CHAPTER 1

INTRODUCTION

Membrane processes are gaining momentum in view of their wide application in various industries such as chemical, food, pharmaceutical and metal finishing industries (porter 1972). Even though membranes are normally fabricated from commercial polymers, (Guiver 1992) the adaptability of membrane processes to a wide range of application stems from the development of new polymers or modifications of the existing polymers (portnis 1992).

Efficient separation processes are needed to get high grade products (Bhattacharjee and Datta 1996, Rosberg 1997 and Huang and Koseoglu 1993). Membrane Technology is a type of filtration process, which possesses wide range of applications towards separation, purification and concentration of various chemicals such as microvalent ions, macrovalent ions, suspended solids, proteins, metal ions, paints, pigments, viruses, bacteria etc,.

Membrane separation Technology, is more superior process compared to other conventional separation processes, as it is a highly selective, efficient process and cost effective process. Further, there is no environmental hazard in this non-conventional technique.

1.1   MEMBRANES

Membrane in a broader sense is a region of discontinuity interposed between any two phases. This implies that membranes can be gas, liquid, solid or combination of these phases. Thus, the interfaces of two immiscible liquids, of a gas and a liquid, or of a gas and a solid would not ordinarily be

considered as membrane structures. Membranes vary in their make up from relatively crude structure of a screen to extremely fine configurations only one molecular layer thick, as in the fatty acid spreading in water (Hwang and Kammermeyer 1975).

1.1.1 Historical Overview and Evolution of Polymeric Membranes

The studies on biological membranes, their properties and performances led to the origin and growth of synthetic membranes. The first series of synthetic polymeric membranes were prepared from cellulose nitrate of varying concentrations (Bechhold 1906). The osmotic phenomena was studied by Traube, Pfeffer and Vont-Hoff in membranes prepared by precipitating cupric ferrocyanide in a thin layer of unglazed porcelain. By the early 1930s microporous collodion membranes were commercially available. During the next 20 years, the early microfiltration membrane technology got extended to other polymers such as cellulose acetate, polysulfones etc, and the membranes found their significant applications to obtain drinking water followed by industrial applications during 1960s by Sourirajan and Loeb.

1.2 MEMBRANE SEPARATION PROCESSES

Membrane processing is a technique that permits concentration and separation without the use of heat. Particles are separated on the basis of their molecular size and shape with the use of pressure (microfiltration, ultrafiltration, reverse osmosis and/or gas separation), a concentration gradient (dialysis) or an electrical gradient (electrodialysis) with a specially designed semi-permeable membranes.

Membrane separation is a kind of filtration technique. When effluent enters the system, two streams are formed namely concentrate, containing contaminate and permeate, containing dilute amounts of contaminate (Cartwright 1994) as shown in the Figure 1.1.
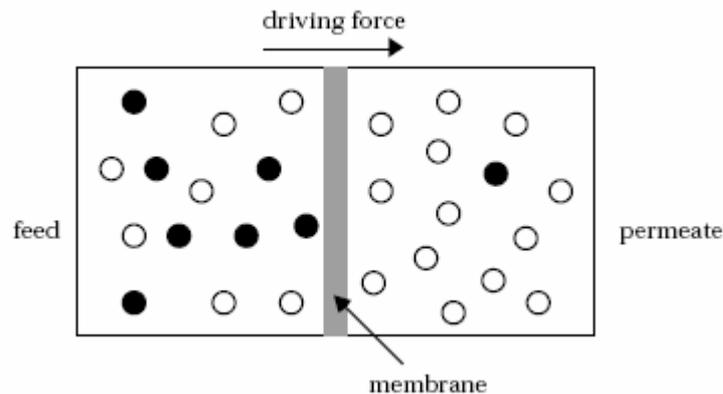

Figure 1.1 Schematic representation of the membrane separation process

A general illustration of all types of membrane separation processes is provided in Figure 1.2. However there are some differences existing between the various processes. The actual separation mechanism can be based on differences in the size of the permeating components (sieving effect), or in the membrane affinity towards the feed solution constituents.

The solute chemical nature or electrical charges, as well as the vapour pressure of the different components in a mixture often play an important role in membrane separation processes. The two phases separated by the membrane, i.e., the feed and the permeate, may present either in the liquid or in the gaseous state. The driving force that is necessary for the transport may be transmembrane pressure gradient ΔP, or a concentration gradient ΔC or activity gradient or Δa, respectively, or an electrical potential gradient ΔE, or a temperature gradient ΔT. Based on these driving forces, the membrane separation processes using membranes can be classified as shown in Table 1.1 (Mulder 1991).
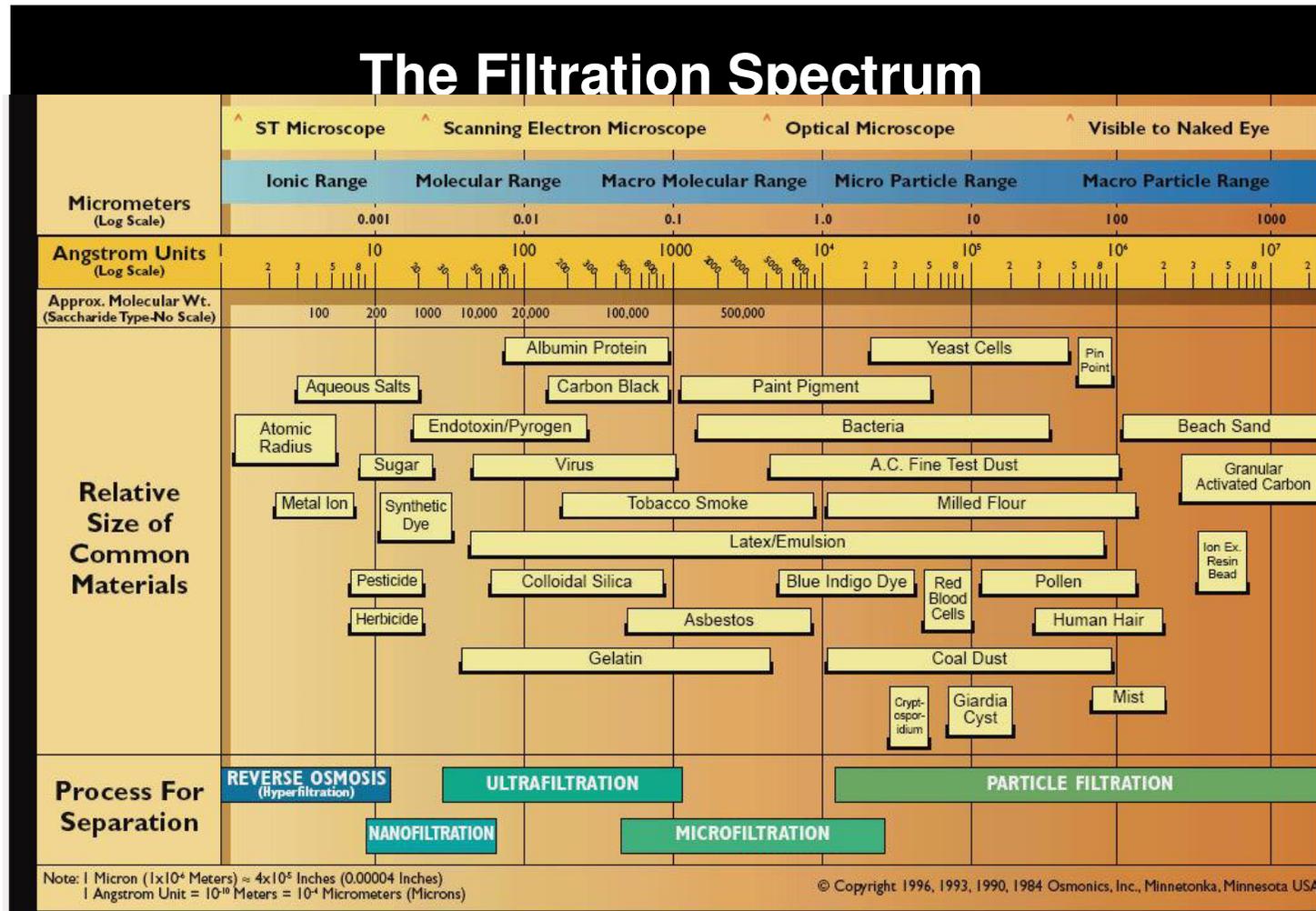
Figure 1.2 Filtration spectrum

Industrially important membrane separation processes and their operating principles are given in Table 1.2

Table 1.1   Overview of membrane processes, driving force, separation mechanism, and states of feed and permeate

Membrane process	Driving force	Feed state	Permeate state	Separation Mechanism
Microfiltration (MF)	ΔP	Liquid	Liquid	Size
Ultrafiltration (UF)	ΔP	Liquid	Liquid	Size
Nanofiltration (NF)	ΔP	Liquid	Liquid	Size/Affinity
Reverse Osmosis (RO)	ΔP	Liquid	Liquid	Size/Affinity
Piezo Dialysis (PD)	ΔP	Liquid	Liquid	Affinity
Gas separation (GS)	ΔP	Gas	Gas	Affinity/Size
Pervaporation (PV)	ΔP	Liquid	Gas	Affinity
Dialysis (D)	ΔC	Liquid	Liquid	Size
Osmosis (O)	ΔC	Liquid	Liquid	Affinity
Liquid membranes (LM)	ΔC	Liquid	Liquid	Chemical Nature
Electrodialysis (ED)	ΔE	Liquid	Liquid	Charge
Membrane Distillation (MD)	$\Delta T, \Delta P$	Liquid	Liquid	Vapour Pressure

The first four processes mentioned in Table 1.1 utilize a hydrostatic pressure difference as driving force and are closely related to each other. The ability to separate solutes, based on the pore size of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis is given in Table 1.2 (Lonsdale 1982, Cadotte et al 1988, Eriksson 1988, Petersen 1993).

Ultrafiltration (UF) designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. Due to the low energy

requirement ultrafiltration is superior to the other conventional separation processes (Ilias et al 1995)

Table 1.2 Comparison of pressure-driven membrane processes

Membrane process	Pore size (nm)	Material retained	Material passed	Pressure (bar)	Type of membrane
MF	> 50	Particles (bacteria, yeasts etc.)	water, salts macromolecules	< 2	Porous
UF	1 – 100	Macromolecules, water, colloids, lattices solutes $M_w > 10,000$	water, salts and sugars	1-0	Microporous
NF	≈1	Solutes $M_w >$ 500, di- and multivalent ions	water, sugars, monovalent ions	5-20	Microporous
RO	Not relevant	All dissolved and suspended solutes (salts, sugars)	water	15-80	Nonporous

1.3 POLYMER MEMBRANES

For the separation of water from wine using animal bladder by Abbe Nollet and Fick prepared artificial and semi permeable membranes made from an ether-alcohol solution of cellulose nitrate called collodion during 1855. Efforts to control membrane pore size led to the development of artificial membranes. Manegold, Michaels and McBain in 1920s prepared membranes, using regenerated cellulose or cellophane. Those cellophane membranes were used for kidney dialysis, which became the first practical application of synthetic membranes. This has paved the way for many researchers to look into polymers for the preparation of membranes. Lloyd and Meluch (1985) have listed over 90 different homopolymers, copolymers

and blends that have been investigated for use as membranes. The simple conditions for polymers to be eligible for the preparation are governed by their availability, capable of forming dense or porous film, correct hydrophilic/hydrophobic balance and a moderate ionic character/dielectric constant. During 1950s, due to the technological breakthrough,scientists, engineers and entrepreneurs intensified the research on the preparation of polymeric membranes, classifications were carried out as microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

1.4   MEMBRANE PREPARATION

Several membrane preparation techniques are available which could be applied depending on the type of membranes required. Few important membrane preparation techniques are discussed as follows.

Symmetric membranes are uniformly isotropic in nature through the cross section of the membrane. These membranes can be porous or dense, but the permeability of the membrane material does not change from point to point within the membrane. The dense membranes are prepared by solution casting and thermal melt pressing and the porous membranes 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 a micro porous support membrane. In this method an aqueous solution of reactive prepolymer is deposited in the pores of the micro porous support membrane followed by immersion in a water immiscible solvent solution containing a reactant. This results in a densely cross linked thin membrane layer.

Solution cast composite membranes are prepared by preparing the thin water insoluble layer and then packing it on a micro porous support. In plasma polymerization, a support membrane is kept in an inert gas atmosphere at low pressure. When monomer vapour is introduced in the atmosphere at 200-300 milli torr for 1-10 min, an ultrathin 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 an asymmetric membrane preparation and it has also been employed in our investigation. In this method, polymer solution is first cast using a 'doctor's blade' to produce a thin uniform film on a glass plate and the solvent is allowed to evaporate. After a predetermined evaporation time, the cast film is immersed in a bath of non-solvent, containing considerable amount of solvent and surfactant. The water rapidly precipitates the top surface of the cast film forming an extremely dense permselective skin. As the cast film, which was in homogeneous sol phase, is converted to gel by non-solvent, 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 formations.

1.5   MEMBRANE MODULES

A variety of membrane types and configurations has been developed. The types of ultrafiltration modules commercially (Strathmann 1990) produced are:

- Flat sheet membrane

- Tubular membrane modules

- Spiral wound membrane modules

- Hollow fibre membrane elements

The immersion type flat membrane module operates suction or gravity filtration while the membrane is being rinsed by aeration. Tubular membranes are based on either PVDF (polyvinylidene fluoride) or PSf (polysulfone). They are capable of continuous, reproducible processing cycles, which means they are cleanable, durable, easy to operate and a proven advance in technology. Spiral wound membrane technology was first introduced more than 30 years ago. Some of the many applications that employ the spiral wound membranes are Seawater desalination, Brackish Water treatment and Recovery of High purity water production, Dairy processing, Whey protein concentration.

Hollow fiber membranes have been successfully employed in a wide variety of industries including food, juice, pharmaceutical, metalworking, dairy, wine and most recently municipal drinking water. Depending on the application, hollow fiber membranes can be highly practical and cost effective alternatives to conventional chemical and physical separation processes.

1.6 HOMO POLYMERIC MEMBRANES AND MODIFIED POLYMERIC MEMBRANES – A REVIEW

1.6.1 Cellulose Acetate Membranes

The development of cellulose acetate (Figure 1.3) membranes of asymmetric structure has found wide applications 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 pretreatment 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). 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-6000 using a 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 (Bhattacharjee and Datta 1996).

On the basis of separation curves, the pore size and pore size distribution of cellulose acetate ultrafiltration membranes are determined (Schwarz and Hicke 1989). Recently there is an increasing need for separation of proteins and peptide drugs from biological broths due to the development of Biotechnology. In the pharmaceutical and food industry, ultrafiltration membrane is required to with stand high temperature and have solvent resistances. Cellulose acetate membrane has high water permeability. However, a fairly narrow pH range, compaction and biodegradation properties restricts its application (Kurihara and Himeshima 1991).
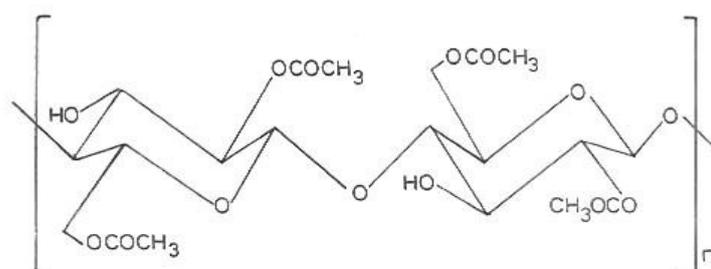

Figure 1.3 Cellulose Acetate (CA)

The effects of pretreatments on morphology and performance of cellulose acetate membranes were investigated by Wang et al (1994). The buoyancy studies of macro void pore formation in dry-cast cellulose acetate membranes were investigated by Matthew et al (2002). Flat sheet cellulose acetate membranes were prepared and the compaction at modest pressure and loss of permeability were 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

- Relatively easy to manufacture and cost effective

- Renewable source of raw material

- Non-toxicity

1.6.2 Polyethersulfone

The development of polyethersulfone membranes of asymmetric structure has found wide range of applications in many separation industries due to their high tolerance towards chemicals, extreme pH and environments and thermal stability. However, it is more susceptible to fouling due to its hydrophibic character. This fragility of the membrane material results in loss of flux over a period of time. Even the membrane life is reduced due to fouling and the choice of cleaning agents is extremely limited (Brousse et al 1976).

The performance of the polyethersulfone membranes are highly hinderd by the fouling effects. This type of fouling can be reduced by modifying the membrane with hydrophilic monomer or a polymer. Many

researchers modified the polyethersulfone membranes adopting various techniques such as functionalization, blending, surface modification etc. In order to check the performance of the membranes a   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 (Bhattacharjee and Datta 1996).

Recently there is an increasing need for separation of proteins, humic substances, toxic metals and sediments from water source due to the increasing pollution. In the pharmaceutical and food industry, ultrafiltration membrane is required with stand high temperature and have solvent resistances respectively. Polyethersulfone (Figure 1.4) membranes has high water permeability high resistance towards wide range of pH, chemical tolerance and are thermal stability. However, fouling during filtration restricts its application (Van der Bruggen et al 2009).
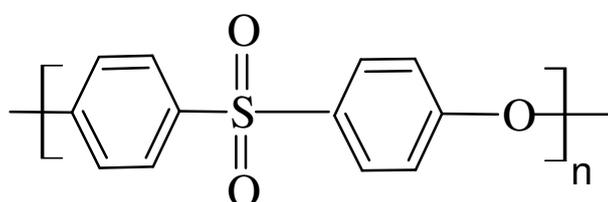

Figure 1.4 Polyethersulfone (PES)

The effects of modification on morphology and performance of polyethersulfone membranes were investigated by (Van der Bruggen et al 2009).

The following advantages of polyethersulfone and its derivatives made it suitable for selecting it as membrane material.

- Wide temperature limit: typically temperatures rang of 90-320°C can be used, which would be an advantage for microbial and biotechnological applications.

- pH tolerances: pH range of 1-13, which is an advantage for cleaning purpose.

- Fairly good chlorine resistance: up to 200 ppm chlorine for short term sanitation purposes and up to 50 ppm chlorine for long-term storage of the membranes.

- Easy to fabricate membranes in a wide variety of configurations and wide range of pore size, ranging from 10 to 200 Å and molecular cut-off from 1000 up to 500,000 Da.

- Longer shelf-life for dope solution in processing industries

- Longer life

- Less shut-downs for cleaning

- Longer continuous run

- Lower surface defects

However, the limitations of polyethersulfone membranes are:

- More hydrophobic

Lau and Jiang (1994) studied the performance of membranes made from miscible blends of polysulfone (PSf) and carboxylated polysulfone (CPSf) having an average of 0.45 and 0.87 –COOH groups per repeat unit. Membranes made from PSf/CPSf of varied blend composition showed higher separation factors for NaCl, glucose, polyethyleneglycol (PEG) and bovine serum albumin (BSA) under an applied pressure of 345 kPa and higher. UF membranes have been prepared and characterized by Thomas et al (1992)

from aromatic polysulfone and CA polymers individually using appropriate polymers, solvent and additive compositions.

A brief summary of selected polymer properties and results obtained from UF, NF and RO membranes made from carboxylated polysulfone, was presented by Guiver and Tam (1992). Rangarajan et al (1991) have discussed the processes occurring during the preparation of polyester fabric reinforced polysulfone membranes based on a simple model. The relationship between the porosity of the fabric, the extent of penetration of the PSf casting solution, the time that elapses between the completion of casting and the onset of gelation and the thickness of the PSf membranes above the surface of the fabric were theoretically deduced and the results were verified experimentally.

Korbutowicz et al (1994) have investigated the performance of UF membranes based on polysulfone and sulfonated polysulfone blend for the removal of humic matter from water. Both membranes were found to reject humic matter in the 91-98% range and a flux decline of 5-30% as a result of surface fouling. Jitsuhara and Kimura (1983) worked on charged UF membranes made of sulfonated PSf for the separation of inorganic solutes. Rejections are high when solute concentration is low, and become lower with high concentration.

Han and Battacharyya (1995) have observed that a polymer film, cast from a homogeneous polysulfone solution (15 wt %) in dimethylformamide, demixes by liquid-liquid phase separation due to nucleation of polymer-poor phase with sorption of water vapor from atmosphere. The separation of the liquid phases continued to grow until the polymer rich phase solidified.

Wang et al (1995) have determined the relationship between the mass ratio of non solvent additive to solvent in a membrane casting solution and its coagulation value in preparing asymmetric membranes by wet or dry/wet phase inversion process. The equation developed may be used to indicate a variation of phase separation behavior of the membrane casting solution with a coagulant by the introduction of a nonsolvent additive in the solution.

Boom et al (1992 and 1992a) have prepared membranes from a casting solution of a water soluble polyether, PVP and PES in 1-methyl-2-pyrrolidone (NMP) as solvent by immersing them in mixtures of water and NMP. Using a model for mass transfer in the quaternary system, it was possible to explain the effect of the additive in macrovoid formation.

1.6.3   Aminated Polyethersulfone and Carboxylated Polyethersulfone

Modified polyethersulfone membranes were found to possess less fouling behavior, than their unmodified analogues and the protection is extended to wide range of retentate pH values (Gancarz et al 2000, Potnis 1992). The impetus for development of new polymers or modification for existing polymers has been proved by the need for higher flux with high permselectivity. Cellulose acetate/aminated polyetherimide blend ultrafiltration membranes were prepared successfully and characterized (Lawrence et al 2008).

Cellulose acetate/carboxylated polysulfone blend ultrafiltration membranes were prepared successfully and characterized Sajitha et al (2002, 2003 and 2005)
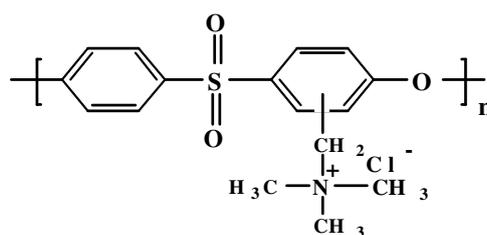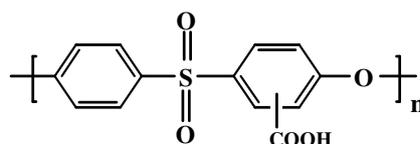
Figure 1.5 Aminated polyethersulfone

Figure 1.6 Carboxylated polyethersulfone

Aminated, carboxylated polyethersulfone possesses excellent mechanical, biological, tolerance to high temperature, pH and chemical stability. Cellulose acetate and carboxylated polysulfone, sulfonated polysulfone blend ultrafiltration membranes were prepared successfully and characterized (Latha et al 2005, Malaisamy et al 2002).

Transformation of neutral polymers into charged ones is a reason for introducing chemically active groups on membrane polymers. In case of polymers with excellent film-forming properties like aminated polyethersulfone, these properties should not be lost by chemical reaction. Membranes prepared from these ion exchange polymers provide higher water content. Thus chemical modification improves the hydrophilicity of the hydrophobic base polymer. Rejections are high when the solute concentration is low and become lower with higher concentration, which is the typical trend of the charged membranes. Thus, these membranes can remove low content of inorganic solute at low pressure of ultrafiltration range, resulting in energy saving.

The membranes modified by direct amination and carboxylation had the lowest surface energy and the shortest grafted chain length and

exhibited the highest volumetric flux with BSA solution. It was also easier to clean and exhibited the highest flux (Nabe et al 1997). The chemical modifications for the modification are membrane preserving i.e., they do not alter the membrane characteristics considerably. The surface charges of the membranes are changed and it depends on the substitute and on the completion of the reaction. The charged ultrafiltration membranes are more interesting than non-charged membranes for practical applications, as they have three variables: sign, density of charges and pore size (Kobayashi and Fujii 1992). The charged membrane is able to expel charged solutes and colloids having the same sign as the membrane surface, so that it is less fouled than the non-charged membrane, by the gel layer formation on the membrane surface (Nakao et al 1988). It is therefore useful to apply a charged ultrafiltration membranes to the separation and permeation of constituents such as proteins, enzyme and water-soluble polymer.

1.6.4   Polymer Blends as Membrane Material

Membranes prepared from homopolymers lack certain qualities such as low flux, poor mechanical strength, hydrophopic nature etc., These drawbacks could be eliminated by blending two or more polymers having desired properties. Blending is used to modify the polymeric material, developing new types of materials and it shows great potential for applications in membranes too (Bikson et al 1994, Baoguo and Hongliang 1996 and Xiuli and Hua 1997). Blending of a miscible hydrophilic polymer with a chemically or thermally stable hydrophobic polymer has been investigated for achieving stable polymeric materials with improved hydrophilicity (Chiou and Paul 1994).

Polyvinylpyrrolidine (PVP), a hydrophilic polymer is known to form blends with polysulfone (Tam et al 1993), polyethersulfone, polyimide, and polyetherimide (Roesink 1989). Membranes from homogeneous blends of

these polymers can be prepared by phase inversion. Chen et al (1996) have prepared mechanically stable, partially charged hydrophilic membranes from blends of aminated polysulfone or sulfonated polysulfone with polysulfone.

Blends of CA and polysulfone have been prepared by (Sivakumar et al 1995). They characterized the blends by pure water permeability and separation of metal ions in aqueous medium.

Fundamental studies on a new series of anion exchange membranes: effect of simultaneous amination-crosslinking processes on membranes ion-exchange capacity and dimensional stability carried out successfully by Xu Tongwen, F.F. Zha 2002)

Polymer blends have provided an efficient way to fill new requirements for material properties. Blending is done for a variety of reasons including creating materials with enhanced thermal and mechanical behavior. 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).

Cellulose acetate as a matrix polymer was blended with polyethyleneimine in a mixture of solvents to prepare a modified microfiltration membrane (Chen et al 2004). The prepared membranes have homogeneously microporous structure, large internal surface area, high pore interconnectivity and mechanical stability. Solution mixing of PSf with CA is already reported by Fukai et al (1994) for semi-permeable membranes with improved chemical resistance and is used for separation of serum albumin. Various polymeric blends based on polyethersulfone/ sulfonated polysulfone

and polyethersulfone/ sulfonated poly (ether ether ketone) have been prepared and characterized (Manea et al 2002).

1.7   CHARACTERIZATION OF MEMBRANES

The characterization of the membranes is essential in order to enhance their performance in the separation and technology processes. Membranes were characterized in terms of compaction, pure water flux, water content, membrane resistance, contact angle, molecular weight cut-off and morphological studies. The pore sizes of the membranes play an important role in deciding the type and performance of membranes. Since membrane performance is governed by its characterization, many attempts were made on characterization of membranes. The necessity and effect of compaction on the water flux of ultrafiltration membranes have been studied by Persson et al (1995). The effect of various concentrations of additives on the formation and performance of polyethersulfone ultrafiltration membranes in terms of water permeability and solute rejection has been studied in detail Chaturvedi et al (2001) and Khan et al (2000)

Kim et al (1990) examined the effect of the density of the hydrophilic group on the pure water flux and water content of membranes. The change in flux was elucidated by considering pore volume change and the site of graft chains. The membrane performance was evaluated by the water flux and the rejection of dextran using a polyacrylonitrile ultrafiltration membranes by Nouzaki et al (2002). Johnson and Johnson (1995) determined the water flux for hydrophobic/hydrophilic ultrafiltration membranes with increasing time. Mulder (1991) concluded that membrane compaction would lead to a denser structure with smaller pores. Transmembrane 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 (Nguyen et al 1980).

The performance of ultrafiltration and microfiltration is an important role and determined by deposition of protein layer Opong and Zydney (1990). The hydraulic permeability of the protein deposit decreased with increasing the filtration pressure. Water content is directly dependent on the porosity of membranes and an index of membrane hydrophilicity and flux and studied by Prabhakar and Misra (1986), Tamura et al (1981), and also Mohan group, Mahendran et al (2004).

The molecular weight cut-off (MWCO) was constructed by measuring the separation values of polyethylene glycol solutes of varying molecular weights. The method for determining the concentration of polyethylene glycol was given by Sabde et al (1997).

1.8 APPLICATIONS OF ULTRAFILTRATION PROCESSES

Conventional separation techniques such as precipitation, ozonation, biological treatment possesses lots of disadvantages such as usage of chemicals, man power consumption, usage of chemicals, energy expensive etc,. Whereas, the advanced membrane technology finds widespread applications in the areas of ultrapure water, food technology, animal blood processing, clarification of juice, down stream processing, membrane bio reactors, electrodeposition of paints, oil and latex emulsion treatment, pulp and paper industry etc., (Jonnson and Tragardh 1990). The physical process of separation by ultrafiltration membranes was studied to improve the colour and turbidity removal of the textile effluent (Rosa Maria Ribeiro, 2002).

Cellulose acetate and polysulfone based membranes have been largely used for the treatment of sea water for the production of drinking

water. (Jones and Wilson 1998 and Pryor et al 1998). In microbiology, ultrafiltration finds wider usage in the separation and concentration of foot-and-mouth virus. Stirred cell, flat sheet and spiral configurations of 50 -300 K MWCO ultrafiltration membranes made of acrylate polymers were used for the concentration of virus and a maximum of 94% recovery has been achieved (Adikane et al 1997).

Ultrafiltration provides macro-molecular separation for particles in 20 - 1000 Å. All the dissolved salts and smaller molecules pass through the membrane. Items rejected by the membrane include colloids, proteins, microbiological contaminants and large organic molecules (Vigneswaran and Fane 1998). Further, impetus for the application of membranes comes from biotechnology, there is an increasing need for the separation of proteins and peptide drugs from biological broths and blood (Higuchi et al 1991). The treatment of distillery effluent and removal of color is a major problem with sugar industries. Satyajai Mayor (1999) has studied the use of membranes at various stages of effluent treatments in detail. It has been proved that the economics works out to be reasonably satisfactory to the distillery.

Membranes were used to treat waste waters in various mining and mineral sectors like metal leaching solutions, ore washing, floatation process water, acid mine drainage, refinery operations etc., (Awardalla and Kumar 1994). Precious and rare earth metals such as Au, Se and U etc., have been extracted from their dilute solutions. Juang et al (1993) have conducted low-pressure batch ultrafiltration for the removal of dyes from aqueous solutions at 22ºC and reported that ultrafiltration is an ideal way to achieve these goals by selection of a membrane with appropriate molecular weight retention characteristics.

1.8.1   Rejection of Proteins by Ultrafiltration Membrane Process

The rapid growth in the field of biotechnology has led to an increase in the demand for efficient, large-scale protein rejection processes. The major advantage of ultrafiltration processes over conventional processes is high throughout of product. Fane et al (1983) explained ultrafiltration of proteins through partially-permeable membranes. The flux and rejection are time-dependent, flux shows an initially rapid and then a more gradual decline that is attributable to loss of porosity by internal adsorption followed by surface adsorption.

Iritani et al (2002) examined the dynamic behavior of dead-end ultrafiltration of dilute aqueous BSA protein solution. The concentration distributions in the filter cake, accumulated on the membrane surface in dead-end ultrafiltration of protein solutions, were measured using the principle of inclined ultrafiltration where a large amount of filter cake is formed. Balakrishnan and Agarwal (1996) concluded that a high degree of protein separation is generally obtained at low fluxes, corresponding to low transmembrane pressures.

Dynamic ceramic ultrafiltration membrane was characterized in terms of ovalbumin protein solution, the linear velocity along the membrane, bulk protein concentration, pressure and pH in the feed solution were studied in detail (Matsuyama et al 1994). In various industrial fields, such as food and medical industries and bio industry, it becomes increasingly important to separate solution constituents such as proteins, enzymes, antibodies, hormones, and blood proteins (Nakao et al 1988).

Magueijo et al (2002) have reported protein ultrafiltration (UF) and its dependence on UF operating conditions. Cellulose acetate (CA) asymmetric membranes are made in laboratory by the phase-inversion method

and characterized in terms of pure water permeability and molecular weight cut-off (MWCO) (10000 Da for 98% of rejection). Permeation experiments were carried out for solutions of reference solutes in order to characterize the membranes and for lysozyme solutions under different operating conditions. The influence of the ionic strength in the permeation flux and protein rejection is studied by performing permeation tests with a solution of lysozyme (0.3 kg/m^3) containing different NaCl concentrations.

The transmission of the major chicken egg with proteins ie., ovalbumin and conalbumin, were found to depend on the transmembrane pressure; transmission decreased with increase in transmembrane pressure (Gosh et al 2000). Mukai et al (1998) have conducted ultrafiltration of mixtures of bovine serum albumin and egg white lysozyme using membranes which were almost completely retentive for BSA but permeable for lysozyme. Chiang et al (1993) have reported a two-step process involving diafiltration and affinity separation for purification of lysozyme.

The contributions of individual protein species to the apparent critical flux were evaluated as well as the separation performance by Ghan et al (2002). For mixtures of globulin/lysozyme and BSA/lysozyme the larger retained protein tended to control the critical flux behaviour. Causseranda et al (2002) determined the apparent MWCO of ultrafiltration membranes using a mixture of dextran protein solutions. Tests were conducted with a flat-sheet membrane with an effective filtration area.

1.8.2 Separation of Toxic Heavy Metal Ions by Ultrafiltration Membrane Process

Many industrial wastewaters, including mining, mineral processing, metal finishing and battery industries, contain metals as multicomponent mixtures (Fane et al 1992). Many metals, especially heavy metals are toxic

and provide a major environmental hazard. In addition they have potential economic value as non-renewable natural resources. The increasing awareness of the environmental dangers posed by discharge of toxic heavy metals into the environmental and the accumulation of heavy metals in sewage sludge has resulted in progressively stricter legislation regarding effluent quality standards.

Conventional treatment methods for removal of heavy metals from metal finishing operations are usually energy intensive and costly. Micellar-enhanced ultrafiltration (MEUF) with water soluble polymer is a recently developed technique which can remove heavy metals and other small molecular weight ions from waste streams at relatively lower costs and without a phase change. Heavy metals such as cadmium, lead, copper, nickel and zinc in a simulated wastewater, alone and together, were substantially removed by surfactant – based ultrafiltration using natural surfactants (Hung et al 1994), (Mahendran et al 2004). The permeation behavior of several kinds of metal complex solutions was investigated with cellulose acetate membranes annealed at 65-76°C (Kamizawa 1978).

Muslehiddinoglu et al (1998) investigated the performance of polymer enhanced ultrafiltration (PEUF) method for removal of mercury and cadmium from binary mixtures. The method includes the addition of polyethyleneimine (PEI) as a water-soluble   polymer to bind the metals to improve separation. The influence of various operating parameters such as temperature, metal/polymer ratio and pH on retention of metals and permeate flux was investigated.

Chromium as chromate is one of the most serious environmental problem in all over world. Sriratana et al (1996) studied the removal of chromate from aqueous solution using poly (diallyldimethyl ammonium chloride) with an average molecular weight of 240K as the polyelectrolyte.

The solution was then treated using ultarfiltration with membrane pore sizes small enough to reject the polymer bound ion.

Saffaj et al (2004) evaluated the efficiency of ceramic ultrafiltration membranes in rejecting the toxic heavy metal ions such as Cr(III), Cd(II) and Pb(II).

A process for purifying wastewaters containing heavy and toxic metal such as chromium has been studied. A batch complexation–ultrafiltration process was used to concentrate and recover chromium from sulphate solution. As the chromium ions are too small to be retained by the filter, they are first complexed with a water-soluble macroligand (polyethylene-imine). Factors affecting the rejection rate and permeate flux such as pH, concentration ligand, chloride and sulphate concentration, membrane pore size, applied pressure and extraction factor were investigated by Aliane et al (2000)

Rivas et al (2001) studied the binding capacity of various completely water soluble co polymers with metal ions such as metal ions Ag(I), Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), and Cr(III). Further, they investigated retention of metal ions in an aqueous solution with water-soluble polymers.

1.9 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Through there are several reports on the properties and performance of various membranes which are available, membranes suitable for specific environment and applications with improved properties such as flux, hydraulic resistance, and rejection, mechanical, thermal and chemical stability have not been attempted to. Hence, in the present investigation, an

attempt has been made to develop UF membranes with improved properties such as high flux, fouling resistant, thermal and chemical resistance for desired applications such as removal of macromolecular proteins and toxic metal ions removal. In this study, CA has been chosen as the base polymer and blend with APES and CPES with PEG 600 have been chosen as an additive and its influence on membrane performance was investigated.

In order to prepare membranes with superior properties, an investigation on preparation of novel polymeric membranes was made.

The present work includes the preparation of blend membranes. In this work, CA has been chosen as the base polymer and blended with APES and CPES in the absence and presence of additive, PEG 600 with DMF as a solvent.

The objectives of the investigation are

1) Functionalisation of PES by Amination and Carboxylation.

2) Characterization of aminated and carboxylated PES polymer.

3) To Study the effect of additive concentration and blend polymer composition on the performance of blend membranes.

4) Characterization of the polymeric membranes in terms of

(i) Compaction

(ii) Pure water flux

(iii) Water content

       (iv)   Hydraulic resistance

       (v)   Contact angle

       (vi)   Molecular weight cut – off (MWCO) and

       (vii)   Membrane morphology

5)   Application of the membranes in the separation of proteins such as trypsin, pepsin, egg albumin and bovine serum albumin and removal of toxic heavy metal ions such as Copper (II), nickel (II), Zinc (II), and cadmium (II) from aqueous streams.