CHAPTER 1

INTRODUCTION

Membrane technology is an important tool in the quest for advances and improvements in various industries such as pharmaceutical, chemical food, metal processing and finishing etc. In these process industries the production of wide variety of chemicals and components generally require a need for separation, concentration and purification of a range of materials including reagents and chemicals used in manufacture, the resulting intermediate and products and undesirable by-products from waste streams.

Traditional chemical methods are being used for separation of valuable chemicals from waste streams. However, such separation processes such as distillation, crystallization, ion-exchange, adsorption, precipitation etc., are very often found to be tedious and inefficient in product recovery (Illias et al 1995). Further they also contribute to various environmental problems. With the advent of membranes, separation and effluent treatment processes have become industrially viable unit operations because of the energy efficiency involved in the technique. With membrane technology, waste treatment processes has become environmental friendly process and also it need not be restricted to conversion of waste from one form to another. A variety of purification processes supported by membrane technologies can be a cost-effective way to satisfy the increase demand for quality. Since membrane separation involves no change of phase for solvent removal, no latent heat is produced. Hence it is possible to obtain products with functional properties superior to those produced by conventional processes.
Membrane separation in its modern incarnation is energy efficient and highly adaptive for a wide range of applications stemming from the development of new polymers as membrane materials (Potnis 1992); (Endoh et al 1997). Membrane technology is a cost-effective means of complying with increasingly stringent federal, state and local environmental regulations concerning industrial waste water treatment and discharge. With tougher regulations, increases in landfill costs and raises in environmental-related insurance, a more environmental-friendly process can also be a sound economic investment.

With membranes the separation, concentration and purification is faster and it is simple to operate using modern compact modules with added advantages of recycling and reuse of chemicals.

1.1 MEMBRANES

A membrane, in a broader sense is a region of discontinuity interposed between two phases. This implies that membranes can be gaseous, liquid or solid or combination of these phases. The term region in the definition is used to eliminate ordinary interfaces. Thus, the interfaces of two immiscible liquids or of a gas and a solid would not be ordinarily considered as membrane structure. Membranes vary in their make up from the relatively crude structure of a screen to extremely fine configurations in the order of thickness of a molecular layer thick, as in the fatty acid spreading in water (Hwang and Kammermeyer 1975). The term ‘Synthetic Membrane’ refers to those polymeric barriers, irrespective of the void volume or physical state, which have been restructured prior to utilization in a membrane separation process (Kesting 1971).
Scientists have succeeded in developing synthetic membranes in order to get the following desired properties; temperature resistance, pressure resistance, required mechanical strength, pH stability, solvent and microbial resistance (Michaels 1976).

1.1.1 Historical Overview and Evolution of Membranes

Biological membranes including the membranes of skin, lungs, heart collagen liver collagen, kidney glomerular etc., are composed primarily of lipids and proteins (Jain and Wagner 1980). A schematic representation of the biological membrane is shown in Figure 1.1. The lipids vary in composition and generally consist of a polar head group and non-polar aliphatic tail conferring surface activity. In aqueous environment, lipids align in tail – to –tail continuous bilayer with the polar head groups in contact with the water phase. Generally water, gases, H^+ and hydrophobic toxic molecules are transported through the biological membranes (Fendler 1982).

Figure 1.1 Schematic representation of biological membrane
History of synthetic membranes began with the development of cellulose nitrate semi-synthetic polymers. Systematic studies on membrane properties started from studies on membrane properties started from 1748 onwards.

The studies on biological membranes, their properties and performance led to the origin and growth of synthetic membranes. The versality of the biological membrane is a result of the evolutionary process of the living system, whereas the science and technology of synthetic membrane is linked to the short history of polymer science (Cabasso 1989). In the year 1748 Abbe Nollet discovered that after immersing an animal bladder filled with wine in pure water. Water permeated into the bladder causing it swell and even burst. That demonstrated the existence of a semi permeable membrane which was more permeable to water than to wine as well as the build up of osmotic pressure.

The demand for more membranes and membrane processes for various industries resulted in preparation synthetic membranes. The work of Lpeb and sourirajan (1964) resulted in the development of efficient Reverse Osmosis (RO) membranes. The mechanism of formation of asymmetric membranes has been studied by Kesting (1971) and Strathmann et al (1975). This formed the basis of ultrafiltration and microfiltration membranes with different properties from various polymers.

With the need for efficient and economic separation process and the increasing demand for production of potable water the importance of membranes and its industrial applications increased which in turn resulted in enhanced interest in research and development.
1.2 MEMBRANE PROCESS

A membrane process basically requires a circuit containing a pump to pressurize and re-circulate the process stream and a membrane module for filtration. As the effluent enters the system, two streams are formed; concentrate containing the contaminant in the concentrate and permeate, containing dilute amounts of contaminant (Cartwright 1994) as shown in Figure 1.2.

![Figure 1.2 Schematic representation of a membrane process](image)

Though membrane processes differ in their basic operating mode and areas of application they share several features that make them attractive in the separation of molecular mixtures in various industries such as food, pharmaceutical etc., where separation is done by physical means at ambient temperature without damaging or chemically altering the constituents. They are also used for large scale continuous operations like desalination of sea water and batch-wise treatment of very small quantities like isolation and purification of valuable drugs (Strathmann 1990).

Based on the size, application, structure and mechanism of transport, membrane processes are classified as gas diffusion, dialysis, reverse osmosis, electrodialysis, ultrafiltration, microfiltration, coarse filtration, liquid
membranes etc. Various membrane processes, membrane pore size, their concept, the materials that diffuse through the membrane, the driving force for separation and the materials retained by membranes are tabulated in Table 1.1.

Table 1.1 Size of materials retained, driving force and type of membranes

<table>
<thead>
<tr>
<th>Process</th>
<th>Size of materials retained</th>
<th>Driving force</th>
<th>Type of membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>0.1 – 10 µm microparticles</td>
<td>Pressure differences (0.5 – 2 bar)</td>
<td>Porous</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>1 – 100 nm macromolecules</td>
<td>Pressure differences of (1 – 10 bar)</td>
<td>Microporous</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>0.5 – 5 nm molecules</td>
<td>Pressure differences of (10 – 70 bar)</td>
<td>Microporous</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>&lt; 1 nm molecules</td>
<td>Pressure differences of (10 – 100 bar)</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Dialysis</td>
<td>&lt; 1 nm molecules</td>
<td>Concentration difference</td>
<td>Nonporous or Microporous</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>&lt; 1 nm molecules</td>
<td>Electrical potential difference</td>
<td>Nonporous or Microporous</td>
</tr>
<tr>
<td>Pervapouration</td>
<td>&lt; 1 nm molecules</td>
<td>Concentration difference</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Gas permeation</td>
<td>&lt; 1 nm molecules</td>
<td>Partial pressure Difference (1 – 100 bar)</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Membrane Distillation</td>
<td>&lt; 1 nm molecules</td>
<td>Partial pressure difference</td>
<td>Microporous</td>
</tr>
</tbody>
</table>
There are many different ways of classifying and cross-correlating membranes and membrane separation processes. Useful range of separation processes showing the range of particle or molecular size covered by each process, visualization techniques and the relative sizes of materials are illustrated in Figure 1.3.

Membrane separations are now effectively used in separation of particles from solutions, salt from water, toxins from blood, separation of gas from a mixture of gases etc. Since membranes are used in various industries such as chemical, food, drug, metal finishing industries etc., focus has been made on preparation of polymer based ultrafiltration membranes for specific applications.

Ultrafiltration has been an industrial process over two decades. With the advances in asymmetric membranes and improved engineering designs of ultrafiltration modules in many industrial applications, ultrafiltration systems are preferred over conventional separation processes due to their low energy requirement (Illias et al 1995).

1.3 POLYMER MEMBRANES

Though there are membranes made from every available materials (Brock 1983), polymer membranes are effectively employed when compared with membranes prepared from other materials. Polymers can be tailored for specific applications. As a result of specific needs for certain permselective membranes, only few polymers were developed until mid 1980s. Difficulties concerning the material selection process are frequently due to the elusive nature of the amorphous phase in polymers.
1.3.1 Membrane Mechanism

The most important property of membranes is their ability to control the rate of permeation of different species. The models used to describe the mechanism of are:

(i) Solution – Diffusion model and
(ii) Pore – flow model

In the solution diffusion model, the permeate dissolves in the membrane material and then diffuses through the membrane down the concentration gradient. The permeants are separated be of the differences in the solubilities of the materials in the membranes and the differences in the rates at which the material diffuse through the membrane.

The other model pore-flow model, in which permeants are transported by pressure-driven convective flow through tiny pores. Separation occurs because one of the permeants is filtered from some of the pores in the membrane through which other permeants move.

The difference between the solution diffusion model and pore-flow model lies in the relative size and permeance of the pores. For membranes in which transport is described by solution – diffusion model and Fick’s law, the free–volume pores in the membrane are tiny spaces between polymer chains caused by thermal motion of polymer molecules.

On the other hand, for a membrane in which transport is described by a pore-flow model and Darcy’s law the free-volume pores are relatively large and fixed and do not fluctuate in position or volume on the time scale of permeant motion.

Ultrafiltration, microfiltration and microporous gas separation membranes are all clearly microporous and transport occurs by pore-flow model.
Figure 1.3  Filtration spectrum - Various membrane processes, range of particles, membrane pore size and scanning region
The selection process of materials for the preparation of membranes requires a thorough understanding of the structure-property relationship which affects segregative mass transport. Hitherto most permselective membranes have been prepared through an empirical process of trial and error. A systematic method is needed for the classification of group interactions between solvents, nonsolvents and polymers, providing a framework for the selection of polymer membranes. In order to bring the casting formulation closer to the solubility boundary, numerous formulations employ swelling agents (Sourirajan 1991).

Based on the separation of water from wine using animal bladder by Abbe Nollet and Fick prepared artificial semi permeable membranes made from ether – alcohol solution of cellulose nitrate called colloidion during 1855. Development of artificial membranes started with the efforts to membrane pore size. Cellophane membranes were used for kidney dialysis, which became the first practical application of synthetic membranes. This paved the way for many other researchers to look into polymers for the preparation of membranes. Lloyd and Meluch (1985) have listed over 90 different homopolymers, co polymers and blends that have been investigated for membrane application. The conditions for polymers to be used as membranes are capability to form a dense or porous film, their availability, hydrophilic/hydrophobic balance and moderate ionic character and dielectric constant. Based on the pore size of the membranes, classifications were done as microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

1.4 MEMBRANE PREPARATION

Membranes are prepared by several techniques depending upon the type of membranes required. The important membrane preparation techniques are discussed below.
Symmetric membranes are isotropic in nature through the cross section of the membranes. They can be porous or dense, but the permeability of the membrane remains same at all points within the membrane. The dense membranes are prepared by solution casting and thermal melt pressing, while the porous membrane by irradiation, stretching and leaching. The surface layer performs the separation and is the principal barrier to flow through the membrane. Asymmetric membranes are prepared by the following techniques.

- Interfacial composite membranes
- Solution cast composite membranes
- Plasma polymerization
- Phase inversion

Interfacial composite membranes are prepared on micro porous support membrane. An aqueous solution of reactive prepolymer is deposited in the pores of a micro porous support membrane followed by immersing in a water immiscible solvent solution containing a reactant. This results in a densely cross linked thin membrane layer.

Solution cast composite membranes are obtained by preparing a thin water insoluble layer and then packing it on the microporous support. In the plasma polymerization, a support membrane is kept in an inert gas atmosphere at low pressure. When the monomer vapour is introduced in the atmosphere at 200 - 300 milli torr for 1 - 10 min, an ultra thin polymer film is deposited on the porous membrane sample held in the plasma field.

Though several methods are available phase inversion is a versatile technique for asymmetric membrane preparation and it has also been employed in our present study. The polymer solution is spread as thin film and the solvent is allowed to evaporate casting of the polymer solution is done
by using a ‘doctor blade’ to produce a thin film on a glass plate. After a predetermined evaporation time the cast film is immersed in a bath containing a non-solvent, some considerable amount of the solvent and a surfactant. The water rapidly precipitates the top surface of the cast film forming an extremely dense permselective skin. The cast film which was in homogenous sol is converted to gel by non-solvent, and the process of formation of membrane is called phase inversion. Since the casting solution and the conditions of formation can be varied widely to get controlled structures, the phase inversion process is an extremely versatile technique for asymmetric membrane formation.

1.5 MEMBRANE MODULES

It is essential to set up effective membrane modules to achieve high membrane performance. Many types of membrane modules such as tubular, plate and frame, spiral would and capillary membranes are produced commercially (Strathmann 1990). The membranes may be prepared in any one of these modules based on the nature of feed. Important economic consideration in their design and operation include the cost of the supporting and containing vessels, power consumption in fluid pumping and how much of the module hardware can be reused when the membrane is replaced.

1.6 ASYMMETRIC MEMBRANES FOR ULTRAFILTRATION APPLICATION

Ultrafiltration dominates other separation processes colloidal separations. Ultrafiltration has advantages over competing processes; no heat is added and hence heat liable substances are not harmed. Energy requirements are also lower than that for lyophilization or evaporation and no chemical denaturation as in the case of salt precipitation or solvent extraction,
concentration and purification may be achieved in one step, eg., enzyme recovery, using diafiltration to wash away unwanted or excess media; the permeate is especially suitable for specialized fermentation broths or final product recovery systems, eg., by ion – exchange chromatography, adsorption etc., the ultrafilter may be used either directly as a continuous reactor by attaching cells or enzymes to the membrane or by retaining cells and enzymes with the membrane.

1.6.1 Cellulose Acetate Membranes

Cellulose acetate membrane has wide application in desalination. However, it is more susceptible to chemical and bacteriological agents. This fragility of the membrane material results in heavy and costly installations for the treatment of water, difficulties in the storage of the membrane and in the case of accidental clogging or blocking, the choice of cleaning agents is extremely limited (Brousse et al 1976).

Traditionally, cellulose derivatives with a degree of substitution greater than 2.75 i.e. with acetyl content greater than 42.3% have been termed as cellulose triacetate (Cheryan 1986). Prabhakar and Misra (1986) have measured the hydraulic permeability and osmotic permeability for cellulose acetate membranes of varying water contents. A mathematical model based on steady-state mass balance over a boundary layer, coupled with the results from irreversible thermodynamics, is proposed for ultrafiltration of PEG 600 using cellulose acetate membrane. The model has been developed by taking into account the solvent permeability, solute permeability and reflection coefficient and can be utilized to predict the value of rejection at any operating condition (Bhattacharya and Datta 1996).
Recently, there is an increasing need for the separation of proteins and peptide drugs from biological booths due to the development of biotechnology. Ultrafiltration membrane is required to have high temperature resistance and solvent resistance, especially in pharmaceutical and food industry. Cellulose acetate membrane has high water permeability and easy manufacturing as an advantage. However, due to narrow pit range, compaction and biodegradation, it is limited to expand its applied field (Kurihara and Himeshima 1991).

Bal (1992) prepared CA membranes for RO separations and tested in order to evaluate the optimum casting conditions. The effect of thermal shrinkage treatment and pre-pressurization on the morphology and performance of CA membranes have been investigated by Wang et al (1994).

Kumar et al (1995) have prepared and characterized asymmetric CA membranes in the laboratory with the view to use them in membrane bioreactors. Enzymatic hydrolysis of sucrose has been investigated in a dead end stirred cell type bioreactor using these membranes.

The effects of pretreatments on morphology and performance of cellulose acetate membranes were investigated by Wang et al (1994). Cellulose membranes were also prepared and used to effect separation of proteins such BSA and Immuno-γ-globulin (Net et al 1994). The buoyancy studies of macrovoid pore formation in dry-cast cellulose acetate membranes were investigated by Mathew et al (2002). Flat Sheet cellulose membranes were prepared and compaction at modest pressure and loss of permeability was reported recently. The results show the range of hydraulic pressure suitable for maximum efficiency.
The following advantages of cellulose acetate and its derivatives made it suitable for selecting it as membrane material.

- Moderate flux and high salt rejection properties.
- Relative ease of manufacture;
- Cost effective and more hydrophilic;
- Renewable source of raw material;
- Non-toxicity.

Disadvantages of cellulose acetate membranes are:

- a fairly narrow temperature range of applicability (maximum 30°C);
- Reduced pH range (perfectly restricted to pH 2-8);
- Poor resistance to chlorine;
- Highly biodegradable;
- Gradual loss of membrane properties under pressure over its operating lifetime.

In order to meet the requirements of more aggressive cleaning, better chemical resistance and mechanical strength modification of cellulose acetate by blending with polymers with improved properties. Solution blending can be employed in order to achieve membranes with different hydrophilic / hydrophobic ratio along with other desired properties.

1.6.2 Polymethylmethacrylate Membranes

Polymethylmethacrylate (PMMA) is a thermoplastic which is transparent, mechanically rigid, tough and exhibits excellent thermal
oxidative resistance. It is one of the hardest polymers and possess good weathering resistance, dimensional stability and is highly scratch resistant. In view of their chemical, mechanical, thermal and hydrostatic stability PMMA membranes are widely used in variety of ultrafiltration applications. The effect of tensile strength of the PMMA membrane was studied by Dar jong et al. the following characteristics are exhibited by polymethylmethacrylate.

- Wide temperature limit: typically temperature range is 75 - 125°C can be used, which would be an advantage for microbial and biotechnological applications.
- Wide pH tolerances: can be exposed to range of 1-13
- Fairly good chlorine resistance: Most manufactures permit the use of up to 200 ppm chlorine for short sanitation purposes and up to 50 ppm for long-term storage of the membranes.
- Wide range of pore sizes ranging from 10 to 200 Å and molecular cut-off from 1000 to 500,000 Da are available for ultrafiltration applications.

1.6.3 Polystyrene Membranes

Polystyrene is also a thermoplastic, rigid and transparent polymer. It possesses good dimensional stability and it also has good electrical properties. Polystyrene provides enhanced stability and extended utility to the end products. Polystyrene membranes are used in various industrial and biomedical applications. They have different physicochemical properties, high porosity, low weight to volume ratio, good abrasion resistance etc.

Preparation of asymmetric membranes from polystyrene blends were studied by Chiria et al. Franco D.R. Armado et al have worked on the
synthesis and characterization of high impact polystyrene blend composite membranes for electrodialysis. The presence of polystyrene hinders the organization of regions responsible for crystallinity originally existing in pure CA. Application of graft polystyrene membranes in pervaporation was studied by Khajet et al. Lopez et al have worked on the proton transport properties of modified polystyrene membranes. Hao Zhang et al have investigated the effect of chemical groups of polystyrene on pervaporation performance. By combining the advantageous properties of polystyrene and cellulose acetate, membranes with improved properties can be made for various applications.

Blending of polystyrene with CA may lead to membrane with improved properties like high flux and high microbial resistance and better separation process due to its aromatic nature.

1.6.4 Polymer Blends as Membrane Materials

Polymer blending is a proven tool to obtain new type of materials with a wide diversity of properties intermediate between those of pure components along with economic advantages. The term polymer blend is used for any mixture of two or more homo polymers or copolymers brought together by physically mixing the polymers in the require amount, though a degree of compatibility between the polymer is necessary for interpenetrating networks (IPNS) (Thomas and Sperling 1978). The properties of the blend depend upon the compatibility of the individual polymers with each other and the method of mixing.

Polymer blends have provided an efficient way to fulfill new requirements for material properties. Blending is done for a variety of reasons including creating materials with enhanced thermal and mechanical behavior.
Membranes used in ultrafiltration applications often need to possess both good thermal and chemical resistance. Unfortunately polymers fulfilling these requirements like polysulfone, polycarbonate, polymethylmethacrylate, polystyrene, polyethersulfone etc., exhibit high hydrophobicity and in practice leads to loss of performance due to the effects of adsorption. Often polymers do not fit the demand for special applications when they are used in their original form. This can be overcome either by blending the polymers or by chemical modification (Hinke and Staude 1990).

The great majority of useful blends are immiscible and in these blends mechanical properties can be optimized by controlling the blend morphology (Sundararaj and Macosko 1995). The synthesis of a polymer blend membrane is motivated by the desire to superimpose requisite properties upon the transport properties of a base polymer (Sivakumar et al 1996).

Compatibility is achieved if the blend displays homogeneity with regard to the desired properties such as optical clarity, single Tg (Malik 1992) and mass transport properties (Nguyen et al 1980). The absolute rate at which a permeate traverses a membrane is known as permeability and the rate at which two different species permeate relative to each other is selectivity. Permeability and selectivity together determine the practicability of any membrane separation. The permselectivity/permeability of the membranes based on a miscible polymer blend pair is very much higher than that of membrane composed of the individual polymers. Hydrophilicity can be imparted to membranes by blending the hydrophobic polymer with a hydrophilic polymer and casting the modified polymer into a membrane.

The homogenous blends of polyanions and polycations forming polyelectrolyte complexes represent a class of novel materials, characterized
as miscible blends that are suitable for preparation of structurally asymmetric ultrafiltration and dialysis membranes.

Lu yan et al have worked on the preparation and characterization of PVDF/PMMA blend ultrafiltration membrane and studied their antifouling effects. Dar jong Lin et al (2006) have investigated on the preparation and characterization of PVDF/PMMA composite membranes. Effect of surfactants on the structure of PMMA membranes have been studied by Lin et al (1997).

Chiria et al (2005) have worked on asymmetric membranes from Polystyrene /polyolefin blends. Meenakshi et al have worked on the mechanical and microstructure studies on the CA/Polystyrene blend membranes.

In view of better performance of cellulose acetate, polymethylmethacrylate and polystyrene as membrane material these polymers have been chosen in the present study to prepare asymmetric, microporous, flat-sheet membranes by phase inversion technique for ultrafiltration applications.

1.7 MEMBRANE CHARACTERIZATION

The characterization of membranes is a very essential part as it decides the performance of the membrane for the specific application. The choice of the membrane for a specific application depends on the feed solution to be separated for which the knowledge of pore size distribution and the internal structure of the membrane are essential (Jackson 1995).
Thus membrane characterization is a very important part of membrane research and development because the design of the membrane process and systems depends on reliable data relating to membrane properties.

Characterization of ultrafiltration membranes is very important in the development of new and better membranes (Zhang et al 1989). In addition to chemical compatibility, the supporting layer must have high surface porosity with minimal pore diameter (Walch 1983).

Membrane permeability depends on the chemical nature of the base polymer and also on its morphological structure, i.e., the thickness and porosity of the skin layer and on the structure of the porous sub-layer (Bottino et al 1984). Yulan et al (1987) have developed a mathematical method for the study of the effect of water permeability, solute rejection, and other parameters of synthetic membranes on membrane performance.

Porous microfiltration or ultrafiltration membranes are generally characterized in terms of their trans-membrane flux, pre-size modular weight cut off and pre-size distribution. Water permeability of various ultrafiltration membranes were measured as a function of pressure and temperature and the results have shown that the convective flux of water was proportional to the viscosity (Nguyen et al 1979). Mulde (1991) concluded that membrane compaction will lead to a denser structure with smaller pores. Trans-membrane flux and membrane solute retention are determined in filtration tests. Transmembrane flux is generally measured as a function of applied hydrostatic pressure with ultra-pure water. Molecular weight of the polymer and the casting solution composition could affect the pore size and pore size distribution on the surface of the resulting membrane (Nguyer et al 1980).
Matz (1972) has studied the mechanism of the development of pores structure in anisotripic cellulose acetate membranes using microscopic studies. Pore distribution which is an important characteristic of a membrane, defines selectivity and solvent flow determined in terms of molecular weight cut off. On the other hand rejection of a given membrane for various molecular mass components is determined in filtration tests to investigate the molecular weight transport profiles of ultrafiltration membranes using a synthetic polymer or globular proteins with a distribution of molecular weights (Coope and Van Derveer 1979; Sueoka et al 1983; Issid et al 1992).


Based on the literature survey in the present work characterization of membranes was carried out in terms of compaction, pure water flux, membrane hydraulic resistance by measuring pure water flux of membranes at various pressures, water content, molecular cut off using different globular proteins with varied molar masses and membrane morphology by scanning electron microscopy.

1.8 APPLICATIONS OF ULTRAFILTRATION MEMBRANES

Membrane processes find many scientific and technological applications as they are used in many industries for the production of particle free solutions (Sourirajan and Matsuura 1985). In microbiology membranes are used for separation of micro-organisms from their medium for counting of specific group of micro-organisms and for the rapid diagnostic determination of the presence of indicators or pollution as well as pathogens (Brock 1983).
In Biochemistry, they are used as supporting agents for electrophoresis, and for binding of nucleic acids in hybridization studies.

One of the most sophisticated methods for the preparation of high quality ion free water combines membrane filtration with reverse osmosis through similar but finer membrane. The pharmaceutical industry is one of the biggest users in the preparation of sterile solution of thermally labile materials (Porter and Nelson 1972). Many industries like electronics, computer and aerospace need ultra clear-fluids which can be easily prepared by the use of membrane filtration (Porter 1990). The membrane separation technologies possess characteristics, which make them attractive for industrial pollution control applications (Sweeney 1985; Cartwright 1985).

Ultrafiltration provides macro-molecular separation for particles in the 20 to 1000 Angstrom range (upto 0.1 micron). All dissolved salts and smaller molecular pass through the membrane. Molecules rejected by the membranes include colloids, proteins, microbiological contaminants and large organic molecules (Vigneswaran and Fane 1998). Most ultrafiltration membranes have molecular weight cut off values between 1000 and 100,000. Transmembrane pressures are typically between 1 to 7 bar (15 to 100 psi).

Membranes are used on a large scale to provide 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, to release drugs at a controlled rate of medium (Strathamann 1990, Barker et al 1984).

Further membranes are also used in biotechnology where the substrate and / or products are concentrated and purified by means of synthetic membranes. Due to the development of biotechnology, there is an
increasing need for the separation of proteins and peptide drugs from biological broths and blood (Higuch et al 1991). The advantages are large-scale separation and easy operation of the membranes.

The water reuse of applications involving ultrafiltration include electro deposition primers, oil-water separation in metal cutting operations, color removal from kraft mill effluents and laundry wastes (Bhattacharya et al 1975). Ultrafiltration is one of the best techniques for the concentration of macromolecular solutions (Nakao et al 1986). The concentration, purification and separation of proteins through UF are considered as an unit operation (Opong and Zydney 1991). It is advantageous over other separation processes due to relative non-destructivity, limiting denaturation of proteins etc. (Medda et al 1981). An experimental study was carried out by Bellucci et al (1975) on the UF of protein containing solutions under different conditions, as compared with a solution of a linear synthetic polymer.

Ultrafiltration is a process applied on liquid industrial waste treatment, food processing and pharmaceutical industries (Ahner et al 1993). In various industries such as food, medicine and bio industry, it is essential to separate solution constituents such as proteins, enzymes, antibodies, hormones and blood proteins (Nakao et al 1988). Rodgers and Sparks (1991) studied the effect of negative transmembrane pressure (TMP) pulsing on solute rejection for an albumin and gamma-globulin mixture in Mukai et al (1998) have conducted ultrafiltration of mixture of bovine serum and egg white lysozyme using membranes which were almost completely retentive for bovine serum albumin but permeable for lysozyme. Li et al (1997) and Li et al (1998) have worked on the effects of gas sparging on permeate flux, single protein transmission and protein fractionation.
Conventional treatment methods for removal of heavy metals from metal finishing operations are usually energy-intensive and costly (Ahmad et al 1994). When Huang and Koseoglu (1993) have presented a review of the membrane operating principles, economics of membrane design and applications of membrane systems in the separation of heavy metals from industrial waste streams. When comparatively low concentration of high toxic or valuable constituents is to be removed from an industrial wastewater stream containing mixture of other salts, ultrafiltration can be applied. Unfortunately, ordinary ultrafiltration methods are not effective in removing solutes having molecular weights less than about 300Da (Sriratana et al 1996). Micellar enhanced ultrafiltration with synthetic surfactants is a recently developed technique which can remove heavy metals and other low molecular weight ions from waste streams at relatively lower cost without a phase change (Smith et al 1995, Hanra and Prabhakar 1996, Kim et al 1998, Fillipi et al 1998).

Concentration and recovery of heavy metals such as Hg (II), Co (II), Pb (II), Ni(II), Ca (II) etc. have been carried out using various complexing agents including polymethacrylic acid (Mandel and Leyte 1964), Carboxy methyl cellulose (Mandkur and Walters 1993). Acrylic acid (Bodzek et al 1999), polyethyleneimine (Nguyen et al 1981), (Juang and Chen 1996), Uludag et al 1997).

Polyethyleneimine (PEI), a polymeric amine, has often been used in many studies as a complexing ligand as well as a versatile source of chelating derivatives for removing metal ions from aqueous solutions by means of complexation - UF (Chaufer and Deratani 1988). PEI has quite a number of advantages such as good water solubility, sufficient number of functional groups, good physical and chemical stability and suitable molecular weights. The aim of the present work is to examine the per cent toxic metal ion
separation using PEI as complexing ligand by ultrafiltration using the blend membranes based on (CA/PMMA and CA/PS systems.

Kim and Vigneswaran (1991) have conducted studies on the treatment of starch wastewater by anaerobic digestion coupled with membrane separation process. Juang et al (1993) have conducted the low pressure batch ultrafiltration for removal of dyes from aqueous solutions at 22 °C and reported that ultrafiltration is an ideal way to achieve these goals by selection of a membrane with appropriate molecular weight retention characteristics. Vigneswaran and Fane (1998) have used ultrafiltration membranes to remove bacteriological and dissolved organics from water and reported 100% removal of bacteria and virus (Phages of Shigella and E. coli) and a significant removal of organics (60-70%).

Thus ultrafiltration membranes find a wide range of applications from food and pharmaceutical to waste water reclamation and hence in the present work attempts have been made to study the performance of membranes based on cellulose acetate, polymethyl methacrylate and polystyrene for specific applications of proteins and metal ion rejections.

1.9 SCOPE OF THE PRESENT INVESTIGATION

Membrane separation techniques such as reverse osmosis and ultrafiltration, play an important role in industrial separation technology. However, many ultrafiltration membranes have been affected by membrane fouling, which reduces the efficiency during operation.

To develop high performance UF polymeric membranes for specific application, it is difficult to find a polymer which satisfies both excellent aqueous permeability aqueous resistivity. Hence based on the
properties of CA, PMMA and PS individually, blends based on these materials may yield membranes with suitable hydrophilic / hydrophobic and appropriate crystalline/amorphous ratios with suitable resistance/processibility.

Hence an attempt has been made to modify CA by blending it with PMMA and PS individually. In order to get membranes with good properties, an investigation on preparation of novel polymeric membranes with the following objectives were made:

- Solution blending of cellulose acetate-polymethylmethacrylate and cellulose acetate-polystyrene.
- Preparation of blend ultrafiltration membranes based on cellulose acetate, polymethylmethacrylate and polystyrene.
- Study on the effect of polymer composition and concentration of additive PEG 600 on performance of membranes.
- Characterization of the modified membranes in terms of
  - Compaction
  - Pure water flux
  - Water content
  - Membrane hydraulic resistance
  - Molecular weight cut-off
  - Membrane morphology
- Applicability of the membranes for the.
  - Separation of proteins such as trypsin, pepsin, egg albumin and bovine serum albumin
  - Separation of toxic heavy metal ions such as Copper (II), Nickel (II) and Zinc (II) ions from aqueous streams.