained from the reaction of TMC with *m*-PDA.

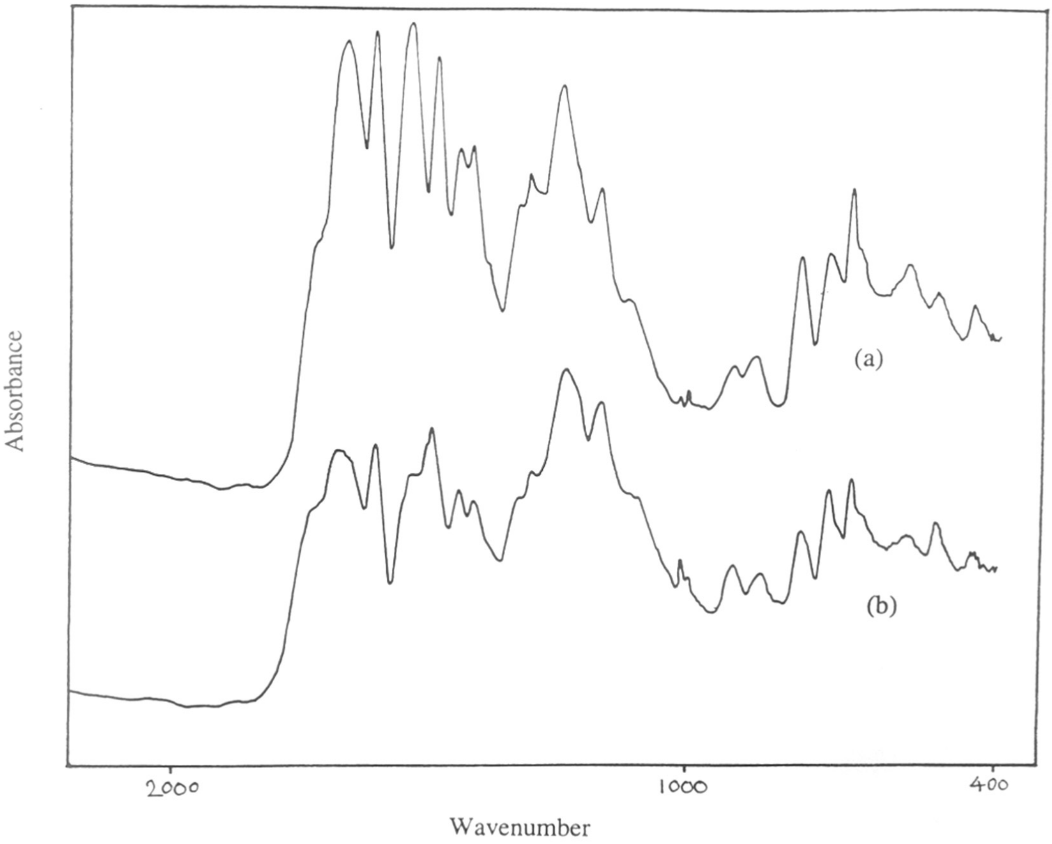


Fig. 5.6 : FTIR spectra of (a) polyesteramide obtained from the reaction of TMC with 50:50 HQ : *m*-PDA and (b) physical mixture of polyester obtained from the reaction of TMC with HQ and polyamide obtained from the reaction of TMC with *m*-PDA.

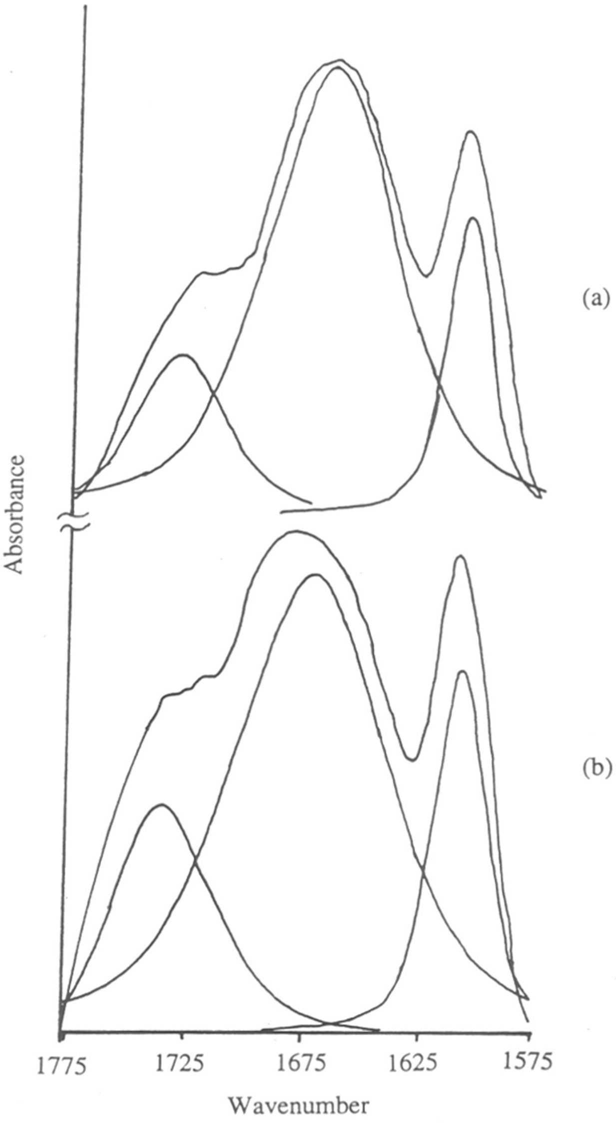


Fig. 5.7 : Deconvoluted FTIR spectra of (a) polyesteramide obtained from the reaction of TMC with 50:50 HQ : *m*-PDA and (b) physical mixture of polyester obtained from the reaction of TMC with HQ and polyamide obtained from the reaction of TMC with *m*-PDA.

estimation. For example, the physical mixture A based on 58.2% (w/w) of polyesteramide from *m*-AP and TMC and 41.8 % (w/w) of polyamide from *m*-PDA and TMC is estimated by the FTIR procedure to have an ester : amide ratio of 0.401 which matches well with the calculated value of 0.407. Similarly, in the case of the physical mixture based on the *m*-AP polyesteramide, the estimated ester : amide ratio by FTIR is 0.709 while the calculated value is 0.700. There is a discrepancy in the case of the physical mixture based on HQ polyester and this is attributed to an artifact in sample preparation. This sample could not be dispersed properly in the KBr pellet owing to difficulty encountered in grinding.

Following the above method of estimation the polyesteramide samples prepared by interfacial polymerization shows the following results :

(i) the polyesteramide obtained from the reaction of TMC with 50:50 *m*-AP : *m*-PDA contains 9.9 % ester while the amide is 90.1%.

(ii) the polyesteramide obtained from the reaction of TMC with 50:50 Bis-A : *m*-PDA contains 22.4% ester while the amide is 77.6%.

(iii) the polyesteramide obtained from the reaction of TMC with 50:50 HQ : *m*-PDA contains 21.8% ester while the amide is 78.2%.

These measurements indicate that the ratio of percent ester linkages in polymer : percent hydroxyl groups in the aqueous phase reaction mixture is approximately 0.4 - 0.45. This may be attributed either to the higher reactivity of the amine compared to the ester or its higher partitioning into the organic phase to react with the TMC. Since this ratio is approximately the same for both the diols as well as *m*-AP, it appears to be related to the reactivity difference.

5.5 CHLORINE EXPOSURE STUDIES

The chlorine exposure studies monitored the changes in the rate of water flux and salt passage through the TFC membrane after continuous exposure to chlorinated water. Chlorine exposure studies were conducted by addition of requisite amount of NaOCl (4 - 6%) to feed solution comprising of 2000 ppm NaCl so as to maintain a residual chlorine concentration of 200 ppm. This was immediately followed by stabilizing the pH at 6 - 6.5 with HCl addition. The chlorine level was maintained with continuous monitoring of the feed solution and adding fresh NaOCl as necessary.

Since the same feed was recirculated, this led to a gradual rise in the feed conductivity. The rate of solute passage after chlorine addition was therefore measured as the transmission rate T (= C_p/C_f), based on conductivity measurements. The chlorine tolerance (ppm-hours) is defined as the product of time (hours) of exposure to a specified concentration (ppm) of chlorine solution which a membrane tolerates before it starts to degrade i.e. the transmission rate for a previously rejected solute increases by a specified amount (2x). The transmission rate, T_o, for a particular membrane sample, in the absence of chlorine was first established. The increase in the value of T/T_o as a function of chlorine ppm-hours was then monitored.

Ideally, the chlorine tolerance of the membrane should have been measured over an extended time period and at low concentrations (1 - 5 ppm). Since such extended trials were not logistically possible, accelerated trials were made at 200 ppm chlorine levels. Another experimental problem was the need to continuously monitor and add NaOCl. In order to ensure that experimental artifacts did not lead to false conclusions regarding the chlorine tolerance of the new membranes, in each chlorine exposure run, a TFC membrane based on the standard polyamide formulation (*m*-PDA reacted with TMC) was used as a reference. The membrane samples for the reference polyamide and polyesteramide TFC membranes were chosen so as to have similar initial T_o values. Since high rejection TFC membranes could not be made from either the 1,5-naphthalene diamine or 2,6-diaminopyridine, these were not included in the chlorine tolerance study.

The polyesteramide TFC membranes chosen for the chlorine exposure studies were based on the reaction of TMC with the following aqueous phase compositions :

(i) 50:50 *m*-AP : *m*-PDA

(ii) 25:75 HQ : *m*-PDA

(iii) 50:50 HQ : *m*-PDA

(iv) 50:50 Bis-A : *m*-PDA

Details of the aqueous phase and organic phase compositions for the above are mentioned in Tables 10g, 11c and 12c,d (Appendix 2). Based on the FTIR spectra of the interfacially synthesized polymer, we expect the last two compositions to contain ~ 21% ester linkages while the first two would contain ~10% ester linkages. The results of the chlorine tolerance studies with these systems are discussed below. The tabulated data for the various systems are presented in Tables 16 - 19 (Appendix 2), while the changes in the transmission rates and water permeabilities are shown in Figs. 5.8 - 5.13 .

5.5.1 TFC Membrane Based on 50:50 *m*-AP : *m*-PDA

The water and salt passage rates as a function of chlorine exposure time for this system is presented in Table 16 (Appendix 2). Fig. 5.8a shows the plot of T/T_o Vs the chlorine ppm-hours for the polyesteramide membrane obtained from a 50:50 *m*-AP : *m*-PDA composition using TMC as the acid chloride. The membrane was prepared from a 15 sec. dip time in the organic phase as listed in Table 10g (Appendix 2). The T/T_o profile for this polyesteramide membrane is similar to that of the standard polyamide membrane. The transmission for the standard polyamide membrane (shown in Fig. 5.8a) increases 2x in ~315 ppm hours. The transmission for the polyesteramide membrane also shows a similar increasing trend and would be expected to double around 500 ppm-hours. The chlorine tolerance of both these membranes is thus comparable. The incorporation of ester groups via the use of *m*-AP is thus only marginally effective towards improving chlorine tolerance.

As shown in Fig. 5.8b the water permeability (calculated from equation 1.2) for both these membranes initially decreased considerably on chlorine addition. This is indicative of N-chlorination which destroys the hydrogen bonding potential of the membrane followed by ring chlorination that imparts hydrophobicity to the membrane. Continued chlorination would eventually have resulted in chain cleavage leading to structural breakdown which would be indicated by an increase in water flux through the membrane.

5.5.2 TFC Membrane Based on 25:75 HQ : *m*-PDA

The plot of T/T_o Vs the chlorine ppm-hours for the polyesteramide membrane synthesized from a 25:75 HQ : *m*-PDA composition using TMC as the acid chloride is shown in Fig. 5.9a. The water and salt passage rates as a function of chlorine exposure

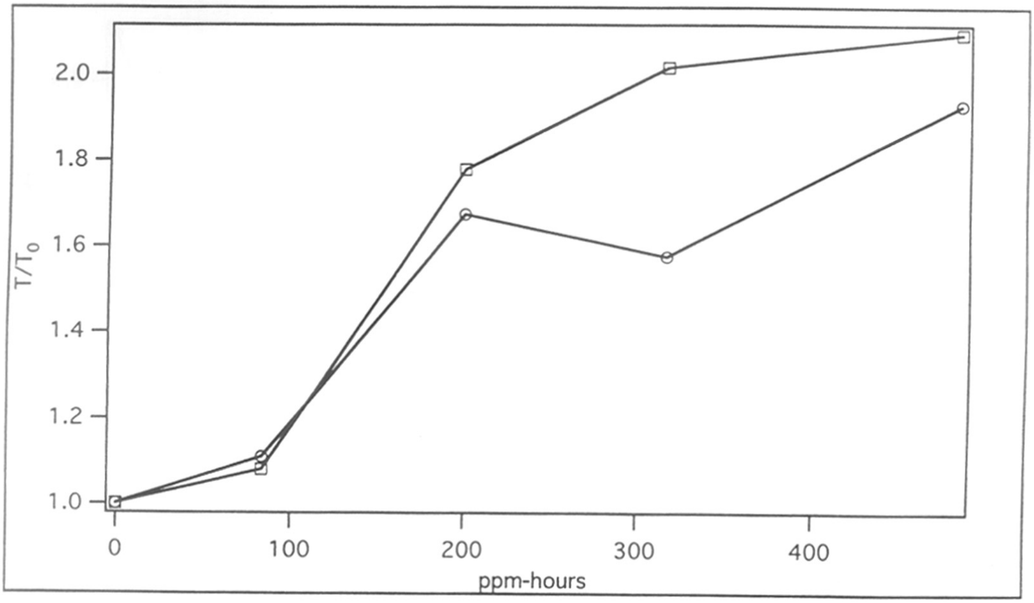


Fig. 5.8a : Plot of T/T$_o$ Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 *m*-AP : *m*-PDA (○) and for the reference polyamide TFC membrane (□).

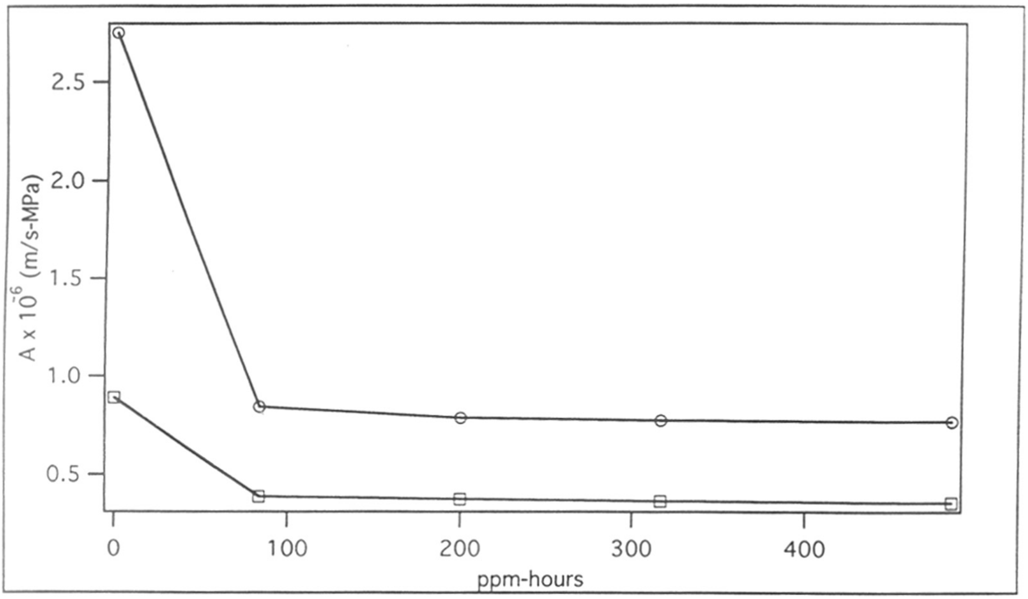


Fig. 5.8b : Plot of water permeability coefficient A Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 *m*-AP : *m*-PDA (○) and for the reference polyamide TFC membrane (□).

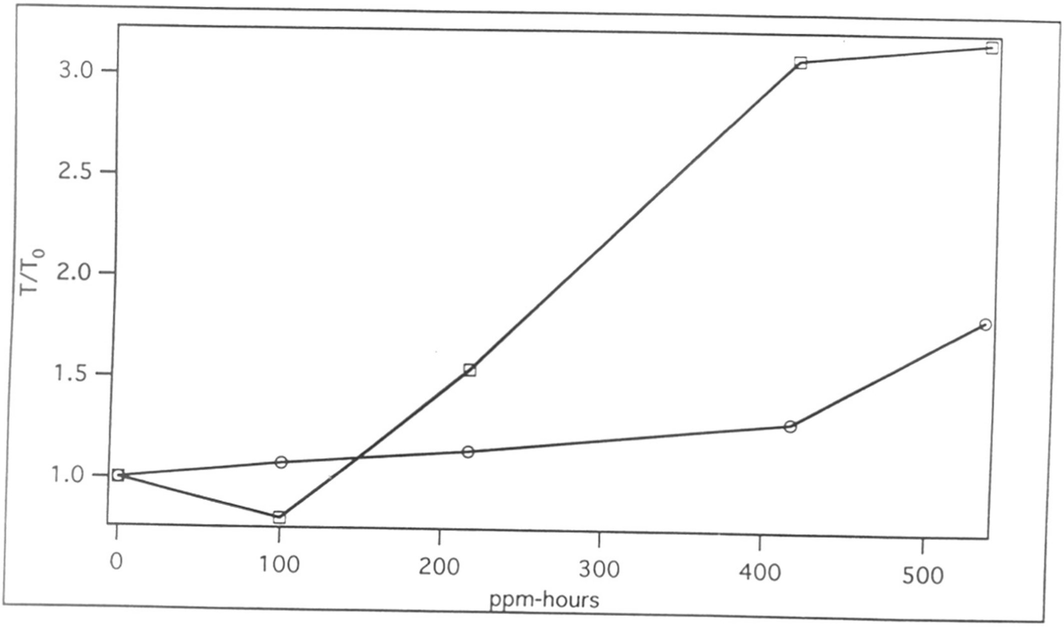


Fig. 5.9a : Plot of T/T_o Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 25:75 HQ : *m*-PDA (O) and for the reference polyamide TFC membrane (□).

time for this system is presented in Table 17 (Appendix 2). The membrane was prepared from a 30 sec. dip time in the organic phase as listed in Table 12d (Appendix 2). This composition was specifically chosen in order to compare the chlorine tolerance of this system with that of the 50:50 *m*-AP : *m*-PDA system. In both these systems, the percent ester linkages incorporated would be similar (10%). The effect on chlorine resistivity of having both ester linkages on the same phenyl ring (HQ) as opposed to both amine and ester linkages on the same phenyl ring (*m*-AP) can thus be compared.

As shown in Fig. 5.9a, the conductivity transmission for the standard polyamide membrane initially decreased slightly and then increased; T/T_o doubled at ~280 ppm-hours. For the polyesteramide membrane, the transmission increased only marginally till 400 ppm-hours and then showed an increase wherein T/T_o would appear to double at ~600 ppm-hours. Thus, the polyesteramide membrane formed from 25:75 HQ : *m*-PDA shows a marginally better chlorine tolerance than the standard polyamide membrane.

Fig. 5.9b shows the corresponding changes in water permeability as a function of chlorine exposure for both the reference polyamide and the polyesteramide membrane. The water flux for both the standard polyamide and the polyesteramide membrane shows an initial rapid decrease on chlorination and then continues to show a very slow gradual decline until the end of the study. The trend is quite similar to that of the *m*-AP based system.

5.5.3 TFC Membrane Based on 50:50 Bis-A : *m*-PDA

The plots of T/T_o Vs the chlorine ppm-hours for two of these polyesteramide membranes based on 50:50 Bis-A : *m*-PDA compositions are shown in Figs. 5.10a and

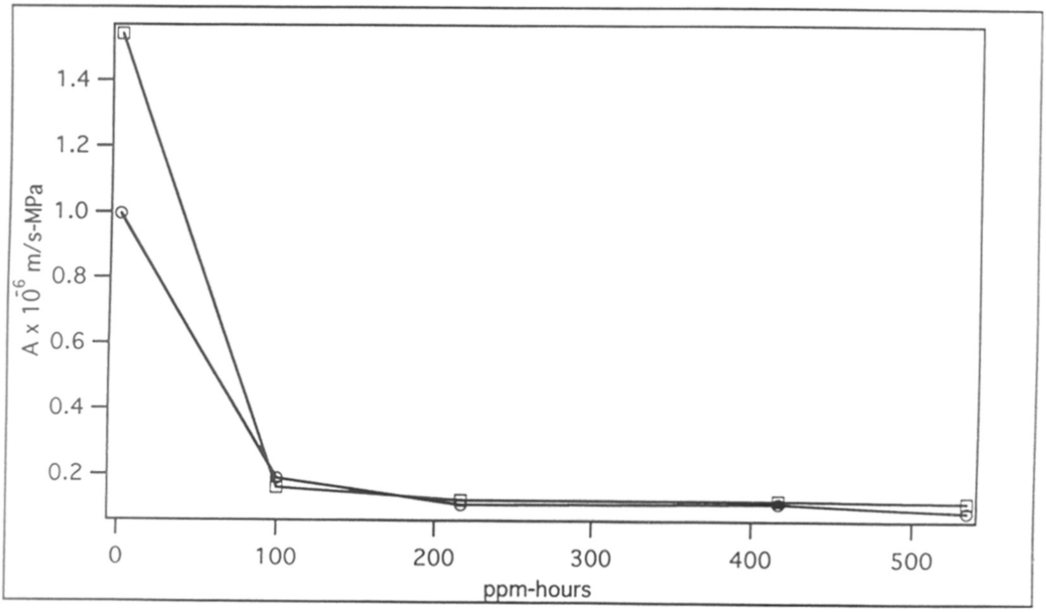


Fig. 5.9b : Plot of water permeability coefficient A Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 25:75 HQ : *m*-PDA (O) and for the reference polyamide TFC membrane (□).

5.11a. The membranes were synthesized from a 45 sec. dip time in the organic phase as listed in Table 11c (Appendix 2). They were tested in two separate runs with two reference polyamide samples having similar initial NaCl rejections. The water and salt passage rates as a function of chlorine exposure time for these two systems corresponding to Figs. 5.10a,b and 5.11a,b are presented in Tables 18a and 18b (Appendix 2).

In both these sets of chlorine tolerance experiments, the standard polyamide membranes showed rapid deterioration in conductivity rejection. The transmission for the standard polyamide membranes showed an initial decline followed by a rapid increase beyond 100 ppm-hours; T was found to double at ~130 and 150 ppm-hours respectively. For the polyesteramide membranes, the T/T_0 values are much lower as compared to those for the standard polyamide membrane. Transmission increased slowly after 100 ppm-hours and would appear to double only after 600 ppm-hours. Thus, the chlorine tolerance of the polyesteramide membranes formed from 50:50 Bis-A : *m*-PDA is far better than that of the standard polyamide membrane. Since ring chlorination proceeds via N-chlorination, no ring chlorination is expected on the aromatic rings contributed through Bis-A.

Both polyesteramide membranes showed a decline in water permeability upon chlorination (see Fig. 5.10b and 5.11b). This trend is again quite similar to the 50:50 *m*-AP : *m*-PDA and 25:75 HQ : *m*-PDA systems. One standard polyamide also showed similar flux behavior while the other showed an initial flux decline and then a rapid increase in flux beyond 100 ppm-hours. This rapid flux increase is indicative of chain cleavage resulting in a breakdown of the membrane structure.

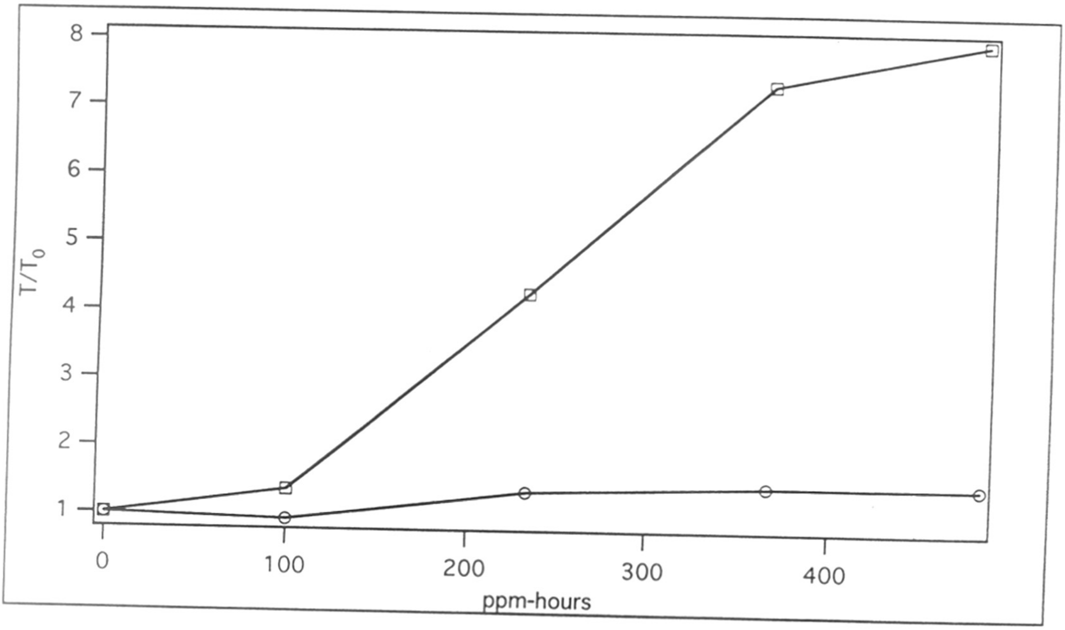


Fig. 5.10a : Plot of T/T$_0$ Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA (○) and for the reference polyamide TFC membrane (□).

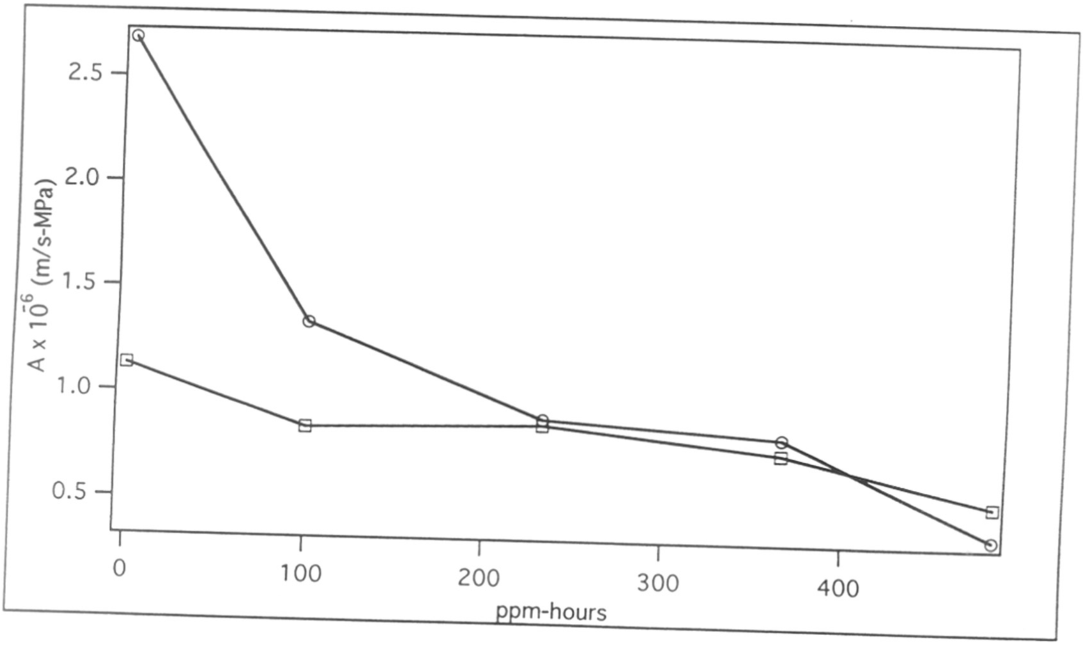


Fig. 5.10b : Plot of water permeability coefficient A Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA (○) and for the reference polyamide TFC membrane (□).

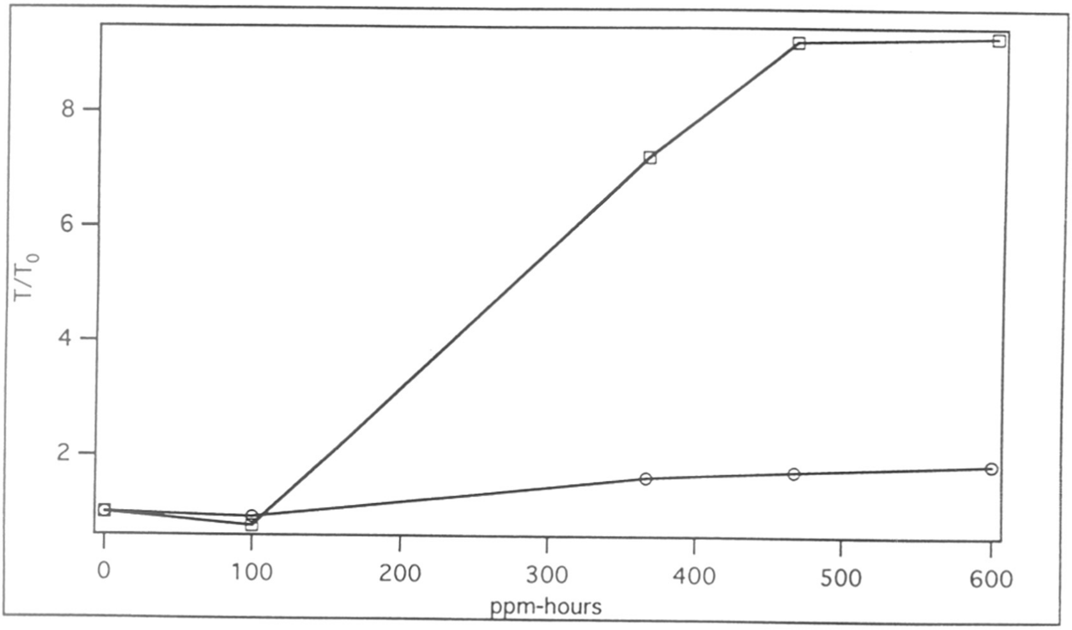


Fig. 5.11a : Plot of T/T_o Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA (o) and for the reference polyamide TFC membrane (□) (Repeat study).

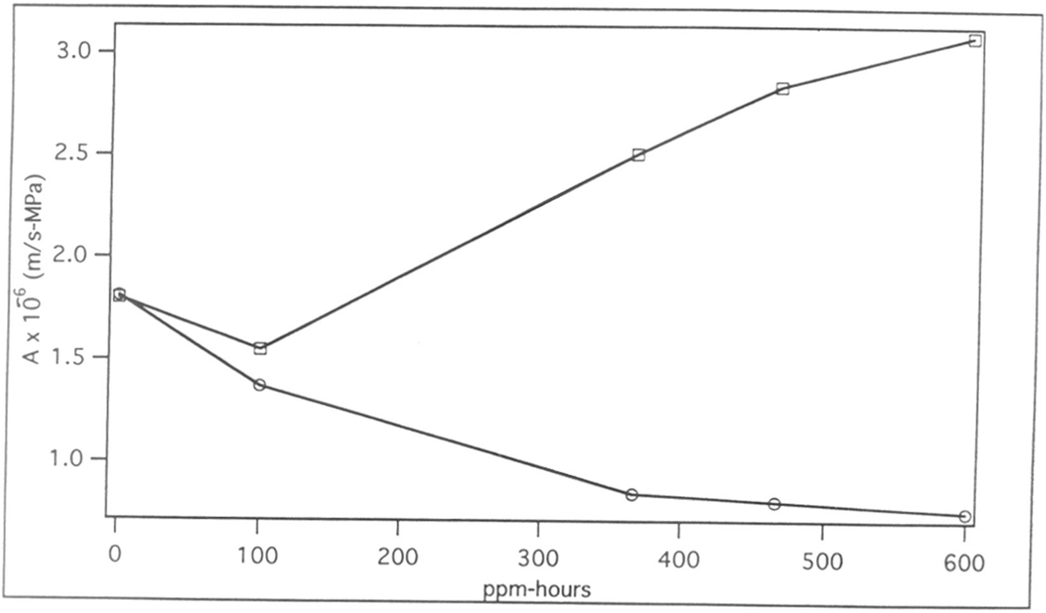


Fig. 5.11b : Plot of water permeability coefficient A Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA (O) and for the reference polyamide TFC membrane (☐) (Repeat study).

5.5.4 TFC Membrane Based on 50:50 HQ : *m*-PDA

Figs. 5.12a and 5.13a show the plots of T/T_o Vs the chlorine ppm-hours for the two polyesteramide membranes synthesized from a 50:50 HQ : *m*-PDA composition using TMC as the acid chloride. The membranes were synthesized from a 1 minute dip time in the organic phase as listed in Table 12c (Appendix 2). Both membranes had different initial transmission rates and ideally needed to be directly compared with reference standard polyamide membrane with similar selectivities. The comparison in this case is slightly damaged as membranes of similar selectivities were not compared in the same run. The polyesteramide membrane with lower rejection (87.6%) was tested along with a standard membrane sample with higher rejection (98.5%) in the first run (refer Table 19a - Appendix 2); while, in the second run, the polyesteramide membrane with higher rejection (97.6%) was tested with a standard polyamide membrane sample with lower rejection (91.1%) (refer Table 19b - Appendix 2).

In the first case as seen in Fig. 5.12a , the value of T/T_o for the polyesteramide membrane doubled at ~770 ppm-hours while in case of the reference standard polyamide membrane this value was found to double at ~155 ppm-hours. In the second run shown in Fig. 5.13a, the high rejection polyesteramide membrane showed a chlorine tolerance of ~780 ppm-hours and in comparison, the low rejection standard polyamide sample exhibited a chlorine tolerance of ~580 ppm-hours. As seen in Fig. 5.13b, this polyamide membrane exhibited lower water permeability than the other three samples which may be indicative of a thicker film which is responsible for retaining the membrane selectivity for a longer period. Even though the comparison is not as direct as desired, it is clear that polyesteramide membranes based on 50:50 HQ : *m*-PDA systems are superior to the

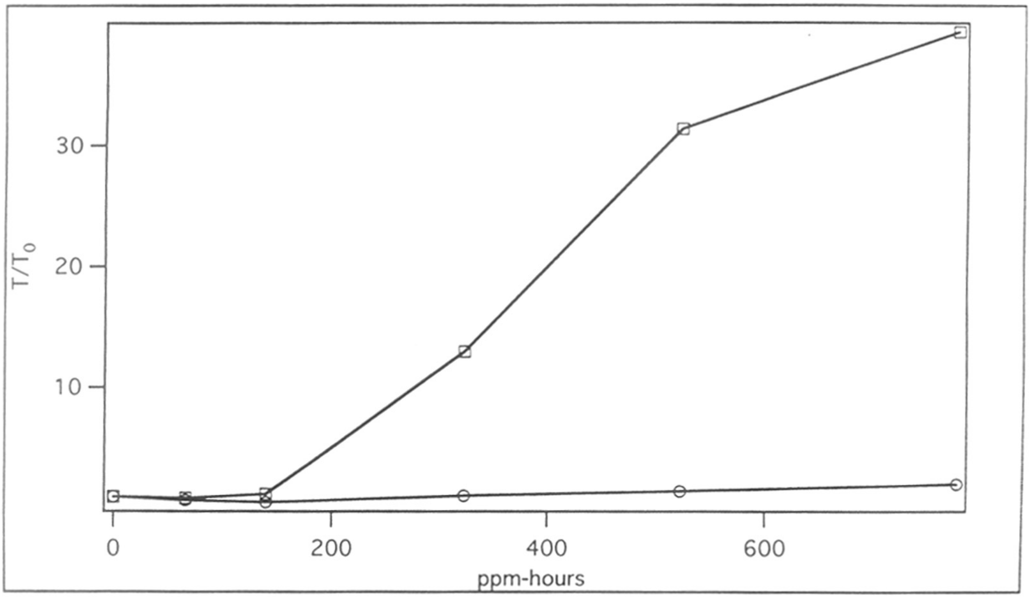


Fig. 5.12a : Plot of T/T$_o$ Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 HQ : *m*-PDA (○) and for the reference polyamide TFC membrane (□).

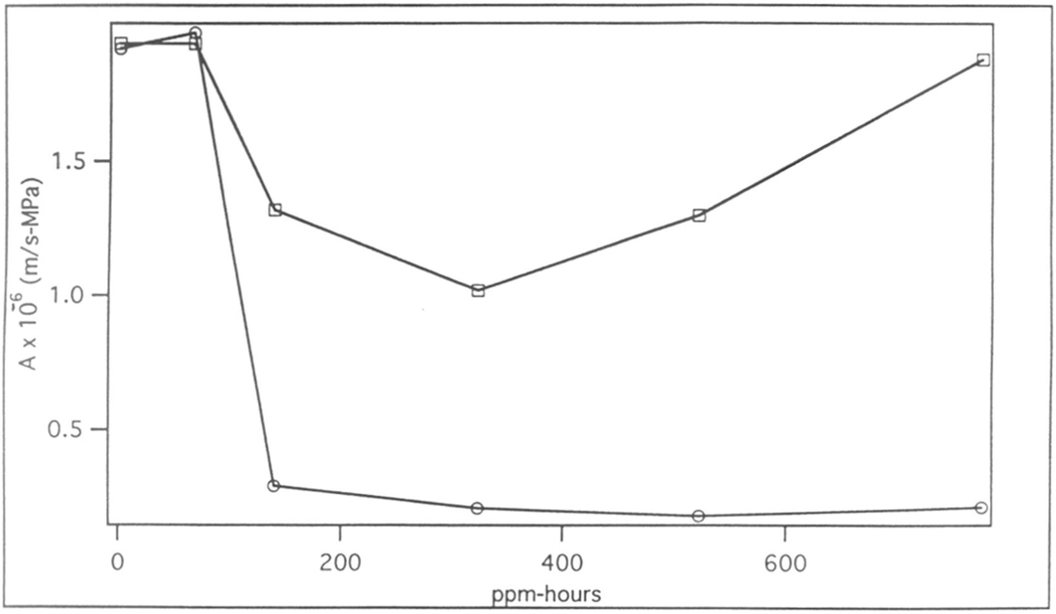


Fig. 5.12b : Plot of water permeability coefficient A Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 HQ : *m*-PDA (○) and for the reference polyamide TFC membrane (□).

standard polyamide membranes in terms of chlorine tolerance.

From Figs. 5.12b and 5.13b it is observed that both the polyesteramide membranes show a flux decline upon chlorination similar to the other systems discussed above. In case of the reference standard polyamide membranes, both membranes show a similar initial flux decline and then an increase in flux at higher chlorination times. This increase in flux is indicative of the start of membrane degradation by oxidative chain cleavage.

5.6 COMPARISON OF CHLORINE TOLERANCE OF THE POLYESTERAMIDE MEMBRANES WITH EACH OTHER AS WELL AS WITH THE STANDARD POLYAMIDE MEMBRANE

The chlorine tolerance studies of the polyesteramide TFC membranes bring out several interesting comparisons which identify that the main variable in increasing the chlorine tolerance is simply the increasing number of ester linkages which replace amide linkages. As shown by the adduct studies in chapter 4, the ester linkages provide substantially more chlorine resistance than the amide linkages. Since N-chlorination is avoided in the ester case, ring chlorination can only take place by direct electrophilic substitution which is a less favorable chlorination route than Orton rearrangement. The relevant comparisons are discussed below :

1) Effect of combined ester and amide linkages on the same ring : Both the 50:50 *m*-AP : *m*-PDA and the 25:75 HQ : *m*-PDA based TFC membranes have the same proportion of ester linkages (10%). However, in case of the HQ monomer, the diol aromatic ring has

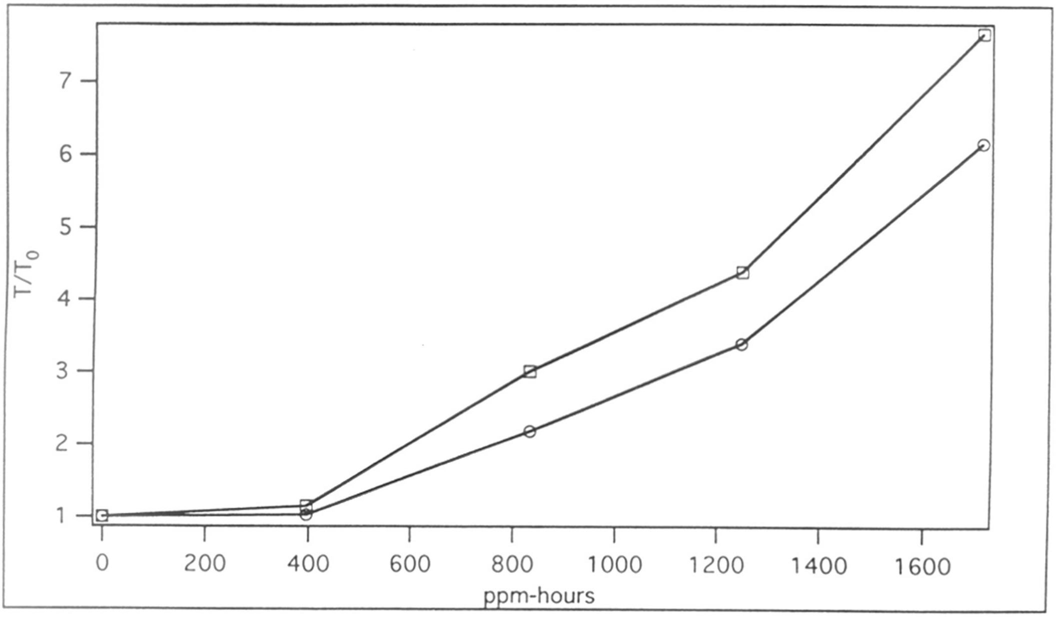


Fig. 5.13a : Plot of T/T_0 Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 HQ : *m*-PDA (○) and for the reference polyamide TFC membrane (□) (Repeat study).

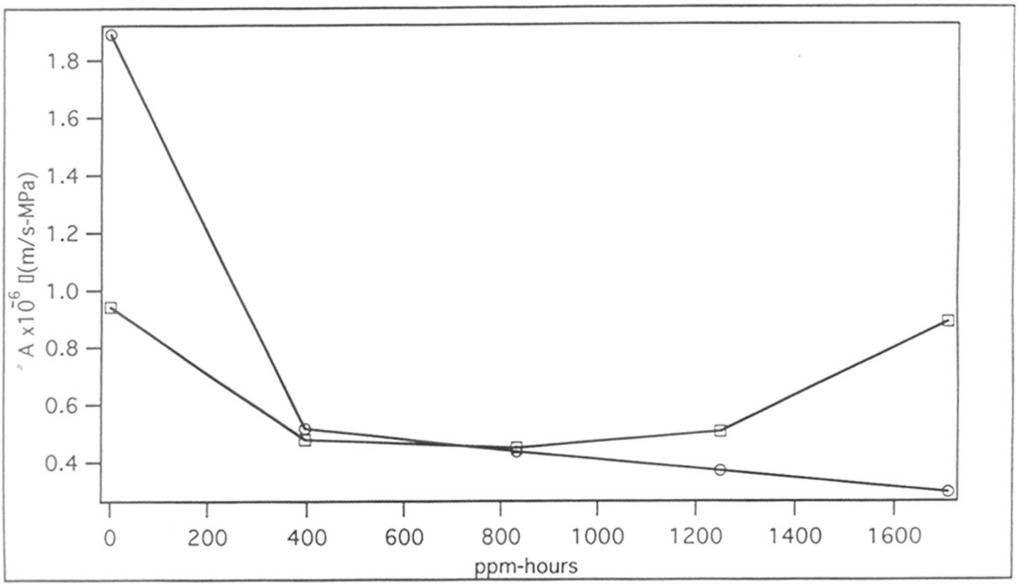


Fig. 5.13b : Plot of water permeability coefficient A Vs the chlorine ppm-hours for the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 HQ : *m*-PDA (○) and for the reference polyamide TFC membrane (□) (Repeat study).

only ester linkages while in the case of *m*-AP, the amide functionality on the same ring as the ester offers scope for N-chlorination and subsequent ring chlorination by Orton rearrangement.

The chlorine tolerance of the polyesteramide membrane obtained from a 50:50 *m*-AP : *m*-PDA composition is only about 1.58x higher than the standard polyamide membrane tested under the same conditions. This is consistent with the model compound study (chapter 4) wherein the esteramide adduct obtained by the benzoylation of *m*-AP exhibited only a minimal degree of chlorine tolerance. The polyesteramide membrane obtained from the 25:75 HQ : *m*-PDA composition showed a slightly higher (1.96x) chlorine tolerance than the standard polyamide membrane tested under the same conditions.

Thus the polyesteramide membranes formed from both 50:50 *m*-AP : *m*-PDA and 25:75 HQ : *m*-PDA which both contain low amounts (10%) of ester linkages result in only a slight improvement in the chlorine tolerance of the membrane in comparison to the chlorine tolerance of the standard polyamide membrane. At these low levels of ester linkages, the effect of *m*-AP is similar to HQ. However, chlorine tolerance of the polyesteramide membrane formed from the 25:75 HQ : *m*-PDA system is a little better than that formed from the 50:50 *m*-AP : *m*-PDA system. Also, the transmission through the 25:75 HQ : *m*-PDA remained mostly unaffected till 400 ppm-hours while that for the *m*-AP system deteriorated at the same rate as the standard polyamide membrane.

2) Higher proportion of ester linkages : The effect of increasing the proportion of ester linkages can be seen by comparing the chlorine tolerance of membranes based on 25:75 and 50:50 HQ : *m*-PDA systems. As seen above, the 25:75 HQ : *m*-PDA composition

increases the chlorine tolerance by a factor of 2 at most. By contrast, the degree of chlorine tolerance for the polyesteramide membrane obtained from the reaction of a 50:50 HQ : *m*-PDA composition with TMC is 4x higher than the standard polyamide membranes (~ 780 ppm-hours as compared to ~155 ppm-hours, when comparing high rejection samples). This is clearly related to the higher proportion (21% as opposed to 10%) of ester linkages in the 50:50 HQ : *m*-PDA system as compared to the 25:75 system.

3) Effect of diol type : Both the 50:50 HQ : *m*-PDA and Bis-A : *m*-PDA systems have approximately the same proportion (21%) of ester groups incorporated into the TFC membrane. In the HQ case, the -OH groups are situated on the same aromatic ring while in the case of Bis-A, these groups are located on two separate rings separated by a bridge carbon. Though the exact chlorine tolerance time (ppm-hours) for the 50:50 Bis-A : *m*-PDA membrane could not be estimated, it appears that both polyesteramides have at least 4x higher chlorine tolerance than the standard polyamide membrane. No significant difference is seen between the chlorine tolerance of these two TFC membranes.

The comparisons above indicate that unless there is a certain minimum level of ester functions (20%) incorporated in the membrane, marginal improvement in chlorine tolerance is seen. To a first approximation, the chemistry through which these ester linkages are introduced into the TFC structure is less important for determining the increase in chlorine tolerance. The concentration of the -OH groups in the aqueous mixture has the major effect on increasing the chlorine tolerance of the resulting polyesteramide. Diols are preferable to aminophenols because twice the number of ester linkages are introduced into the structure per monomer unit.

The trend in the water flux in all cases is similar for both polyesteramide and standard polyamide membranes. In all these membranes, initial chlorination leads to a rapid flux decline. This may be indicative of rapid N-chlorination which disrupts H-bonding and causes a decrease in water permeability by compaction. The slower decline after the initial chlorine exposure may be attributed to a more gradual ring chlorination process which increases the membrane hydrophobicity. While some of the standard polyamide membranes showed signs of increased flux at high chlorination times, indicative of chain cleavage; none of the polyesteramide membranes showed this type of extreme structural breakdown. However, it is probable that with still increased chlorination times, the same effect would have been seen for the polyesteramide membranes as well.

CHAPTER 6

CONCLUSIONS

This chapter summarizes the experimental observations and correlates the results from the adduct and TFC membrane studies.

The main objectives of the thesis were to develop correlations of the polymer structures with the RO separation characteristics and the chlorine resistance of the resulting TFC membranes. In this study, model compounds were synthesized and their susceptibility to chlorine attack was studied by means of IR, NMR and melting point measurements. This was followed by the synthesis of TFC membranes, and data regarding salt and sucrose rejections and water flux of these membranes was collected. The chlorine tolerance on certain fixed compositions of these systems was examined by monitoring the solute transmission with increased chlorine exposure time. The results are correlated with that obtained from the adduct study.

6.1 ADDUCT STUDY

The structures of adducts synthesized by benzoylation of various diamines, diols and aminophenols were confirmed by IR and NMR spectral analysis. The reactivity of these adducts when subjected to varying levels of chlorine treatment was monitored by ^{1}H NMR. This study gave information regarding the mechanism of diamide chlorination, the effect of substitution pattern in primary aromatic diamines and aminophenols and the reactivity to chlorination of ester linkages in diol and aminophenol based adducts vis-à-vis amide linkages.

Ring chlorination has been detected only at the positions either ortho or para or both to the amide function. Thus, even though N-chloro amide formation could not be specifically detected by ^{1}H NMR, the overall results are consistent with N-chlorination followed by molecular rearrangement via Orton rearrangement to yield an irreversibly chlorinated ring.

The chlorine resistance of a particular class of adducts is greatly influenced by the substitution pattern. The diamide obtained from *o*-PDA could not be chlorinated even at the most severe chlorination conditions (treatment C). This is attributed to steric hindrance at the -NH- position or possible hydrogen bonding between the amide proton and the carbonyl group. This effect is consistent with the above postulated reaction mechanism.

The other diamides obtained from *m*-PDA and *p*-PDA showed susceptibility to chlorination. The diamide obtained from *p*-PDA was chlorinated to a lesser extent as compared to the diamide formed from *m*-PDA. In the diamide obtained from *m*-PDA, each ortho and para position is doubly activated by both -NH- groups. By contrast, in case of the diamide obtained from *p*-PDA, the ortho position is only singly activated by the adjacent -NH- group. Thus, the diamide adducts showed the following increasing order of chlorine tolerance :

diamide formed from *m*-PDA < diamide formed from *p*-PDA < diamide formed from *o*-PDA.

In case of the esteramides, the esteramide obtained from *p*-AP was affected even at the mildest chlorination conditions where no change was observed with that obtained from *m*-AP. Both the esteramide adducts are susceptible when exposed to more severe chlorination and the extent of chlorination was more with the esteramide formed from *m*-AP than that formed from *p*-AP. In case of the esteramide obtained from *m*-AP the formation of a dichloro- and a trichloro- product can be attributed to the two ortho and one para positions that are activated by the -NH- group. In the esteramide obtained from *p*-AP, only the two positions ortho to the -NH- group are activated, which in turn leads to the formation of only mono- or dichloro- products as was confirmed from the COSY study.

The esteramide adducts showed a lower level of chlorine tolerance as compared to the diamide adducts. While both the diamides (except for that obtained from *o*-PDA) and esteramides are susceptible to chlorination, all the diesters resisted chlorination even on most severe chlorination conditions (treatment C). In the case of the diesters, it was not possible to differentiate between various substitution patterns i.e. comparison of diesters formed using HQ and Res or the effect of the bridge aliphatic carbon in the case of the diester formed using Bis-A since all these adducts were unaffected by chlorination. The lack of chlorine attack in case of the diesters and the susceptibility in case of the esteramides also supports the reaction mechanism in which chlorine attack in the case of diamides takes place via the N-chlorination scheme proposed by Orton.

6.2 RO STUDY OF VARIOUS TFC MEMBRANES

An existing successful TFC membrane is based on a crosslinked aromatic polyamide layer (formed by the reaction of *m*-PDA with TMC) supported on a PSF (ultrafiltration) membrane. Though these polyamide membranes are known to have excellent intrinsic separation characteristics for RO, their main drawback has been the lack of chlorine resistance. Based on the adduct study, it is expected that the chlorine tolerance of polyamide membranes can be improved if ester groups are introduced into the polymer backbone.

While the adduct study identifies the chemistries likely to give chlorine tolerant membranes, the monomer reactivity is also a key issue. For example, though the diamide obtained from *o*-PDA has excellent chlorine tolerance, the monomer reactivity is likely to be hindered. Based on the chlorination reaction mechanism, other diamines (1,5-naphthalene diamine and 2,6-diaminopyridine) would also be expected to have good chlorination tolerance. Hence, these amines were investigated to examine their ability to form high performance TFC membranes.

Similarly, though as a class the adducts formed using diols showed excellent chlorine tolerance as compared to the adducts formed using diamines and aminophenols, it was expected that the hydroxyl reactivity with the acid chloride would be less than that of the amine group. For this reason, both *m*-AP and the two diols (HQ and Bis-A) were investigated to examine their ability to form high performance TFC membranes. *m*-AP was preferred over *p*-AP due to its better resistance at low chlorination levels.

In all cases, when TFC membranes were prepared from the reaction of any of the experimental diols or *m*-AP alone with TMC, the resultant membranes exhibited high fluxes and poor solute rejections. Hence, TFC membranes were prepared as copolymers based on the reaction of TMC in the organic phase with the experimental monomers and *m*-PDA in varying proportions in the aqueous phase. The two diamine systems i.e. 1,5-naphthalene diamine and 2,6-diaminopyridine were investigated without the addition of *m*-PDA. Generally, at each composition of the reacting phases, the dip times in each phase and the curing conditions were optimized so as to get the best performance corresponding to that particular composition.

6.2.1 Polyesteramide TFC Membranes Based on *m*-AP : *m*-PDA

In case of the polyesteramide membranes obtained from the reaction of varying compositions of *m*-AP : *m*-PDA with TMC it was noted that as the proportion of *m*-AP decreases, the salt rejection of the membrane increases. Thus, it is difficult to obtain reasonably good RO membrane performance with significant incorporation of *m*-AP. Using *m*-AP, it may be possible to obtain useful membranes capable of separating large organics from salt. The membranes formed using a 90:10 *m*-AP : *m*-PDA composition showed high water permeability of 10 - 12 x 10^{-6} m/s-MPa as well as high salt permeability of 10 - 34 x 10^{-6} m/s. Though the sucrose rejections were not absolute (82-86%), the sucrose permeability was 10x lower than that of NaCl, thereby indicating the applicability of these membranes towards separation of organics from monovalent salts. However, since the chlorine tolerance study showed no advantage in using *m*-AP over *m*-PDA, even this system does not appear promising.

As the *m*-AP : *m*-PDA ratio is decreased, the membrane permeabilities decrease and solute rejection increases. In case of the 80:20 *m*-AP : *m*-PDA system the difference in permeability coefficients for sucrose over salt is also considerably reduced compared to the 90:10 system. The best membrane obtained with 70:30 *m*-AP : *m*-PDA composition exhibited complete sucrose rejection combined with a salt permeability of 0.6 x 10^{-6} m/s corresponding to a rejection of 91%. This is combined with a reasonable water permeability of 3.1 x 10^{-6} m/s-MPa. The membranes formed from 50:50 and 30:70

compositions showed overall lower solute permeabilities that are comparable with the standard polyamide membrane but with even lower water fluxes.

It was observed that the addition of the surfactant SLS to this system generally caused all the permeability coefficients to decrease by 2x and there was no improvement in the separation ability of the membrane to compensate for the loss in water flux.

6.2.2 Polyesteramide TFC Membranes Based on Bis-A : *m*-PDA

Polyesteramide membranes formed from the reaction of varying Bis-A : *m*-PDA compositions with TMC typically have complete rejection for sucrose coupled with high water permeabilities. The NaCl rejection is also reasonably high (more than 90%) and thus this system could be developed as a loose RO membrane. Chlorine tolerance of the membrane can also be increased considerably by incorporating ester linkages via the use of Bis-A moiety.

At the highest Bis-A : *m*-PDA ratios (>80:20), the membrane solute rejection is poor. It is, however, interesting to note that the membrane performance is not sensitive to the Bis-A proportion within a wide composition range of 80:20 to 30:70 (Bis-A : *m*-PDA). Within this range of Bis-A : *m*-PDA compositions, fabrication variables could be found which gave TFC membranes with similar permeability profiles. No simple trends relating membrane performance with the fabrication variables could be identified. As an example of the best type of RO performance possible with this system, consider the membrane prepared with 70:30 Bis-A : *m*-PDA composition from a 15 sec. dip time in the organic phase which exhibited 100% sucrose rejection; a salt permeability of 0.2×10^{-6} m/s corresponding to rejection of 96%, and water permeability of 2.4×10^{-6} m/s-MPa.

In comparison to the standard polyamide membrane, the membranes formed using Bis-A : *m*-PDA compositions exhibit similar sucrose and water permeabilities; however, the salt permeabilities are at least 2x higher. Thus, it is apparent that the incorporation of ester functionalities via the Bis-A moiety decreases salt rejection of the resulting membranes as compared to the standard polyamide membrane. This effect could be related to the size of the Bis-A monomer.

6.2.3 Polyesteramide TFC Membranes Based on HQ : *m*-PDA

The HQ : *m*-PDA system shows considerable potential for forming useful RO membranes. This system could be used to fabricate both loose RO or NF membranes as well as tighter RO membranes with NaCl rejections up to 98% at 2.76 MPa and 2000 ppm salt. The sucrose rejection is complete and the water permeability of these membranes is only slightly lower being about 70% of the best values for the standard polyamide membrane samples. TFC membranes made from compositions with 50% or higher levels of HQ also have considerably enhanced chlorination resistance of about 4x compared to the standard polyamide membrane.

Though there is a slight trend towards increasing salt rejections with decreasing ratios of HQ : *m*-PDA, within a range from 80:20 to 25:75, the salt rejections are not very sensitive to this composition. Membranes formed from 70:30 compositions showed lower salt permeabilities than those formed from 80:20 compositions. The salt permeabilities of the membranes formed from 70:30 and 50:50 compositions are comparable to that of the standard polyamide membrane although the water permeabilities are slightly lower (70% of best values). Salt rejections as high as 95 - 97% were obtained for membranes prepared at either low (15 sec.) or high (60 sec.) organic phase dip times while intermediate dip times gave poorer salt rejections. Lowering the concentration of HQ further to a 25:75 composition gave membranes that exhibited much lower permeabilities for both salt as well as water.

As compared to membranes formed from the Bis-A : *m*-PDA system, those formed from HQ based compositions yield membranes with higher salt rejection values. This may be attributed either to the greater colinearity of the polymer chain with HQ compared to that with Bis-A (additional kink at the bridge carbon) or to the smaller size of the HQ monomer as compared to the HQ monomer, which thus allows a tighter polymer matrix packing in the HQ case.

6.2.4 Polyamide TFC Membranes Formed using 1,5-Naphthalene

In case of the polyamide membranes formed from the reaction of 1,5-naphthalene diamine with TMC, the salt rejections could not be improved beyond 85%. Even though the water permeability was very low, the sucrose rejections too could not be improved beyond 95%. This indicates the formation of thick but defective polyamide layers. Due to the poor solubility of 1,5-naphthalene diamine in water, a water : methanol (50:50) solution was used as the aqueous phase, wherein, even here, the diamine concentration could not be increased beyond 0.2%. As described in section 5.3.1, it was not possible to find a set of fabrication conditions which could sufficiently improve the RO performance of TFC membranes made by incorporating this diamine.

6.2.5 Polyamide TFC Membranes Formed using 2,6-Diaminopyridine

TFC polyamide membranes incorporating 2,6-diaminopyridine also did not exhibit sufficiently high salt rejections to be considered a RO membranes (max. 89 - 92% NaCl rejection). Though the water permeability and sucrose rejection of these membranes were better than with the 1,5-naphthalene diamine system, they were much lower than that of the standard polyamide membrane. At certain conditions (3% 2,6-diaminopyridine and 0.35% TMC in hexane) membranes could be made which exhibited reasonably high salt and water permeabilities with low sucrose permeabilities. Further variations (see section 5.3.2) in the amine or acid chloride concentrations and other fabrication variables did not improve the salt rejection nor were any further improvements seen for increasing the separation between salt and sucrose.

6.3 CHLORINE TOLERANCE STUDIES

6.3.1 Effect of Ester Incorporation on Chlorine Tolerance of Polyesteramide TFC membranes

Chlorine tolerance studies, based on the chlorine exposure required to double the salt passage rate, were conducted on membranes prepared with 50:50 compositions based on *m*-AP : *m*-PDA, Bis-A : *m*-PDA and HQ : *m*-PDA and 25:75 HQ : *m*-PDA reacted with TMC in each case. At the 50:50 composition ratio, FTIR analysis showed that the final membrane would contain ~10% ester linkages in the *m*-AP case and ~22% ester linkages in the case of the two diols. The adduct study had already shown that aromatic ring chlorination is less feasible for the diesters compared to adducts prepared with diamines or aminophenols.

The study shows that the most important variable affecting the chlorination resistance of the polyesteramide membranes is simply the level of ester linkages incorporated into the copolymer. Unless there is a certain minimum level of ester functions (22%) incorporated in the polyesteramide membrane, no significant improvement in chlorine tolerance is seen. To a first approximation, the chemistry through which these ester linkages are introduced into the TFC structure is less important for determining the increase in chlorine tolerance. Diols are more effective than aminophenols in increasing chlorine tolerance, primarily because twice the number of ester linkages are introduced into the structure per monomer unit and the fact that the aromatic rings contributed by the diols are not susceptible to chlorine attack as was evidenced from the adduct study. As a result, the available sites for N-chlorination attack are reduced considerably for the diol based systems in comparison to the *m*-AP based system and the standard polyamide.

6.3.2 Effect of Lower Percent Ester Incorporation

Both the polyesteramide membranes formed from the 50:50 *m*-AP : *m*-PDA and the 25:75 HQ : *m*-PDA based systems contain a similar low proportion of ester linkages (10 – 11%) and show low chlorination resistance, that is only slightly better than that of the standard polyamide membrane. The polyesteramide membrane formed from the 50:50 *m*-AP : *m*-PDA composition exhibited a chlorine tolerance that was only 1.58x higher while that formed from the 25:75 HQ : *m*-PDA composition showed 1.96x higher as compared to the standard polyamide membrane tested under the same conditions separately in each case. The lower chlorine tolerance of the *m*-AP based composition in this case as compared to the HQ case is consistent with the model compound study wherein the esteramide obtained by the benzoylation of *m*-AP exhibited only a minimal degree of chlorine tolerance while the diester obtained from HQ showed no chlorination effect even on the most severe treatment C. Also, the salt transmission through the polyesteramide membrane formed from the *m*-AP based system deteriorated at the same rate as the standard polyamide membrane while that formed from the HQ based system remains mostly unaffected till 400 ppm-hours.

6.3.3 Effect of Increased Percent Ester Incorporation

Increasing the HQ : *m*-PDA ratio from 25:75 to 50:50 resulted in polyesteramide membranes that gave a substantial increase in chlorination resistance. Both the polyesteramide membranes formed from 50:50 Bis-A : *m*-PDA and HQ : *m*-PDA systems showed enhanced chlorine tolerance of about 4x as compared to the standard polyamide membrane. This is encouraging as useful RO membranes can be prepared from these systems at even higher levels of diol incorporation. Though the HQ based system gives better salt rejection than the Bis-A system, there is no significant difference between either monomer in terms of chlorine tolerance of the resultant membranes.

6.3.4 Change in Water Flux on Chlorination

All the membranes showed an initial rapid decline in the water permeability on initial chlorination. This indicates rapid N-chlorination which destroys the H-bonding potential of the membrane followed by a more gradual ring chlorination process. Both these processes render the membrane hydrophobic. In certain instances, the reference standard polyamide membranes did show an increase in the water permeability values at higher chlorination times which is indicative of chain cleavage that results in polymer structural breakdown. Comparatively, the polyesteramide membranes do not show the increasing flux regime corresponding to structural degradation of the membrane. However, it is probable that with still increased chlorination times, than that reported in this study the same effect would have been observed for the polyesteramide membranes as well.

REFERENCES

Akcatel, P. and B. Jasse, J. Polym. Sci., Polm. Chem. Ed. 14(6), (1976), 1537.

Allegrezza Jr., A.E., B.S. Parekh, P.L. Parise, E.J. Swiniarski and J.L. White, Chlorine resistant polysulfone reverse osmosis modules, Desalination, 64 (1987), 285.

Arthur, S.D., Structure-property relationship in a thin film composite reverse osmosis membrane, J. Membrane Sci., 46 (1989), 243.

Avlonitis, S., W.T. Hanbury and T. Hodgkiess, Chlorine degradation of aromatic polyamides, Desalination, 85 (1992), 321-334.

Bell, A.T., T. Wydeven and C. Johnson, A study of the performance and chemical characteristics of composite reverse osmosis membranes prepared by plasma polymerization of allylamine, J. Appl. Polym. Sci., 19 (1975), 1911.

Bhattacharyya, D. and M. E. Williams, Separation of hazardous organics by low pressure reverse osmosis membranes, NTIS Report No. PB91-234625 (1991).

Bourganel, J., U.S. Pat. 4, 026, 977 (May 31, 1977).

Buck, K.R. and V.R. Davar, Application of glow discharge polymerization to the preparation of reverse osmosis membranes, Polymer J., 2 (1970), 238.

Cabasso, I., E. Klein and J.K. Smith, Polysulfone hollow fibers. I. Spinning and properties, J. Appl. Polm. Sci., 21 (1977), 165.

Cadotte, J.E., U.S. Pat. 3, 926,798 (Dec. 16, 1975).

Cadotte, J.E., K.E. Cobian, R.H. Forester and R. J. Petersen, Continued evalutation of in-situ formed condensation polymers for reverse osmosis membranes, NTIS Report No. PB-253193 (Apr. 1976).

Cadotte, J.E., M.J. Steuck and R.J. Petersen, Research on in-situ-formed condensation polymers for reverse osmosis membranes, NTIS Report No. PB-288387 (Mar. 1978).

Cadotte, J.E., R.S. King and N.A Newkumet, Advanced poly(piperazineamide) reverse osmosis membranes, NTIS Report No. PB-80-127574 (Sep. 1979).

Cadotte, J.E., R.J. Petersen, R.E. Larson and E.E. Erickson, A new thin-film composite seawater reverse osmosis membrane, Desalination, 32 (1980), 25.

Cadotte, J.E and R.J. Petersen, Thin-film composite membranes: origin, development and recent advances, in: A.F. Turbak (Ed.), Synthetic membranes, Vol. 1, Desalination, ACS Symp. Ser. No. 153, (1981), 305.

Cadotte, J.E., U.S. Pat. 4, 259, 183 (Mar. 31, 1981).

Cadotte, J.E., U.S. Pat. 4, 277, 344 (1981).

Cadotte, J.E., Evolution of composite reverse osmosis membranes, in: R.L. Douglas (Ed.), Materials Science of Synthetic Membrane, ACS, Washington DC, (1985).

Cadotte, J., R. Forester, M.Kim, R. Petersen and T. Stocker, Nanofiltration membranes broaden the use of membrane separation technology, Desalination, 70 (1988), 77.

Cadotte, J.E. U.S. Pat. 4, 895, 661 (Jan. 23, 1990).

Carothers, W.H. and J.W. Hill, J. Amer. Chem. Soc., 54 (1932), 1566.

Chakravorty, B. and A. Srivastava, Application of membrane technologies for recovery of water from pulp and paper mill effluents, Deasalination, 67 (1987), 363.

Challis, B.C. and J.A. Challis, Reactions of the carboxamide group, In : J. Zabicky (ed.), The Chemistry of Amides, Wiley Interscience, New York, (1970), 775.

Chan, W.H., S.Y. Lam-Leung and C.F. Ng, Poly. Comms., 32 (1991), 503.

Credali, L., A. Chiolle and P. Parrini, New polymer materials for reverse osmosis membranes, Desalination, 14 (1974), 137.

Comstock, D.L., Desal-5 membrane for water softening, Desalination, 76 (1989), 61.

Davis, R.B., D.K. Schiffer and C.E. Kramer, Hollow fiber reverse osmosis composite membranes: process and properties, Synthetic membranes, Vol. 1, Desalination, ACS Symp. Ser. 153, (1981).

Eriksson, P., Water and salt transport through two types of polyamide composite membranes, J. Membrane Sci., 36, (1988), 297.

Francesco, P., B. Francesco and F.Otello, Manufacture of asymmetrical membrane of polyesteramide, Eur. Pat. Appl. EP 251, 376 (Jan 7, 1988).

Francis, P.S., Fabrication and evaluation of new ultrathin reverse osmosis membranes, NTIS Report No. PB-177083 (Feb. 1966).

Frommer, M.A., R. Matz and U. Rosenthal, Ind. Eng. Chem. Prod. Res. Dev., 10 (1971), 193.

Gao, C., X. Lu and Z. Bao, Polysulfone amide (PSA) asymmetric RO membrane, Desalination, 83 (1991), 271.

Gittens, G., P. Hitchcock and G. Wakely, Desalination, 2 (1973), 315.

Glater, J., J.W. McCutchan, S.B. McCray and M.R. Zachariah, The effect of halogens on the performance and durability of reverse-osmosis membranes, in: A.F. Turbak (Ed.), Synthetic Membranes, ACS series, 153 (1981), 171.

Glater, J., M.R. Zachariah, S.B. McCray and J.W. McCutchan, Halogen interactions with typical RO membranes, Water Reuse Symposium II, Vol. 2, Aug. 23-28 Washington, D.C., (1981), 1399.

Glater, J., M.R. Zachariah, S.B. McCray and J.W. McCutchan, Desalination, 48 (1983), 1.

Glater, J. and M.R. Zachariah, A mechanistic study of halogen interaction with polyamide reverse osmosis membranes, in: ACS Symp. Ser., 281 (1985), 345.

Glater, J., S-K. Hong and M. Elimelech, Search for a chlorine-resistant reverse osmosis membrane, Desalination, 95 (1994), 325.

Gonsalves, K.E. and C. Xiaomao, ACS Symp. Ser. 545 (Polymeric Drugs and Drug Administration), (1994), 181.

Hara, S., K. Mori, Y. Taketani, T. Noma and M. Seno, Reverse osmosis membranes from aromatic polymers, Desalination, 21 (1977), 183.

Hickman, C.E., I. Jamjoon, A.B. Riedinger and R.E. Seaton, Jeddah seawater reverse osmosis installation, Desalination, 30 (1979), 259.

Himeshima, Y. and T. Uemura, Jpn. Kokai Tokkyo Koho JP 01, 254, 203.

Hollahan, J.R. and T. Wydeven, Some experimental parameters affecting performance of composite reverse osmosis membranes produced by plasma polymerization, J. Appl. Polym. Sci., 21 (1977),923.

Hou, T., S. Dong and L. Zheng, The study of mechanism of organic additive action in the polysulfone casting solution, Desalination, 83 (1991), 343.

Hurndall, M.J., E.P. Jacobs and R.D. Sanderson, The performance of novel reverse osmosis membranes made from poly-2-vinylimidazoline.I, Desalination, 86 (1992), 135.

Ikeda, K., S. Yamamoto and T. Takii, Jpn. Kokai Tokkyo Koho JP 60, 255, 109 (1984).

Ikeda, K., S. Yamamoto and T. Takii, Jpn. Kokai Tokkyo Koho JP 60, 255, 110 (1984).

Ikeda, K., S. Yamamoto and H. Ito, Eur. Pat. Appl. EP 165, 077 (1985).

Imasu, K., Wastewater recycle in the plating industry using brackish water reverse osmosis elements, Desalination, 56 (1985), 137.

Jian, S. and S.X. Ming, Crosslinked PVA-PS thin-film composite membrane for reverse osmosis, Desalination, 62 (1987), 395.

Joshi, S.V. and A.V. Rao, Cellulose triacetate membranes for seawater desalination, Desalination, 51 (1984), 307.

Kakimoto, M-A., Y.S. Negi and Y. Imai, Synthesis and characterization of aromatic polyesters and polyamide-esters from bisphenols and aromatic aminophenols, and 2,5-bis(4-chloroformyl)-3,4-diphenylthiophene, J. Polym. Sci., Part A : Polym. Chem., 24 (1986), 1511.

Katz, M. G. and T. Wydeven, Jr., Poly(vinyl alcohol) membranes for reverse osmosis, in: A.F. Turbak (Ed.), Synthetic membranes, Vol. 1, Desalination, ACS Symp. Ser. No. 153, (1981).

Kawada, I., K. Inoue, Y. Kazuse, H. Ito, T. Shintani and Y. Kamiyama, New thin-film composite low pressure reverse osmosis membranes and spiral wound modules, Desalination, 64 (1987), 387.

Kawaguchi, T., Y. Taketani, H. Minematsu, N. Sasaki, Y. Hayashi and S. Hara, U.S. Pat. 4, 242, 208 (Dec. 30, 1980).

Kawaguchi, T. and H. Tamura, Chlorine-resistant membrane for reverse osmosis. II. Preparation of chlorine-resistant polyamide composite membranes, J. of Appl. Poly. Sci., Vol. 29, (1984), 3369.

Kawaguchi, T. and H. Tamura, Chlorine-resistant membrane for reverse osmosis. I. Correlation between chemical structures and chlorine resistance of polyamides, J. Appl. Polym. Sci., 29 (1984), 3359.

Kazuse, N., T. Shintani and A. Iwama, Jpn. Kokai Tokkyo Koho JP 61, 093 806 (1984).

Kesting, R.E., Phase inversion membranes, in: D.R. Lloyd (Ed.), Material science of synthetic membranes, ACS Symp. Ser. No. 269 (1955), 131.

Kesting, R.E., Synthetic polymeric membranes : A structural perspective, 2nd edition, Wiley Interscience, New York (1985).

Kesting, R.E., A.K. Fritzsche, M.K. Murphy, C.A. Cruse, A.C. Handermann, R.F. Malon and M.D. Moore, The second generation polysulfone gas separation membrane. I. The use of Lewis acid: base complexes as transient templates to increase free volume, J. Appl. Polym. Sci., 40 (1990), 1557.

Kesting, R.E., A.K. Fritzsche, C.A. Cruse and M.D. Moore, The second generation polysulfone gas separation membrane. II. The relationship between sol properties, gel macrovoids and fiber selectivity, J. Appl. Polym. Sci., 40 (1990), 1576.

Khanna, Y.P. and E.M. Pearce, Aromatic polyamides. I. Synthesis and characterization of some aromatic polyamides and their model diamides, J. of Polym. Sci. : Polym. Chem. Ed., 19 (1981), 2799.

Kim, J-J., K. Chang and S-Y. Kwak, Composite reverse osmosis membrane having active layer of aromatic polyester or copolymer of aromatic polyester and aromatic polyamide, U.S. Pat. 5, 593, 588 (Jan. 14, 1997).

Kimmerle, K. and H. Strathmann, Analysis of the structure-determining process of phase inversion membranes, Desalination, 79 (1990), 283.

Kinzer, K.E. and D.R. Lloyd, Phase inversion sulfonated polysulfone membranes, J. Membr. Sci., 22 (1985), 1.

Ko, A. and Guy, D., Brackish and seawater desalting, in: B. Parekh, (Ed.), Reverse Osmosis Technology, Chap. 5, New York, Marcel Dekker (1988).

Koo, J-Y., R.J. Petersen and J.E. Cadotte, ESCA characterization of chlorine damaged polyamide reverse osmosis membrane, Polym. Prepr., 27 (2), (1986), 391.

Koros, W., G. Fleming, S. Jordan, T. Kim and H. Hoehn, Polymeric membrane materials for solution-diffusion based permeation separations, Prog. Polym. Sci. 13 (1988), 339.

Korshak, V.V., S.V. Vinogradova, T.M. Frunze and L.V. Kozlov, Vysokomol. Soedin., 4 (1962), 1457.

Korshak, V.V., S.V. Vinogradova and U. Ban-yuan, ibid., 5 (1963), 969.

Idem, ibid., 5 (1963), 1765.

Idem, Izv. Akad. Nauk SSSR, Ser. Chem., (1964), 897.

Korshak, V.V., S.V. Vinogradova, G. Sh. Papava, R.P. Tsiskarishvili and P.D. Tsiskarishvili, Vysokomol. Soedin., Ser. A, 14 (1972), 1699.

Kurihara, M., N. Kanamaru, N. Harumiya, K. Yoshimura and S. Hagiwara, Spiral-wound new thin film composite membrane for a single-stage seawater desalination by reverse osmosis, Desalination, 32 (1980), 13.

Kurihara, M., T. Watanabe and T. Inoue, U.S. Pat. 4, 366, 062 (Dec. 28, 1982).

Kurihara, M., T. Uemura, Y. Nakagawa and T. Tonomura, The thin-film composite low pressure reverse osmosis membranes, Desalination, 54 (1985), 75.

Kurihara, M. and Y. Himeshima, The major developments of the evolving reverse osmosis membranes and ultrafiltration membranes, Polym. J., 23(5), (1991), 513.

Kurihara, M., Y. Fusaoka, T. Sasaki, R. Bairinji and T. Uemura, Development of crosslinked fully aromatic polyamide ultra-thin composite membranes for seawater desalination, Desalination, 96 (1994), 133.

Kwak, S.Y., Effects of bisphenol monomer structure on the surface morphology and reverse osmosis (RO) performance of thin film composite membranes, J. Polym. Sci. Part B-Polym. Phys., 34 (13), (1996), 2201.

Larson, R.E., J.E. Cadotte and R.J. Petersen, Development of the FT-30 thin film composite membrane for seawater desalting applications , NWSIA Journal, 8 (1), (1981), 15.

Larson, R.E., J.E. Cadotte and R.J. Petersen, The FT-30 seawater reverse osmosis membrane-element test results, Desalination, 38 (1981), 473.

Lang, K., T. Matsuura, G. Choudhary and S. Sourirajan, Preparation and testing of polyvinyl alcohol composite membranes for reverse osmosis, The Canadian J. of Chem. Eng., 73 (1995), 686.

Lau, W.W.Y., M.D. Guiver and T. Matsuura, Phase separation in polysulfone/solvent/water and polyethersulfone/solvent/water systems, J. Membrane Sci., 59 (1991), 219.

Lee, E.K., W.C. Babcock, R.P. Brass, P.A. Bresnahan and M.B. Chidlaw, Novel composite membranes, Technical Completion Report for U.S. Department of Interior, Bureau of Reclamation, DWRT, NTIS PB 83-243170 (1983).

Loeb, S. and S. Sourirajan, Sea water demineralization by means of an osmotic membrane, Advan. Chem. Ser., 38 (1962), 117.

Loeb, S. and S. Sourirajan, U.S. Pat. 3, 133, 132 (1964).

Lonsdale, H., U. Merten and R. Riley, Transport properties of cellulose acetate osmotic membranes, J. Appl. Polym. Sci., 9 (1965), 1341.

Lowell, Jr., J.R., D.T. Friesen, S.B. McCray, S.D. McDermott, D.J. Brose and R.J. Ray, Model compounds as predictors of chlorine sensitivity of interfacial polymer reverse osmosis membranes, Proceedings of the 1987 International Congress on Membranes and Membrane Processes, Tokyo, (1987).

Manjikian, S., Ind. Eng. Chem. Prod. Res. Dev., 6 (1967), 23.

March, J., Advanced Organic Chemistry : Reactions, Mechanisms and Structure, 4th ed., John Wiley, New York, (1992).

McKinney, Jr., R., Reverse osmosis separations with aromatic polyamide films and hollow fibers, Separation and Purification Methods, 1 (1972), 31.

McKinney, Jr., R., Properties of aromatic polyamide and polyamide-hydrazide membranes, in: H.K. Lonsdale and H.E. Podall (Eds.), Reverse Osmosis Membrane Research, Plenum Press New York (1972).

Merten, U. (Ed.), Desalination by Reverse Osmosis, MIT Press, Cambridge, Mass. (1966).

Morgan, P.W., Condensation Polymers: By Interfacial and Solution Methods, Interscience Publishers, NY, (1965).

Muirhead, A., S. Beardsley and J. Aboudiwan, Performance of the 12,000 m3/day seawater reverse osmosis desalination plant at Jeddah, Saudi Arabia January 1979 through January 1981, Desalination, 42 (1982), 115.

Mungle, C.R. and R.L. Fox, Method of making asymmetric cellulose triacetate membranes, U.S. Pat. 4, 026, 978 (May 31, 1977).

Murakami, H. and N. Igarashi, PBIL tubular reverse osmosis. Application as low-energy concentrators, Ind. Eng. Chem. Prod. Res. Dev., 20 (1981), 501.

Niwa, M., H. Ohya, E. Kuwahara and Y. Negishi, Reverse osmotic concentration of aqueous 2-butanone (methyl ethyl ketone), tetrahydrofuran and ethyl acetate solutions, J. Chem. Eng. Jpn., 21 (1988), 164.

Orton, K.J.P., F.G. Soper and G. Williams, The chlorination of anilides. III. N-chlorination and C-chlorination as simultaenous side reactions, J. Chem. Soc., (1928), 998.

Panar, M., H. H. Hoehn and R.R. Herbert, The nature of asymmetry in reverse osmosis membranes, Macromolecules, 6 (1973), 777.

Panayotov, I.M., Polyesteramides, in: F. Millich, (Ed.), Interfacial Synthesis, Vol. 2, Marcel Dekker, New York, (1977).

Parekh, B., Reverse osmosis technology, New York : Marcel Dekker (1988).

Parrini, P., Polypiperazineamides: new polymers useful for membrane processes, Desalination, 48 (1983), 67.

Petersen, R.J., R.E. Larson and J.E. Cadotte, Industrial applications of the FT-30 reverse osmosis membrane, World Filtration Congress III, Proceedings, Vol. 2 (1982), 541.

Petersen, R.J., Composite reverse osmosis and nanofiltration membranes, J. Membrane Sci., 83 (1993), 81.

Plummer, C.W., G. Kimura and A.B. LaConti, Development of sulfonated polyphenylene oxide membranes for reverse osmosis, OSW Report No. 551 (1970).

Preston, J., J. Polym. Sci., Part A-1, 8 (1970), 3135.

Pusch, W., Measurement techniques of transport through membranes, Desalination, 59 (1986), 105.

Pusch, W., Efficiency of synthetic membranes in comparison with biological membranes, Desalination, 62 (1987), 5.

Quentin, J.P., U.S. Pat. 3, 709, 841 (Jan. 9, 1973).

Rajinder, S., Characteristics of a chlorine-resistant reverse osmosis membrane, Deaslination, 95 (1), (1994), 27.

Redondo, J.A. and K.F. Frank, Sea water applications with FILMTEC* reverse osmosis membranes from small to large plants in 10 years, Desalination, 82 (1991), 31.

Reid, C.E. and Breton, E.J., J. Appl. Polym. Sci., 1 (1959), 133.

Richter, J.W. and H.H. Hoehn, U.S.Pat. 3, 567, 632 (March 2, 1971).

Riley, R.L., H.K. Lonsdale, L.D. La Grange and C.R. Lyons, Development of ultrathin membranes, Office of Saline Water, Report No. 386 (1969).

Riley, R.L., R. L. Fox, C.R. Lyons, C.E. Milstead, M.W. Seroy and M. Tagami, Spiral-wound poly(ether/amide) thin film composite membrane systems, Desalination, 19 (1976), 113.

Riley, R.L., C.E. Milstead, A.L. Lloyd, M.W. Seroy and M. Tagami, Spiral-wound thin film composite membrane systems for brackish and seawater desalination by reverse osmosis, Desalination, 23 (1977), 331.

Ridgway, Jr. H.F., Microbial adhesion and biofouling of reverse osmosis membranes, In : B.S. Parekh (ed.), Reverse Osmosis Technology, Marcel Dekker, New York, (1988).

Rozelle, L.T., J.E. Cadotte, R.D. Corneliussen and E.E. Erickson, Final report on development of new reverse osmosis membranes, NTIS Report No. PB-206329 (Jun. 1968).

Rozelle, L.T., J.E. Cadotte. K.E. Cobian and C.V. Kopp Jr., Nonpolysaccharide membranes for reverse osmosis: NS-100 membranes, in: S. Sourirajan (Ed.), Reverse Osmosis and Synthetic Membranes, National Research Council Canada, Ottawa, (1977).

Sano, T., A new reverse osmosis membrane made of polyacrylonitrile, CEER, Chem. Econ. Eng. Rev., 12 (5), (1980), 22.

Sano, T., T. Shimomura, M. Sasaki and I. Murase, U.S. Pats. 4, 107, 049 (Aug. 15 1978); 4, 147, 745 (Apr. 3, 1979) and 4, 272, 378 (Jun. 9, 1981).

Satre, M.D. and N.D. Ghatge, Aromatic polyamide-hydrazides for water desalination II-RO membrane performance of terpolymers, Desalination, 91 (1993), 121.

Scala, L.C., D.F. Ciliberti and D. Berg, U.S. Pat. 3, 744, 643 (Jul. 10, 1973).

Shimomura, T., M. Hirakawa, I. Murase, M. Sasaki and T. Sano, Preparation of polyacrylonitrile reverse osmosis membrane by plasma treatment. J. Appl. Polym. Sci., 38 (1984), 173.

Shafer, J.A., Directing and activating effects of the amido group, in: J. Zabicky (Ed.), The Chemistry of Amides, Wiley Interscience, New York, (1970), 689.

She, J. and X. Shen, Crosslinked PVA-PS thin film composite membrane for reverse osmosis, Desalination, 62 (1987), 385.

Silverstein, R.M, G.C. Bassler and T.C. Morrill, Spectrometric identification of organic compounds, Wiley, New York, (1974).

Skoog, D.A. and D.M. West, Principles of Instrumental analysis, Holy, Rinehart and Winston, New York, (1974).

Solomon, T.W.G., Organic Chemistry, 5th ed., John Wiley, New York, (1992).

Soltanieh, M. and W. Gill, Review of reverse osmosis membranes and transport models, Chem. Eng. Comm. 12 (1981), 279.

Sundet, S.A., U.S. Pats. 4, 529, 646 (Jul. 15, 1985); 4, 626, 468 (Dec. 2, 1986); 4, 643, 829 (Feb. 17, 1987); 4, 719, 062 (Jan. 12, 1988); 4, 783, 346 (Nov. 8, 1988); 5, 015, 380 (May 14, 1991); 5, 015, 382 (May 14, 1991).

Sundet, S.A., U.S. Pat. 5, 019, 264 (May 28,1991).

Swedo, R.J. and J.J. Zupancic US Patent 4, 885, 091 (1989).

Tsai, H-B. and Y-D Lee, Polyarylates III. Kinetic studies of interfacial polycondensation, J. Polym. Sci., Part A : Polym. Chem. 25 (8), (1987), 2195.

Tsai, H-B. and Y-D Lee, Polyarylates V. The influence of phase transfer agents on the interfacial polycondensation, J. Polym. Sci., Part A : Polym. Chem., 26 (8), (1988), 2039.

White, G.C., Disinfection of Wastewater and Water for Reuse, Van Nostrand Reinhold, New York, New York (1978).

White, G.C., Handbook of chlorination : For potable water, wastewater, cooling water, industrial processes and swimming pools, (1972).

Williams, J.L.R., J.M. Carlson and G.A. Reynolds, Makromol. Chem., 65 (1963), 54.

Wrasidlo, W.J., U.S. Pat. 3, 951, 815 (Apr. 10, 1976).

Wrasidlo, W.J., U.S. Pat. 4, 005, 012 (Jan. 25, 1977).

Wu, S., G. Zheng, H. Lian, J. Xing and L. Shen, Chlorination and oxidation of aromatic polyamides. I. Synthesis and characterization of some aromatic polyamides, J. of Appl. Poly. Sci., Vol. 61, (1996), 415.

Wu, S., J. Xing, G. Zheng, H. Lian and L. Shen, Chlorination and oxidation of aromatic polyamides. II. Chlorination of some aromatic polyamides, J. of Appl. Poly. Sci., Vol. 61, (1996), 1305.

Yang, M.H. and T. J. Chu, The effect of skin layer composition and operating parameters on the performance of sulfonated polysulfone-poly(vinyl alcohol) composite reverse osmosis membrane, Sep. Sci. and Tech., 28(6), (1993), 1315.

Yasuda, H., H.C. Marsh and J. Tsai, Preparation of composite reverse osmosis membranes by plasma polymerization. II. Copolymerization of unusual monomers, J. Appl. Polym. Sci., 19 (1975), 2157.

Yasuda, H. and H.C. Marsh, Preparation of composite reverse osmosis membranes by plasma polymerization of organic compounds. III. Plasma polymers of acetylene/CO/H_2O, J. Appl. Polym. Sci., 19 (1975), 2981.

Yasuda, H., Composite reverse osmosis membranes prepared by plasma polymerization, in: S. Sourirajan (Ed.), Reverse Osmosis and Synthetic Membranes, National Research Council Canada, Ottawa, (1977).

APPENDIX 1

Table 1 : Water and solute permeabilities of some commercial NF membranes

Membrane	Water flux (lmh)	Salt rej. (%)	Glucose rej. (%)	Pressure (MPa)	A x 10^{-6} (m/s-MPa)	B_{salt} x 10^{-6} (m/s)	$B_{gluc.}$ x 10^{-6} (m/s)
NF-40	43.18	45.00	90.00	1.60	7.83	14.70	1.33
NF-50	77.50	50.00	90.00	0.39	66.6	21.50	2.39
NF-70	34.00	75.00	98.00	0.48	19.60	3.15	0.193
NF-40HF	43.18	40.0	90.00	0.89	14.30	18.00	1.33
XP-45	36.04	50.0	-	0.70	16.10	10.00	-
UTC-20HR	102.00	75.00	85.00	1.50	20.40	9.44	5.00
UTC-20HF	146.20	50.00	-	1.50	28.50	40.60	-
Desal-5	46.07	47.00	83.00	1.00	13.80	14.40	2.62

Table 2 : Specifications of standard equipment used

Equipment	Make
UV-Vis Spectrophotometer (model UV-240)	Shimadzu Corporation, Japan
IR Spectrometer (model 683)	Perkin-Elmer, USA
FTIR Spectrometer (model 60 SXB)	Nicolet, USA
NMR Spectrometer (model 200/300 MHz)	Bruker, USA
Digital Conductivity meter (model 1292)	Systronics, India
Digital pH meter (model DPH 500)	Global Electronics, India
Melting point apparatus	Kumar, India
Chloroscope kit	Water Chem., India

Table 3 : List and specifications of materials used

Material	Acronyms	Grade	Supplier
Acids			
Hydrochloric acid	HCl	AR	S.D. Fine Chem. Ltd., India
Bases			
Sodium hydroxide	NaOH	AR	S.D. Fine Chem. Ltd., India
Triethylamine	TEA	LR	S.D. Fine Chem. Ltd., India
Potassium hydroxide	KOH	AR	S.D. Fine Chem. Ltd., India
Diamines			
o-Phenylene diamine	*o*-PDA	AR	Loba Chemie, India
m-Phenylene diamine	*m*-PDA	AR	Aldrich Chemical Co., USA
p-Phenylene diamine	*p*-PDA	LR	Loba Chemie, India
1,5-Naphthalene diamine		AR	Aldrich Chemical Co., USA
2,6-Diaminopyridine		AR	Aldrich Chemical Co., USA
Diols			
Resorcinol	Res	AR	Qualigens, India
Hydroquinone	HQ	AR	Qualigens, India
Bisphenol-A	Bis-A	AR	Aldrich Chemical Co., USA
Aminophenols			
m-Aminophenol	*m*-AP	AR	Loba Chemie, India
p-Aminophenol	*p*-AP	AR	Fluka Chemie, Switzerland
Acid chlorides			
Benzoyl chloride		AR	Thomas Baker Chemical
Benzenetricarbonyl trichloride (trimesoyl chloride)	TMC	AR	Aldrich Chemical Co., USA
Miscellaneous chemicals/reagent			
Orthotolidine reagent		LR	S.D. Fine Chem. Ltd., India
Sodium hypochlorite solution	NaOCl	LR	Crystal Corporation, India
Sodium lauryl sulfate	SLS	LR	S.D. Fine Chem. Ltd., India
Bovine Serum Abumin	BSA	Purified	Hi Media Labs., India
Sucrose		LR	S.D. Fine Chem. Ltd., India
Sodium chloride	NaCl	AR	S.D. Fine Chem. Ltd., India
Benzyl alcohol		AR	S.D. Fine Chem. Ltd., India
Phase transfer catalyts			
Benzyltriethylammonium chloride	BTEAC	AR	Fluka Chemie, Switzerland
Tetrabutylammonium bromide	TBABr	AR	Fluka Chemie, Switzerland

Table 3 : (contd.).....

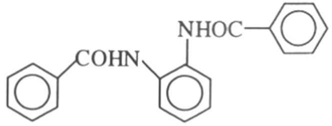
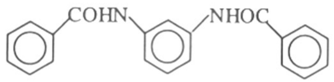
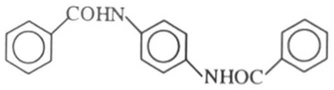
Material	Acronyms	Grade	Supplier
Solvents			
Methanol		AR	S.D. Fine Chem. Ltd., India
Ethyl acetate		AR	S.D. Fine Chem. Ltd., India
Petroleum ether		AR	S.D. Fine Chem. Ltd., India
Hexane		AR	S.D. Fine Chem. Ltd., India
Chloroform		AR	S.D. Fine Chem. Ltd., India
Cyclohexane		AR	S.D. Fine Chem. Ltd., India
1,4-Dioxane		AR	S.D. Fine Chem. Ltd., India
Acetone		AR	S.D. Fine Chem. Ltd., India
N, N-Dimethyl formamide	DMF	AR	S.D. Fine Chem. Ltd., India

Table 4 : Various chlorine treatment levels for the adducts

Treatment	Chlorine conc. (ppm)	No. of days
A	10,000	1
B	35,000	1
C	35,000	7
D (untreated)	No chlorine	-

APPENDIX 2

Table 1 : IR frequencies for absorption bands corresponding to untreated diamides

 Diamide from *o*-PDA	 Diamide from *m*-PDA	 Diamide from *p*-PDA	Assignments
650 690 710 750 (S) 850	700 710 790 (S) 800 860 880	650 680 710 (S) 815 (S)	Out of plane bending of C-H bonds of mono-, ortho-, meta- and para- substituted aromatic rings.
1020 1065 1100	1020	1015 (M) 1060	In plane bending of C-H bonds
1270 (M)	1250 (W)	1260 (M)	Interaction of N-H bending and C-N stretching
1300 (S) 1310 1370	1320 (S) 1370	1305 (S) 1390	Aromatic C-N stretching
1440 (S) 1480 1490	1430 (S) 1450	1430 (M) 1450 1470	C=C ring stretching
1520 (S) 1540	1500 (S) 1530	1500 1520 1530 (S)	Amide (II) band due to interaction of N-H bending and C-H stretching

... contd.

Table 1 (continued)...

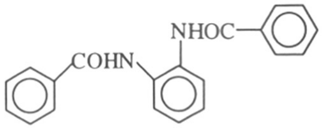
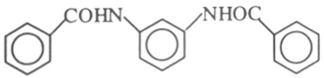
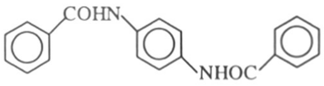
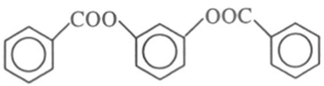
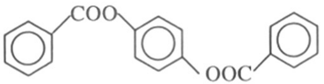
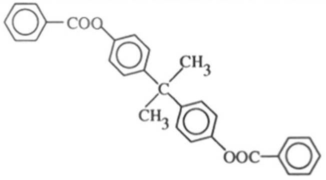
 Diamide from *o*-PDA	 Diamide from *m*-PDA	 Diamide from *p*-PDA	Assignments
1570 1590 (S)	1570 1590 (S)	1570 1590 (S)	C=C ring stretching
1650 (S)	1630 (S)	1630 (S)	Amide (I) band due to C=O stretching
3050 (W)	3040 (W)	3050 (W)	Aromatic C-H stretching
3120 (W)	3100 (W)	3120 (W)	Overtone of Amide (II) band
3250 (S)	3250 (S)	3320 (S)	N-H stretching

Table 2 : IR frequencies for absorption bands corresponding to untreated diesters

 Diester from Res	 Diester from HQ	 Diester from Bis-A	Assignments
500 (M) 555	510 (M) 520 540	527 (S)	In plane and out of plane deformations of ring in benzene derivatives
660	660 670	640	O-C-O bending in esters
690 (S) 770 (S) 790 820 890 (S)	700 (S) 770 790 805 880 (S)	712 (S) 814 (S) 874 (S)	Out of plane bending of C-H bonds of meta- and para-substituted aromatic rings
1010 (S) 1050 1070	1010 (S) 1020 1060 1080	1018 (S) 1058 (S)	In plane bending of C-H bonds
1160 1240 (S) 1260	1170 (S) 1265 (S)	1171 (S) 1206(S) 1261 (S)	C-O-C antisymmetric stretching in esters
1400 1440 (S) 1470	1450 (S)	1376 (S) 1455 (S)	C=C ring stretching

... contd.

Table 2 (continued)...

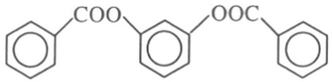
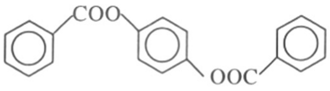
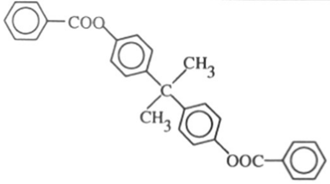
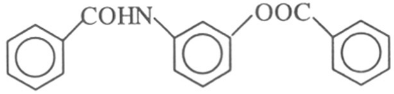
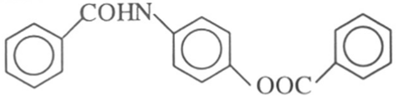
 Diester from Res	 Diester from HQ	 Diester from Bis-A	Assignments
1500 1520 1540 1600 (S)	1500 (S) 1530 1600	1501 1594 (S)	C=C ring stretching
1730 (S)	1735 (S)	1730 (S)	C=O stretching in esters

Table 3 : IR frequencies for absorption bands corresponding to untreated esteramides

 Esteramide from *m*-AP	 Esteramide from *p*-AP	Assignments
510 (S) 530 540	510 (M) 530	In plane and out of plane deformations of ring in benzene derivatives
550 580	560 590 650	O-C-O bending in esters
700 (W) 710 780 890 910	700 (S) 770 810 835	Out of plane bending of C-H bonds of meta- and para- substituted aromatic rings
1020 (S) 1060 1080	1030 1070 (S) 1090	In plane bending of C-H bonds
1140 (S)	1170 1200 (S)	Interaction of N-H bending and C-N stretching
1250 (S)	1280 (S)	C-O-C antisymmetric stretching
1320 (S) 1370 (S)	1325 (S) 1380	Aromatic C-N stretching
1440 1455 (S)	1410 (S) 1450 1465	C=C ring stretching

... contd.

Table 3 (continued)...

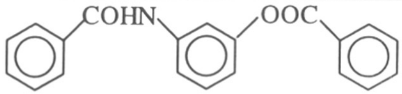
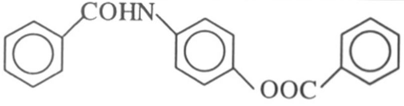
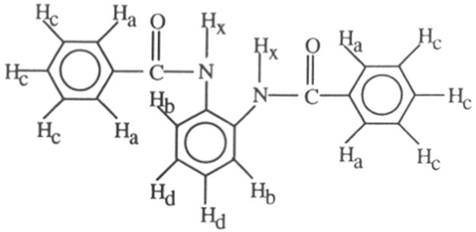
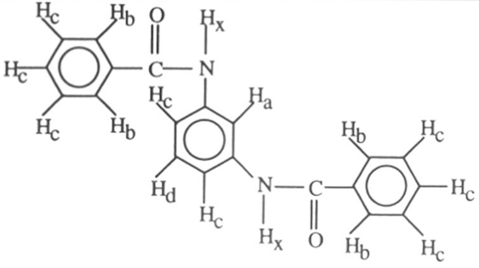
 Esteramide from *m*-AP	 Esteramide from *p*-AP	Assignments
1525 (S)	1510 1530 (S)	Amide (II) band due to interaction of N-H bending and C-N stretching
1590 1600 (S)	1580 1600 (S)	C=C ring stretching
1650 (S)	1660 (S)	Amide (I) band due to C=O stretching
1700 (S)	1720 (S)	C=O stretching in esters
3290 (S)	3310 (S)	N-H stretching

Table 4 : Melting points of the untreated, water treated and chlorine treated adducts

	Melting point (°C)				
Adducts	Recrystallized adduct D (untreated)	Water treated adduct	Adduct subjected to treatment A	Adduct subjected to treatment B	Adduct subjected to treatment C
Diamide from *o*-PDA	286 - 289	286 - 289	286 - 287	286 - 287	284 - 286
Diamide from *m*-PDA	228 - 232	227 - 230	228 - 230	229 - 232	250 - 252
Diamide from *p*-PDA	302 - 305	302 - 306	302 - 306	304 - 307	248 - 251
Diester from Res	110 - 112	110 - 112	110 - 112	110 - 112	110 - 112
Diester from HQ	195 - 199	195 - 199	195 - 199	195 -199	194 - 197
Diester from Bis-A	152 - 154	152 - 154	152 - 154	152 - 154	152 - 154
Esteramide from *m*-AP	146 - 149	146 - 149	146 - 149	117 - 120	105 - 107
Esteramide from *p*-AP	225 - 228	225 - 228	220 - 222	209 - 211	127 - 134

Table 5 : Description of signals in the proton NMR spectra of the untreated diamides in deutrated DMSO

Compound structure	Description of peaks				
	(multiplicity, number of protons, peak assignment)				
 Diamide obtained from *o*-PDA	10.1 (s;2H) H_x	7.95 (d of d;4H) H_a	7.65 (m;2H) H_b	7.55 (m;6H) H_c	7.3 (m;2H) H_d
 Diamide obtained from *m*-PDA	10.3 (s;2H) H_x	8.3 (t;1H) H_a	7.95 (d of d;4H) H_b	7.55 (m;8H) H_c	7.3 (distorted t;1H) H_d

...contd

Table 5 (continued)...

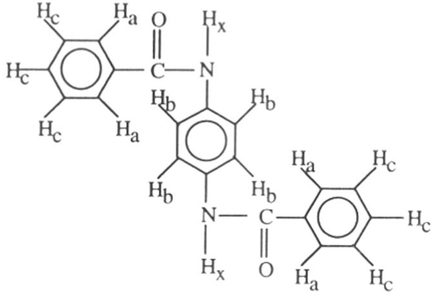
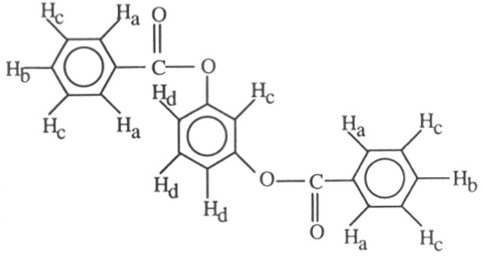
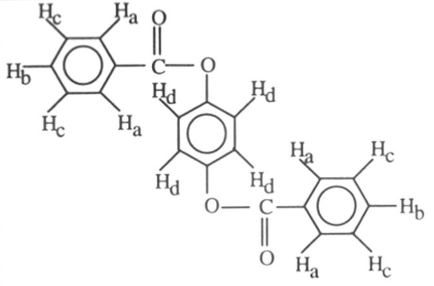
Compound structure	Description of peaks			
	(multiplicity, number of protons, peak assignment)			
 Diamide obtained from *p*-PDA	10.25 (s;2H) H_x	7.95 (d of d;4H) H_a	7.75 (s;4H) H_b	7.55 (m;6H) H_c

Table 6 : Description of signals in the proton NMR spectra of the untreated diesters in deutrated chloroform

Compound structure	Description of peaks			
	(multiplicity, number of protons, peak assignment)			
 Diester obtained from Res	8.2 (d of d;4H) H_a	7.75 (m;2H) H_b	7.6 (m;5H) H_c	7.3 (m;3H) H_d
 Diester obtained from HQ	8.25 (d of d;4H) H_a	7.7 (distorted t;2H) H_b	7.55 (m;4H) H_c	7.3 (s;4H) H_d

... contd.

Table 6 (continued)...

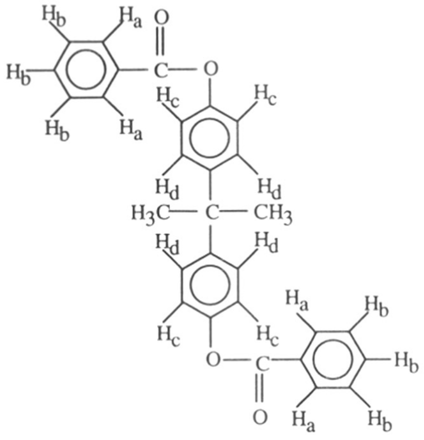
Compound structure	Description of peaks			
	(multiplicity, number of protons, peak assignment)			
 Diester obtained from Bis-A	8.25 (d of d;4H) H_a	7.55 (m;6H) H_b	7.35 (d;2H) H_c	7.15 (d;2H) H_d

Table 7 : Description of signals in the proton NMR spectra of the untreated esteramides in deutrated acetone

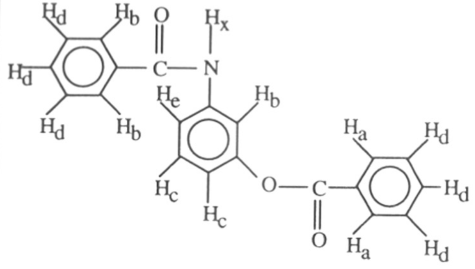
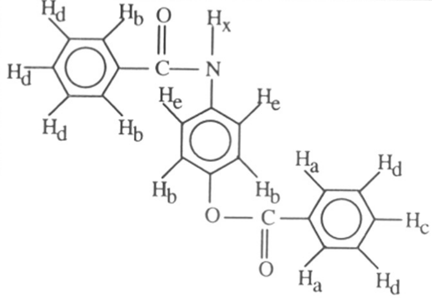
Compound structure	Description of peaks					
	(multiplicity, number of protons, peak assignment)					
 Esteramide obtained from *m*-AP	9.75 (s;1H) H_x	8.2 (d of d;2H) H_a	8.0 (d of d & one t;3H) H_b	7.75 (m;2H) H_c	7.55 (m;6H) H_d	7.05 (d of d of d ;1H) H_e
 Esteramide obtained from *p*-AP	9.7 (s;1H) H_x	8.2 (d of d;2H) H_a	8.0 (m;4H) H_b	7.75 (t of t;1H) H_c	7.6 (m;5H) H_d	7.3 (d of d;2H) H_e

Table 8 : Description of signals in the proton NMR spectra (in deutrated acetone) of the esteramide obtained from *p*-AP after subjection to treatment C showing the presence of mono- and dichlorinated products

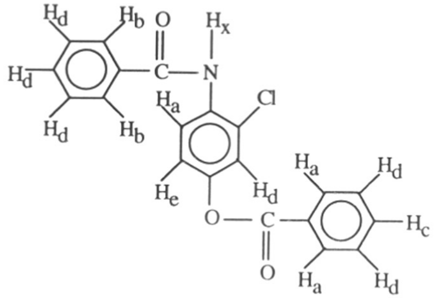
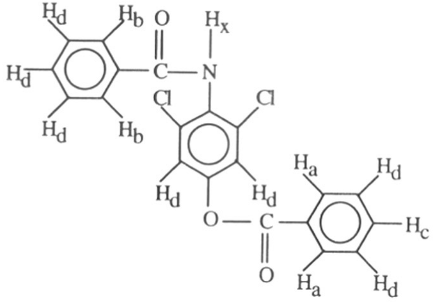
Compound structure	Description of peaks					
	(multiplicity, number of protons, peak assignment)					
 Monochlorinated	9.53 (s;1H) H_x					7.38 (d of d;1H) H_e
		8.2 (m;5H) H_a	8.1 (m;4H) H_b	7.75 (m;2H) H_c	7.6 (m;13H) H_d	
 Dichlorinated	9.17 (s;1H) H_x				7.64 (d;2H) H_d	

Table 9 : TFC membranes based on *m*-PDA alone
Aqueous phase : 2.5% *m*-PDA
Organic phase : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min)	Dip time in org. soln (sec.)	Curing (°C/min)	Salt Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)
2	30	42°C/5m	97.00	34.85	2.76	3.71	0.299
2	30	42°C/5m	97.85	19.73	2.76	2.10	0.12
2	30	42°C/5m	98.54	18.47	2.76	1.97	0.076
2	30	42°C/5m	92.55	15.24	2.76	1.62	0.34
2	30	42°C/5m	91.87	12.87	2.76	1.37	0.32

Table 10a : TFC membranes based on *m*-AP alone
Aqueous soulution : 2.5 % *m*-AP + 1: 0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	10	45°C/5m	36.34	54.79	43.69	2.69	4.97	21.3	10.0
2	35	45°C/5m	64.72	83.56	21.85	2.82	2.49	3.31	1.19
2	45	45°C/5m	23.78	45.20	54.62	2.55	6.44	48.6	18.4
2	60	45°C/5m	8.33	24.65	93.62	2.76	9.79	286	79.5
2	120	45°C/5m	61.02	80.82	16.80	2.89	1.85	2.98	1.11

Table 10b : TFC membranes based on 90:10 *m*-AP : *m*-PDA
Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (90:10) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	10	42°C/5m	27.61	82.43	47.75	1.65	10.0	34.8	2.83
2	35	42°C/5m	52.24	86.48	41.57	1.52	10.2	10.6	1.81
2	60	42°C/5m	53.31	86.48	51.73	1.58	12.0	12.6	2.25
2	30	58°C/5m	28.20	54.28	33.25	1.52	7.20	23.5	7.78

Table 10c : TFC membranes based on 80:20 *m*-AP : *m*-PDA
Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (80:20) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	10	45°C/5m	76.08	91.17	18.48	1.55	4.60	1.61	0.49
2	30	45°C/5m	78.77	90.00	7.92	2.76	0.95	0.59	0.25
2	30	45°C/5m	78.72	92.06	10.14	2.76	1.22	0.76	0.24
2	45	45°C/5m	71.42	82.85	36.94	2.82	4.23	4.11	2.12
2	45	45°C/5m	84.82	97.33	33.25	1.52	8.82	1.65	0.25
2	60	45°C/5m	78.15	91.42	33.25	2.82	3.87	2.58	0.87
2	120	45°C/5m	76.71	86.66	33.61	2.69	4.12	2.83	1.44

Table 10d : TFC membranes based on 80:20 *m*-AP : *m*-PDA with the addition of surfactant
Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (80:20) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP + 0.5% SLS
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	30	45°C/5m	93.21	100.00	3.64	2.76	0.45	0.074	0
2	30	45°C/5m	89.86	100.00	3.45	2.76	0.42	0.11	0
2	30	69°C/5m	87.92	100.00	7.00	2.76	0.86	0.27	0
2	60	45°C/5m	65.80	89.61	7.28	2.76	0.86	1.05	0.23
2	60	69°C/5m	48.01	72.37	12.12	2.76	1.39	3.65	1.29

Table 10e : TFC membranes based on 70:30 *m*-AP : *m*-PDA
Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (70:30) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	10	46°C/5m	76.71	87.14	29.10	2.76	3.46	2.45	1.19
2	30	46°C/5m	78.71	96.82	55.42	2.76	6.70	4.16	0.51
2	45	46°C/5m	79.58	94.29	30.23	2.76	3.64	2.15	0.51
2	60	46°C/5m	91.47	100.00	25.59	2.76	3.13	0.66	0
2	120	46°C/5m	65.27	84.61	66.50	2.76	7.82	9.83	3.36

Table 10f : TFC membranes based on 70:30 *m*-AP : *m*-PDA with the addition of surfactant
Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (70:30) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of m-AP + 0.5% SLS
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	30	46°C/5m	83.30	95.77	9.50	2.76	1.15	0.53	0.12
2	30	71°C/5m	68.88	89.61	6.72	2.76	0.79	0.84	0.22
2	60	46°C/5m	91.42	100.00	12.26	2.76	1.50	0.32	0
2	60	69°C/5m	80.00	93.51	14.45	2.76	1.74	1.00	0.28

Table 10g : TFC membranes based on 50:50 *m*-AP : *m*-PDA

Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (50:50) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP

Organic solution : 0.15% (w/v) of TMC dissolved in hexane

All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	10	42°C/5m	93.11	100.00	6.38	2.76	0.78	0.13	0
2	10	42°C/5m	94.26	100.00	7.77	2.76	0.95	0.13	0
2	15	42°C/5m	93.29	100.00	4.71	2.76	0.58	0.094	0
2	15	42°C/5m	95.32	100.00	3.62	2.76	0.45	0.049	0
2	15	42°C/5m	93.29	-	13.65	2.76	1.45	0.27	-
2	15	42°C/5m	94.81	-	12.12	2.76	1.29	0.18	-
2	15	42°C/5m	94.68	-	11.44	2.76	1.22	0.18	-
2	15	42°C/5m	94.37	-	11.12	2.76	1.18	0.18	-
2	15	42°C/5m	91.13	-	23.21	2.76	2.46	0.63	-
2	30	42°C/5m	93.75	100.00	5.75	2.76	0.71	0.11	0
2	30	42°C/5m	87.19	100.00	12.94	2.76	1.58	0.53	0
2	30	42°C/5m	93.78	100.00	6.66	2.76	0.82	0.12	0
2	30	42°C/5m	92.54	100.00	14.89	2.76	1.82	0.33	0
2	30	42°C/5m	84.82	-	33.83	2.76	3.58	1.68	-
2	30	42°C/5m	85.97	-	22.36	2.76	2.37	1.01	-
2	30	42°C/5m	86.87	-	20.28	2.76	2.15	0.85	-
2	45	42°C/5m	95.36	100.00	9.01	2.76	1.11	0.12	0
2	45	42°C/5m	95.76	100.00	15.57	2.76	1.91	0.19	0
2	45	42°C/5m	83.84	-	30.87	2.76	3.26	1.65	-
2	60	42°C/5m	95.12	100.00	4.44	2.76	0.55	0.063	0
2	60	42°C/5m	96.12	100.00	3.81	2.76	0.47	0.043	0
2	60	42°C/5m	92.37	100.00	8.38	2.76	1.03	0.19	0
2	60	42°C/5m	81.84	-	21.85	2.76	2.31	1.35	-

Table 10h : TFC membranes based on 50:50 *m*-AP : *m*-PDA with the addition of surfactant

Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (50:50) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP + 0.5% SLS

Organic solution : 0.15% (w/v) of TMC dissolved in hexane

All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	15	42°C/5m	91.13	-	4.74	2.76	0.50	0.13	-
2	15	42°C/5m	91.99	-	19.40	2.76	2.06	0.47	-
2	15	42°C/5m	95.19	-	14.01	2.76	1.49	0.19	-
2	15	42°C/5m	91.85	-	9.37	2.76	0.99	0.23	-
2	15	42°C/5m	94.62	-	9.84	2.76	1.05	0.16	-
2	30	42°C/5m	87.69	-	19.11	2.76	2.02	0.75	-
2	30	42°C/5m	88.56	-	19.11	2.76	2.03	0.69	-
2	30	42°C/5m	91.97	-	14.79	2.76	1.57	0.36	-
2	30	42°C/5m	87.36	-	23.89	2.76	2.53	0.96	-
2	30	42°C/5m	91.32	-	12.97	2.76	1.38	0.34	-
2	30	42°C/5m	90.67	-	10.73	2.76	1.14	0.31	-
2	45	42°C/5m	93.73	-	8.87	2.76	0.94	0.17	-
2	45	42°C/5m	92.70	-	7.23	2.76	0.77	0.16	-
2	45	42°C/5m	96.14	-	6.68	2.76	0.71	0.075	-
2	45	42°C/5m	97.38	-	6.63	2.76	0.71	0.049	-
2	60	42°C/5m	94.76	-	9.59	2.76	1.02	0.15	-
2	60	42°C/5m	93.79	-	10.12	2.76	1.08	0.19	-

Table 10i : TFC membranes based on 30:70 *m*-AP : *m*-PDA
Aqueous soulution : 2.5 % *m*-AP : *m*-PDA (30:70) + 1:0.0125 moles of NaOH : BTEAC wrt one mole of *m*-AP
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	15	42°C/5m	96.21	-	13.47	2.76	1.43	0.15	-
2	15	42°C/5m	94.98	-	15.38	2.76	1.64	0.23	-
2	30	42°C/5m	95.16	-	15.44	2.76	1.64	0.22	-
2	30	42°C/5m	95.52	-	17.25	2.76	1.84	0.23	-
2	45	42°C/5m	96.24	-	11.09	2.76	1.18	0.12	-
2	45	42°C/5m	97.88	-	9.89	2.76	1.05	0.059	-
2	60	42°C/5m	97.79	-	6.79	2.76	0.72	0.043	-
2	60	42°C/5m	96.57	-	8.45	2.76	0.9	0.083	-

Table 11a : TFC membranes based on 80:20 Bis-A : *m*-PDA
Aqueous soulution : 2.5 % Bis-A : *m*-PDA (80:20) + 2.74:0.025 moles of NaOH : TBABr wrt one mole of Bis-A
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	40°C/5m	87.18	98.45	20.29	2.76	2.47	0.83	0.089
3	30	40°C/5m	79.26	95.21	25.55	2.76	3.08	1.86	0.36
3	45	40°C/5m	86.22	98.21	19.87	2.76	2.42	0.88	0.10
3	60	40°C/5m	88.91	100.00	18.98	2.76	2.32	0.66	0

Table 11b : TFC membranes based on 70:30 Bis-A : *m*-PDA
Aqueous soulution : 2.5 % Bis-A : *m*-PDA (70:30) + 2.74:0.025 moles of NaOH : TBABr wrt one mole of Bis-A
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	40°C/5m	96.22	100.00	19.99	2.76	2.46	0.22	0
3	30	40°C/5m	89.48	100.00	12.02	2.76	1.47	0.39	0
3	45	40°C/5m	90.24	100.00	5.87	2.76	0.72	0.18	0
3	60	40°C/5m	92.71	100.00	17.05	2.76	2.09	0.37	0

Table 11c : TFC membranes based on 50:50 Bis-A : *m*-PDA
Aqueous soulution : 2.5 % Bis-A : *m*-PDA (50:50) + 2:0.025 moles of NaOH : TBABr wrt one mole of Bis-A
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
1	10	40°C/5m	89.93	100.00	21.73	2.76	2.66	0.68	0
1	15	40°C/5m	91.19	100.00	7.68	2.76	0.94	0.21	0
1	15	40°C/5m	86.05	-	12.48	2.76	1.32	0.56	-
1	15	40°C/5m	86.01	-	23.66	2.76	2.50	1.07	-
1	30	40°C/5m	92.39	100.00	15.52	2.76	1.90	0.36	0
1	30	40°C/5m	83.36	-	25.48	2.76	2.69	1.41	-
1	30	40°C/5m	87.06	-	28.14	2.76	2.98	1.16	-
1	45	40°C/5m	88.21	-	26.98	2.76	2.86	1.00	-
1	45	40°C/5m	90.40	-	25.28	2.76	2.68	0.75	-
1	45	40°C/5m	93.62	-	17.00	2.76	1.81	0.32	-
1	45	40°C/5m	92.18	-	15.50	2.76	1.65	0.37	-
1	60	40°C/5m	89.41	100.00	4.64	2.76	0.57	0.15	0
1	60	40°C/5m	78.29	-	29.43	2.76	3.10	2.27	-
1	60	40°C/5m	76.34	-	31.52	2.76	3.32	2.71	-
1	120	40°C/5m	91.79	-	21.06	2.76	2.24	0.52	-
1	120	40°C/5m	91.70	-	18.04	2.76	1.92	0.45	-

Table 11d : TFC membranes based on 30:70 Bis-A : *m*-PDA
Aqueous soulution : 2.5 % Bis-A : *m*-PDA (30:70) + 2:0.025 moles of NaOH : TBABr wrt one mole of Bis-A
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
1	15	40°C/5m	87.67	100.00	22.17	2.76	2.71	0.87	0
1	30	40°C/5m	93.82	100.00	13.50	2.76	1.66	0.25	0
1	30	40°C/5m	94.77	100.00	13.50	2.76	1.66	0.21	0
1	45	40°C/5m	86.05	100.00	34.49	2.76	4.21	1.55	0
1	60	40°C/5m	87.93	100.00	20.69	2.76	2.53	0.79	0

Table 12a : TFC membranes based on 80:20 HQ : *m*-PDA
Aqueous soulution : 2.5 % HQ : *m*-PDA (80:20) + 2:0.025 moles of NaOH : TBABr wrt one mole of HQ
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	42°C/5m	92.65	100.00	22.47	2.76	2.75	0.49	0
3	15	42°C/5m	91.54	100.00	21.39	2.76	2.62	0.55	0
3	30	42°C/5m	93.39	100.00	21.64	2.76	2.65	0.43	0
3	30	42°C/5m	92.28	100.00	19.31	2.76	2.37	0.45	0
3	45	42°C/5m	89.28	100.00	22.88	2.76	2.80	0.76	0
3	45	42°C/5m	89.00	100.00	20.16	2.76	2.46	0.69	0
3	60	42°C/5m	95.18	100.00	15.93	2.76	1.96	0.22	0
3	60	42°C/5m	95.45	100.00	14.57	2.76	1.79	0.19	0

Table 12b : TFC membranes based on 70:30 HQ : *m*-PDA
Aqueous soulution : 2.5 % HQ : *m*-PDA (70:30) + 2:0.025 moles ofNaOH : TBABr wrt one mole of HQ
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	42°C/5m	95.49	100.00	13.23	2.76	1.62	0.17	0
3	15	42°C/5m	96.10	100.00	12.43	2.76	1.53	0.14	0
3	30	42°C/5m	91.81	100.00	21.01	2.76	2.57	0.52	0
3	30	42°C/5m	91.81	100.00	18.96	2.76	2.32	0.47	0
3	45	42°C/5m	95.88	100.00	18.24	2.76	2.24	0.22	0
3	45	42°C/5m	95.81	100.00	16.75	2.76	2.06	0.20	0
3	60	42°C/5m	95.84	100.00	18.94	2.76	2.33	0.23	0
3	60	42°C/5m	96.96	100.00	17.49	2.76	2.15	0.15	0

Table 12c : TFC membranes based on 50:50 HQ : *m*-PDA
Aqueous soulution : 2.5 % HQ : *m*-PDA (50:50) + 2:0.025 moles of NaOH : TBABr wrt one mole of HQ
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	42°C/5m	94.64	100.00	9.15	2.76	1.12	0.15	0
3	30	42°C/5m	96.38	100.00	7.91	2.76	0.97	0.083	0
3	30	42°C/5m	87.56	-	6.31	2.76	0.67	0.25	-
3	30	42°C/5m	89.88	-	8.57	2.76	0.91	0.27	-
3	30	42°C/5m	79.61	-	5.10	2.76	0.54	0.36	-
3	45	42°C/5m	94.89	100.00	12.27	2.76	1.51	0.18	0
3	45	42°C/5m	92.42	-	23.77	2.76	2.52	0.54	-
3	45	42°C/5m	93.78	-	23.31	2.76	2.48	0.43	-
3	45	42°C/5m	86.26	-	24.04	2.76	2.54	1.06	-
3	45	42°C/5m	86.90	-	23.05	2.76	2.44	0.97	-
3	60	42°C/5m	92.56	100.00	15.93	2.76	1.95	0.36	0
3	60	42°C/5m	97.13	-	17.39	2.76	1.85	0.14	-
3	60	42°C/5m	97.60	-	17.73	2.76	1.89	0.12	-
3	60	42°C/5m	93.29	-	18.16	2.76	1.93	0.36	-
3	60	42°C/5m	94.14	-	17.90	2.76	1.90	0.31	-
3	60	42°C/5m	96.79	-	15.22	2.76	1.62	0.14	-

Table 12d : TFC membranes based on 25:75 HQ : *m*-PDA
Aqueous soulution : 2.5 % HQ : *m*-PDA (25:75) + 2:0.025 moles of NaOH : TBABr wrt one mole of HQ
Organic solution : 0.15% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	30	42°C/5m	96.77	-	9.0	2.76	0.96	0.083	-
3	30	42°C/5m	95.94	-	9.35	2.76	0.99	0.11	-
3	45	42°C/5m	97.79	-	10.21	2.76	1.09	0.064	-
3	45	42°C/5m	97.23	-	9.71	2.76	1.03	0.077	-
3	60	42°C/5m	98.09	-	8.20	2.76	0.87	0.044	-
3	60	42°C/5m	97.56	-	9.55	2.76	1.02	0.066	-

Table 13a : TFC membranes based on 1,5-naphthalene diamine reacted with TPC + IPC
Aqueous solution : 0.2% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 1% (w/w) of TPC : IPC (50:50) dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	15	42°C/5m	17.35	45.68	6.41	2.76	0.69	8.48	2.12
2	45	42°C/5m	1.07	44.44	4.34	2.76	0.46	111.00	1.51

Table 13b : TFC membranes based on 1,5-naphthalene diamine reacted with TMC + IPC
Aqueous solution : 0.2% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 0.15% (w/w) of TMC : IPC (50:50) dissolved in hexane
All membranes were subjected to an air drying period of 12 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	45	42°C/5m	41.05	80.00	2.31	2.76	0.27	0.92	0.16
2	45	42°C/5m	30.46	64.71	12.43	2.76	1.39	0.79	1.88
2	60	42°C/5m	18.73	49.41	6.44	2.76	0.70	7.77	1.83
2	60	42°C/5m	7.28	28.57	4.47	2.76	0.47	15.8	3.11

Table 13c : TFC membranes based on 1,5-naphthalene diamine (0.18%) reacted with TMC (0.2%)
Aqueous solution : 0.18% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 0.2% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 17 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	42°C/5m	63.88	86.05	6.94	2.76	0.82	1.09	0.31
3	30	42°C/5m	67.20	82.95	2.21	2.76	0.26	0.30	0.13
3	45	42°C/5m	46.03	80.22	5.30	2.76	0.61	1.73	0.36
3	60	42°C/5m	73.48	89.53	3.18	2.76	0.38	0.32	0.10
3	180	42°C/5m	58.14	76.92	2.91	2.76	0.34	0.58	0.24

Table 13d : TFC membranes based on 1,5-naphthalene diamine (0.2%) reacted with TMC (0.15% in cyclohexane)
Aqueous solution : 0.2% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 0.15% (w/v) of TMC dissolved in cyclohexane
All membranes were subjected to an air drying period of 17 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	90°C/5m	58.18	76.67	3.55	2.76	0.41	0.71	0.3
3	15	90°C/5m	61.60	74.11	3.50	2.76	0.41	0.61	0.34
3	30	90°C/5m	50.08	69.89	1.73	2.76	0.19	0.48	0.21
3	60	90°C/5m	82.09	93.33	1.72	2.76	0.21	0.10	0.034
3	60	90°C/5m	85.13	97.85	1.82	2.76	0.22	0.088	0.011

Table 13e : TFC membranes based on 1,5-naphthalene diamine (0.2%) reacted with TMC (0.2%)
Aqueous solution : 0.2% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 0.2% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 15 - 17 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	15	42°C/5m	72.72	88.46	4.35	2.76	0.51	0.45	0.16
3	15	42°C/5m	76.67	90.12	2.96	2.76	0.35	0.25	0.090
3	15	42°C/5m	79.27	95.12	3.60	2.76	0.44	0.26	0.051
3	30	42°C/5m	69.41	91.36	2.21	2.76	0.26	0.27	0.058
3	30	42°C/5m	76.83	90.24	2.53	2.76	0.30	0.21	0.076
2	45	42°C/5m	59.08	76.92	4.83	2.76	0.56	0.93	0.40
3	45	42°C/5m	61.14	81.48	7.09	2.76	0.83	1.25	0.45
2	60	42°C/5m	46.92	80.77	6.72	2.76	0.78	2.11	0.44
3	60	42°C/5m	78.03	92.59	2.96	2.76	0.36	0.23	0.066
3	60	42°C/5m	82.36	95.12	3.62	2.76	0.44	0.22	0.052

Table 13f : TFC membranes based on 1,5-naphthalene diamine (0.2%) reacted with TMC (0.2% in cyclohexane)
Aqueous solution : 0.2% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 0.2% (w/v) of TMC dissolved in cyclohexane
All membranes were subjected to an air drying period of 17 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	15	42°C/5m	BAD						
3	30	42°C/5m	38.12	65.48	3.04	2.76	0.34	1.37	0.45
3	45	42°C/5m	54.74	76.19	2.58	2.76	0.29	0.59	0.22
3	60	42°C/5m	48.73	79.76	2.31	2.76	0.27	0.68	0.16

Table 13g : TFC membranes based on 1,5-naphthalene diamine (0.2%) reacted with TMC (0.35%)
Aqueous solution : 0.2% 1,5-naphthalene diamine in water : methanol (50:50)
Organic solution : 0.35% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 17 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
3	5	42°C/5m	47.42	77.54	3.45	2.76	0.39	1.06	0.28
3	15	42°C/5m	72.48	87.78	12.44	2.76	1.48	1.31	0.48
3	15	42°C/5m	71.17	88.51	11.32	2.76	1.34	1.27	0.41
3	30	42°C/5m	66.55	85.06	10.52	2.76	1.24	1.47	0.51
3	30	42°C/5m	67.95	85.56	10.68	2.76	1.26	1.40	0.50
3	45	42°C/5m	61.30	85.56	13.07	2.76	1.54	2.29	0.61
3	60	42°C/5m	69.37	88.51	8.86	2.76	1.05	1.09	0.32
3	60	42°C/5m	71.02	90.00	9.28	2.76	1.10	1.05	0.29

Table 14a : TFC membranes based on 2,6-diaminopyridine (2.5%) reacted with TMC (0.2%)
Aqueous solution : 2.5% 2,6-diaminopyridine
Organic solution : 0.2% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
2	60	42°C/5m	59.87	83.16	18.73	2.76	2.19	3.49	1.05
2	60	42°C/5m	62.97	86.32	18.50	2.76	2.18	3.02	0.81
4	60	42°C/5m	70.38	97.83	10.93	2.76	1.32	1.28	0.067
6	60	42°C/5m	67.08	94.18	8.16	2.76	0.98	1.11	0.14
4	45	42°C/5m	84.49	96.84	6.89	2.76	0.84	0.35	0.062
4	45	42°C/5m	86.08	96.84	6.94	2.76	0.84	0.31	0.063
6	45	42°C/5m	64.30	96.51	9.81	2.76	1.17	1.51	0.099
6	45	42°C/5m	66.59	97.83	10.47	2.76	1.26	1.46	0.065

Table 14b : TFC membranes based on 2,6-diaminopyridine (3%) reacted with TMC (0.35%)
Aqueous solution : 3% 2,6-diaminopyridine
Organic solution : 0.35% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	15	42°C/5m	59.23	94.25	17.56	2.76	2.09	3.36	0.29
4	30	42°C/5m	73.32	98.85	12.78	2.76	1.54	1.29	0.041
4	45	42°C/5m	80.03	98.85	16.93	2.76	2.05	1.17	0.055
4	60	42°C/5m	74.52	98.85	20.13	2.76	2.43	1.91	0.065
4	60	42°C/5m	67.79	91.43	18.41	2.76	2.19	2.43	0.48
4	60	42°C/5m	74.19	90.11	24.58	2.76	2.93	2.38	0.75
4	60	42°C/5m	72.04	90.11	22.13	2.76	2.64	2.39	0.68

Table 14c : TFC membranes based on 2,6-diaminopyridine (3%) reacted with TMC (0.4%)
Aqueous solution : 3% 2,6-diaminopyridine
Organic solution : 0.4% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	30	42°C/5 m	80.16	92.93	10.57	2.76	1.27	0.73	0.22
4	45	42°C/5 m	89.22	100.00	11.88	2.76	1.45	0.39	0
4	60	42°C/5 m	81.19	93.41	14.72	2.76	1.77	0.95	0.29

Table 14d : TFC membranes based on 2,6-diaminopyridine (with 18% CMC value of surfactant) reacted with TMC (0.4%)
Aqueous solution : 3% 2,6-diaminopyridine + 18% CMC value of SLS
Organic solution : 0.4% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	30	42°C/5 m	61.84	85.71	3.16	2.76	0.37	0.54	0.15
4	45	42°C/5 m	92.84	100.00	8.25	2.76	1.01	0.18	0
4	60	42°C/5 m	77.64	92.86	2.14	2.76	0.26	0.17	0.046

Table 14e : TFC membranes based on 2,6-diaminopyridine (with 10 - 90% CMC values of surfactant) reacted with TMC (0.4%)
Aqueous solution : 3% 2,6-diaminopyridine + SLS
Organic solution : 0.4% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Surfactant SLS (% CMC)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	10	45	42°C/5m	64.30	71.11	12.80	2.76	1.48	1.97	1.44
4	30	45	42°C/5m	51.30	71.11	13.06	2.76	1.49	3.44	1.47
4	50	45	42°C/5m	27.83	86.67	2.57	2.76	0.29	1.85	0.11
4	70	45	42°C/5m	30.32	76.25	2.94	2.76	0.33	1.88	0.25
4	90	45	42°C/5m	26.68	61.25	3.72	2.76	0.41	2.84	0.65

Table 14f : TFC membranes based on 2,6-diaminopyridine (3%) reacted with TMC (0.5%)
Aqueous solution : 3% 2,6-diaminopyridine
Organic solution : 0.5% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	30	42°C/5m	87.76	100.00	13.80	2.76	1.69	0.54	0
4	45	42°C/5m	81.21	93.94	12.53	2.76	1.51	0.81	0.23
4	60	42°C/5m	83.99	100.00	12.29	2.76	1.50	0.65	0

Table 14g : TFC membranes based on 2,6-diaminopyridine (with 18% CMC value of surfactant) reacted with TMC (0.5%)
Aqueous solution : 3% 2,6-diaminopyridine + 18% CMC value of SLS
Organic solution : 0.5% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	30	42°C/5m	69.22	90.74	9.20	2.76	1.09	1.14	0.26
4	45	42°C/5m	57.11	65.12	10.27	2.76	1.17	2.14	1.53
4	60	42°C/5m	82.24	94.05	4.83	2.76	0.58	0.29	0.085

Table 14h : TFC membranes based on 2,6-diaminopyridine (3%) reacted with TMC (0.6%)
Aqueous solution : 3% 2,6-diaminopyridine
Organic solution : 0.6% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	30	42°C/5m	74.50	92.45	12.55	2.76	1.50	1.19	0.29
4	45	42°C/5m	80.04	95.28	19.50	2.76	2.35	1.35	0.27
4	60	42°C/5m	59.93	83.81	23.75	2.76	2.78	4.41	1.27

Table 14i : TFC membranes based on 2,6-diaminopyridine (3%) reacted with TMC (0.7%)
Aqueous solution : 3% 2,6-diaminopyridine
Organic solution : 0.7% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	30	42°C/5m	66.80	94.19	7.50	2.76	0.89	1.04	0.13
4	45	42°C/5m	73.21	91.43	22.83	2.76	2.73	2.32	0.59
4	60	42°C/5m	74.50	87.74	26.04	2.76	3.10	2.48	1.01

Table 14j : TFC membranes based on 2,6-diaminopyridine (5%) reacted with TMC (0.25%)
Aqueous solution : 5% 2,6-diaminopyridine
Organic solution : 0.25% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	45	42°C/5m	59.04	92.13	15.42	2.76	1.83	2.97	0.37
4	60	42°C/5m	63.09	95.60	20.30	2.76	2.42	3.30	0.26
4	120	42°C/5m	62.35	92.30	25.14	2.76	2.99	4.22	0.58

Table 14k : TFC membranes based on 2,6-diaminopyridine (5%) reacted with TMC (0.35%)
Aqueous solution : 5% 2,6-diaminopyridine
Organic solution : 0.35% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	45	42°C/5m	70.82	96.47	17.66	2.76	2.12	2.02	0.180
4	60	42°C/5m	61.60	93.41	27.42	2.76	3.26	4.75	0.54
4	90	42°C/5m	44.36	86.47	13.79	2.76	1.60	4.80	0.59
4	120	42°C/5m	55.61	90.11	32.78	2.76	3.86	7.27	0.99

Table 14l : TFC membranes based on 2,6-diaminopyridine (7%) reacted with TMC (0.25%)
Aqueous solution : 7% 2,6-diaminopyridine
Organic solution : 0.25% (w/v) of TMC dissolved in hexane
All membranes were subjected to an air drying period of 10 minutes following the dip time in aqueous phase

Dip time in aq. soln. (min.)	Dip time in org. soln. (sec.)	Curing (°C/min)	Salt Rej. (%)	Sucrose Rej. (%)	Water flux (lmh)	Pressure (MPa)	A x 10^{-6} (m/s.MPa)	B_{salt} x 10^{-6} (m/s)	$B_{sucrose}$ x 10^{-6} (m/s)
4	15	42°C/5m	26.29	61.71	16.05	2.76	1.78	12.5	2.77
4	45	42°C/5m	36.01	78.11	9.04	2.76	1.03	4.46	0.70
4	60	42°C/5m	62.53	92.13	14.62	2.76	1.74	2.43	0.35

Table 15 : Percent ester and amide compositions obtained for the polyesteramide polymers and the physical mixtures from the deconvoluted FTIR spectra

Polymer samples	Area under the signals obtained by deconvolution		Percent ester	Percent amide
	1720-1745 (cm^{-1})	1640-1680 (cm^{-1})		
Polyesteramide polymer obtained using 50:50 *m*-AP : *m*-PDA	1.74	15.88	9.88	90.12
Physical mixture A*	5.12	12.78	28.60	71.39
Polyesteramide polymer obtained using 50:50 Bis-A : *m*-PDA	2.82	9.79	22.36	77.64
Physical mixture B*	4.55	6.42	41.48	58.52
Polyesteramide polymer obtained using 50:50 HQ : *m*-PDA	6.12	22.00	21.76	78.24
Physical mixture C*	3.98	8.52	31.84	68.16

* Physical mixture A: 0.57 mg of polyesteramide from *m*-aminophenol and TMC + 0.41 mg of polyamide from *m*-phenylene diamine and TMC

* Physical mixture B : 0.45 mg of polyester from bisphenol-A and TMC + 0.45 mg of polyamide from *m*-phenylene diamine and TMC

* Physical mixture C : 0.58 mg of polyester from hydroquinone and TMC + 0.45 mg of polyamide from *m*-phenylene diamine and TMC

Table 16 : Water and salt passage rates as a function of chlorine exposure for the reference polyamide TFC membrane and the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 *m*-AP : *m*-PDA

Feed solution : 2000 ppm NaCl solution

Data obtained at 200 ppm chlorine concentration at pH = 6.3±0.2

T_o (polyamide TFC membrane) = 0.0951

T_o (polyesteramide TFC membrane) = 0.0887

Chlorine exposure time (ppm-hours)	Pressure (MPa)	Polyamide TFC membrane based on *m*-PDA		Polyesteramide TFC membrane based on 50:50 *m*-AP : *m*-PDA	
		A x 10^{-6} (m/s-MPa)	T/T_o	A x 10^{-6} (m/s-MPa)	T/T_o
0	2.76	0.889	1.00	2.75	1.00
83.33	2.76	0.386	1.080	0.844	1.109
200.00	2.76	0.374	1.779	0.786	1.673
316.67	2.76	0.362	2.015	0.775	1.576
483.33	2.76	0.355	2.094	0.769	1.927

Table 17 : Water and salt passage rates as a function of chlorine exposure for the reference polyamide TFC membrane and the polyesteramide TFC membrane formed from the reaction of TMC with 25:75 HQ : *m*-PDA

Feed solution : 2000 ppm NaCl solution

Data obtained at 200 ppm chlorine concentration at pH = 6.3±0.2

T_o (polyamide TFC membrane) = 0.0301

T_o (polyesteramide TFC membrane) = 0.0406

Chlorine exposure time (ppm-hours)	Pressure (MPa)	Polyamide TFC membrane based on *m*-PDA		Polyesteramide TFC membrane based on 25:75 HQ : *m*-PDA	
		A x 10^{-6} (m/s-MPa)	T/T_o	A x 10^{-6} (m/s-MPa)	T/T_o
0	2.76	1.54	1.00	0.995	1.00
100.00	2.76	0.161	0.806	0.188	1.079
216.67	2.76	0.123	1.548	0.110	1.146
416.67	2.76	0.124	3.089	0.114	1.296
533.33	2.76	0.119	3.180	0.089	1.816

Table 18a : Water and salt passage rates as a function of chlorine exposure for the reference polyamide TFC membrane and the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA

Feed solution : 2000 ppm NaCl solution

Data obtained at 200 ppm chlorine concentration at pH = 6.3±0.2

T_o (polyamide TFC membrane) = 0.0836

T_o (polyesteramide TFC membrane) = 0.0959

Chlorine exposure time (ppm-hours)	Pressure (MPa)	Polyamide TFC membrane based on *m*-PDA		Polyesteramide TFC membrane based on 50:50 Bis-A : *m*-PDA	
		$A \times 10^{-6}$ (m/s-MPa)	T/T_o	$A \times 10^{-6}$ (m/s-MPa)	T/T_o
0	2.76	1.130	1.00	2.68	1.00
100.00	2.76	0.841	1.372	1.340	0.933
233.33	2.76	0.869	4.278	0.896	1.367
366.67	2.76	0.749	7.350	0.824	1.461
483.33	2.76	0.524	7.984	0.367	1.473

Table 18b : Water and salt passage rates as a function of chlorine exposure for the reference polyamide TFC membrane and the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 Bis-A : *m*-PDA (Repeat study)

Feed solution : 2000 ppm NaCl solution

Data obtained at 200 ppm chlorine concentration at pH = 6.3±0.2

T_o (polyamide) = 0.0771

T_o (polyesteramide) = 0.0829

Chlorine exosure time (ppm-hours)	Pressure (MPa)	Polyamide TFC membrane based on *m*-PDA		Polyesteramide TFC membrane based on 50:50 Bis-A : *m*-PDA	
		$A \times 10^{-6}$ (m/s-MPa)	T/T_o	$A \times 10^{-6}$ (m/s-MPa)	T/T_o
0	2.76	1.800	1.00	1.810	1.00
100.00	2.76	1.550	0.767	1.370	0.921
366.67	2.76	2.510	7.229	0.849	1.633
466.67	2.76	2.840	9.232	0.813	1.735
600.00	2.76	3.090	9.318	0.762	1.867

Table 19a : Water and salt passage rates as a function of chlorine exposure for the reference polyamide TFC membrane and the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 HQ : *m*-PDA

Feed solution : 2000 ppm NaCl solution

Data obtained at 200 ppm chlorine concentration at pH = 6.3±0.2

T_o (polyamide) = 0.0146

T_o (polyesteramide) = 0.1224

Chlorine exposure time (ppm-hours)	Pressure (MPa)	Polyamide TFC membrane based on *m*-PDA		Polyesteramide TFC membrane based on 50:50 HQ : *m*-PDA	
		A x 10^{-6} (m/s-MPa)	T/T_o	A x 10^{-6} (m/s-MPa)	T/T_o
0	2.76	1.94	1.00	1.92	1.00
66.67	2.76	1.94	0.875	1.98	0.710
140.00	2.76	1.32	1.196	0.291	0.547
323.33	2.76	1.02	12.963	0.207	1.089
523.33	2.76	1.30	31.372	0.179	1.468
773.33	2.76	1.88	39.386	0.211	2.032

Table 19b : Water and salt passage rates as a function of chlorine exposure for the reference polyamide TFC membrane and the polyesteramide TFC membrane formed from the reaction of TMC with 50:50 HQ : *m*-PDA (Repeat study)

Feed solution : 2000 ppm NaCl solution

Data obtained at 250 ppm chlorine concentration at pH = 6.3±0.2

T_o (polyamide) = 0.0889

T_o (polyesteramide) = 0.0239

Chlorine exposure time (ppm-hours)	Pressure (MPa)	Polyamide TFC membrane based on *m*-PDA		Polyesteramide TFC membrane based on 50:50 HQ : *m*-PDA	
		A x 10^{-6} (m/s-MPa)	T/T_o	A x 10^{-6} (m/s-MPa)	T/T_o
0	2.76	0.942	1.00	1.89	1.00
395.83	2.76	0.478	1.149	0.518	1.027
833.33	2.76	0.450	3.013	0.436	2.186
1250.00	2.76	0.505	4.399	0.370	3.406
1708.33	2.76	0.888	7.665	0.295	6.164

LIST OF PUBLICATIONS/PATENTS

1) Nilima, S.R.; Neepa P.S.; **Jayarani, P.**
Simultaenous determination of mineral nutrients in different varieties of wheat and bengal gram in India by instrumental neutron activation analysis. Int. J. of Radiat. Appl. and Instrmt. Part A : Appl. Radiat. and Isotopes, 41 (6), 579-581, 1990.

2) Jadhav, A.S.; **Jayarani, P.**; Kulkarni, S.S.; Vernekar, S.P.
Silicon containing polyarylates. U.S. Pat. No. 5 606 000 (25 Feb. 1995).

3) Jadhav, A.S.; **Jayarani, P.**; Kulkarni, S.S.; Vernekar, S.P.
A process for the preparation of silicon containing polyarylates, Indian Pat. No. 588/DEL/93.

4) Jadhav, A.S.; **Jayarani, P.**; Kulkarni, S.S.; Vernekar, S.P.
A process for the preparation of semi-permeable membranes useful for the separation of gases, Indian Pat. No. 589/DEL/93.

5) Jadhav, A.S.; **Jayarani, P.**; Kulkarni, S.S.; Vernekar, S.P.
A process for the separation of gases, Indian Pat. No. 590/DEL/93.

6) Kulkarni, S.S.; **Jayarani, M.M.**
A process for the preparation of thin film composite membranes, Indian Pat. No. 2623/DEL/96.

7) **Jayarani.M.M.**; Kulkarni, S.S.
Reverse osmosis applications. Indian Desalination News, 3 (1 & 2), Jan. - June 1995.

MANUSCRIPTS IN PREPARATION

1) **Jayarani, M.M.**; Rajmohan, . ; Kulkarni, S.S; Kharul, U. K.
Synthesis of model diamide, diester and esteramide adducts and studies on its chlorine tolerance. To be submitted to Desalination.

2) **Jayarani, M.M.**; Kulkarni, S.S.
Synthesis of chlorine tolerant thin film composite polyesteramide membranes for reverse osmosis. To be submitted to Desalination.