

CHAPTER II

LITERATURE REVIEW

2.1 Overview and Principle of Membrane Technology

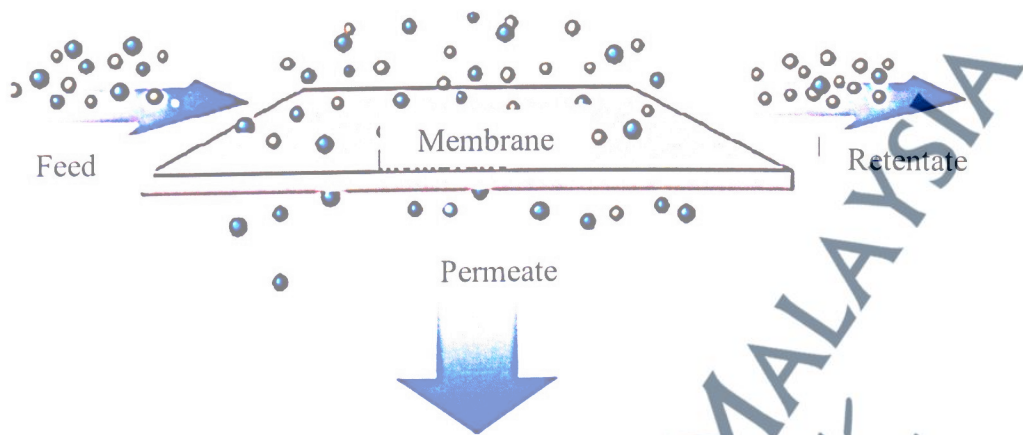
The development of membrane process for commercial or industrial applications lagged far behind scientific research. Even towards the middle of the 18th century, membrane phenomena were observed and studied primarily to elucidate barrier properties and related phenomena rather than to develop membranes for technical or industrial applications. The membrane technology was developing successful in 20 years, from 1960 until 1980. The original Loeb-Sourirajan membrane technology and other process were developed for making ultra-thin, high performance membrane. Besides, interfacial and multilayer composite casting and coating also was used.

Methods of packaging membranes into large-membrane-area such are spiral-wound, hollow-fine-fiber, capillary and plate-and-frame modules were developed and advances were made in improving membrane stability. The membranes used in the various applications were differing widely in their structure, function and the way they are operated. However, all membranes have several features in common that make them particularly attractive tools for the separation or filtration of molecular mixtures. A membrane can be much more complex in both structure and function, also may be

solid or liquid, homogenous or heterogeneous, isotropic or anisotropic in its structure (Strarthmann et al., 2006).

In general, membranes are very thin layers, which can have different structures. They are divided into porous membranes and solution-diffusion membranes. Porous membranes are well established in typical filtration processes for example microfiltration, ultrafiltration and nanofiltration. The particles to be separated have diameters between 10 and 1000 nanometers (nm) and will be held back from the membrane due to the fact that the pores of the membrane are smaller than the particle size. If the size of the components to be separated is less than 1 nm, which is the case for many gaseous, vaporous and also liquid components that have to be removed from process streams then, mainly so called solution-diffusion membranes are used. This type of membrane does not have pores but free volume sites which exist due to restricted motion and packing density of the polymer chains (Schmeling et al., 2010).

Besides, the important things of membrane are their ability to control the rate of permeation of different species. As mentioned, it has two models which are solution-diffusion model and pore flow model. The solution-diffusion model, in which permeate dissolve in the membranes material and then through the membrane down a concentration gradient. The permeate is separated because of the differences in the solubility of the materials in the membrane and the differences in the rate at which the material diffuse through the membrane. The other model is the pore flow model, in which permeates are transported by pressure-driven convection flow through tiny pores. Separation occurs because one of the permeate is excluded (filtered) from some of the pores in the membrane through which other permeates move.

FIGURE 4: Membrane Based Separation Process

Source: Schmeling et al., 2010

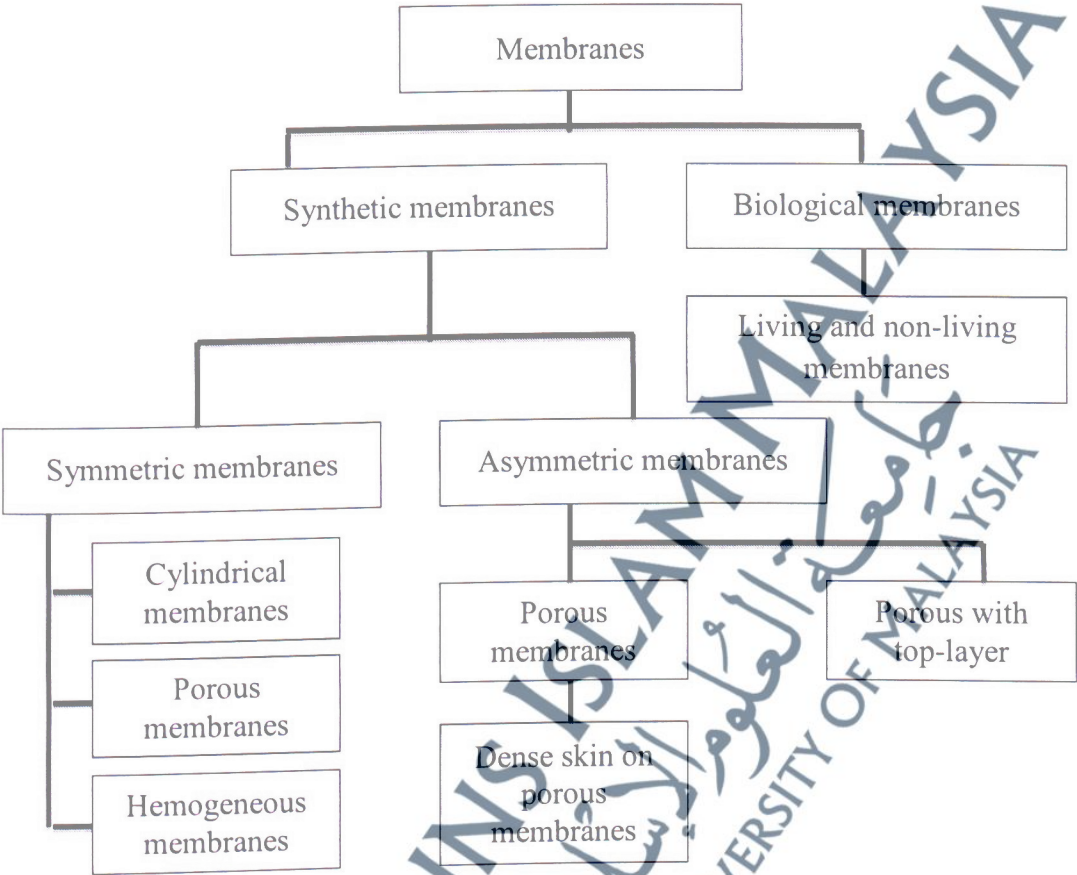
Figure 4 shows the principle of a membrane-based separation process. The feed mixture is transported along one side of the membrane and the different feed components permeate through the membrane at different rates. The stream leaving the membrane unit on the same side as the feed is depleted in the components which permeate preferentially. Consequently the stream, which is collected on the back side of the membrane, is enriched in the preferentially permeating component. The driving force for the mass transport through a polymeric membrane is the difference in the chemical potential between the feed and the permeate side and depends on temperature, pressure and concentration. Moreover, the mass transport through solution-diffusion membranes can be described with the solution-diffusion model. Based on this model, the components permeate through a polymeric membrane in a three-step process which are the sorption of the component on the membrane surface (feed side), the diffusion of the component through the free volume of the polymer and desorption of the component on the permeate side of the membrane (Schmeling et al., 2010).

2.2 Membrane Classification

Membrane can be classified in numerous ways according to different points of view. One of the classifications is by natures which are synthetic membranes and biological membranes. This classification is the clearest distinction possible. Besides, in practice membranes can also be classified by their chemical structure or morphological structure. However, this classification is more illustrative because the membrane structure determines the separation mechanism and hence the applications. Classification of membranes based upon their physical properties has also been proposed. Based on this category, membranes can be divided into homogenous and heterogeneous, or symmetric and asymmetric membranes (Mulder, 1991).

In addition, the symmetric membranes can be either porous or nonporous with their thickness ranging from $10\mu\text{m}$ to $200\mu\text{m}$. the resistance to mass transfer is determined by the actual pore structure and the total membranes thickness. A decreasing in membrane thickness will resulted in increased permeation rate or flux. On the other hand, asymmetric membranes consist of a skin layer fabricated on top of a porous support layer with a thickness of $50\mu\text{m}$ to $150\mu\text{m}$. The membrane performance is normally determined by this dense skin layer. The resistance to mass transfer is normally low compared to the same thickness of a symmetric membrane because the dense skin layer is usually very thin which is between $0.01\mu\text{m}$ and $1.0\mu\text{m}$ (Zhou, 1997). We can see more clearly in Figure 5 for some basic information in order to understand on classification of membrane.

FIGURE 5: Classification by Membrane Structures



Source: Zhou, 1997

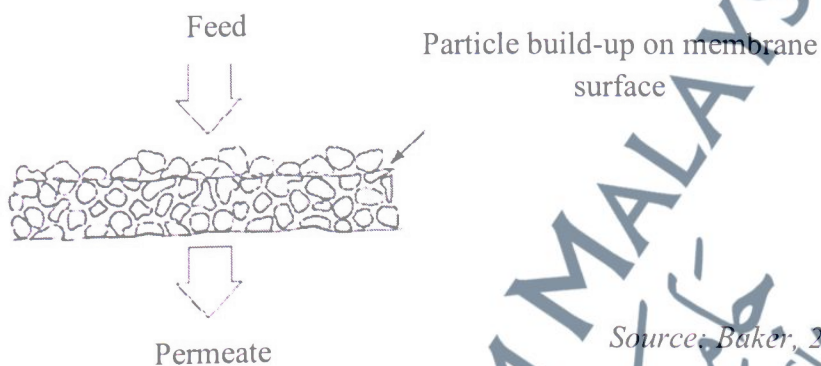
2.2.1 Types of Feed Flow

The filtration styles need to be introduced before introducing the membrane module. The feed flow through the membrane plays a very important role as it effects the permeate flux which determines the performance and efficiency of the process. There are two types of feed flow which are dead-end flow as shown in Figure 6. Dead-end filtration results in a build up of product on the membrane surface that may foul the membrane. The other filtration is cross flow as shown in Figure 7, involves the recirculation of the retentate across the surface of the membrane. This gentle cross flow feed acts to minimize membrane fouling, maintains a high filtration rate and provides higher product recovery since the sample remains safely in solution.

2.2.1.1 Dead-end-Flow

In dead-end filtration (Figure 6), the feed flow enters perpendicular to the membrane surface and essentially all of the flow which can permeate passes through the membrane. As more and more liquid passes through the membrane, more and more materials or particles build up over time forms a layer on the membrane surface until the flow resistance becomes too large for the desired flow rate to be maintained. At that point, the operation must be shut down, the solids removed, and the flow restarted (Humphrey and Keller II, 1997). Hence, the smaller particles concentration in permeate will decreasing while the cost of separation due to the higher operational costs such as pumping cost will increasing (Baker, 2005).

FIGURE 6: Schematic of Dead-End Flow through the Membrane, Showing the Build-Up of Large Particles on the Membrane Surface

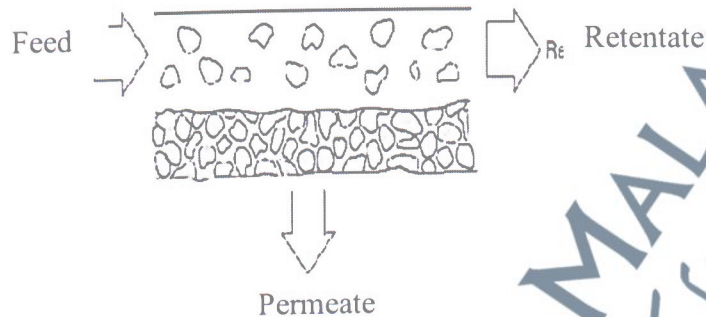


Source: Baker, 2005

2.2.1.2 Cross Flow

The feed flow is parallel to the membrane surface or perpendicular to permeate flow is known as the cross or tangential flow (Figure 7). Cross flow avoids deposition of large particles on the membrane surface by the sweeping effects caused due to the feed flow being parallel to the membrane surface. The non-permeating species tend to be swept along the velocity of the retentate stream (Humphrey and Keller II, 1997). Cross flow filtration results in less fouling and continuous in comparison to the dead-end flow. However, all cross flow filtration processes over time demonstrated the concentration polarization effect. Concentration polarization is where the particle concentration is greater at the membrane surface than in the bulk (Song and Elimelech, 1995).

FIGURE 7: Schematic of Cross Flow or Tangential Flow through the Membrane, Showing the Sweeping Action of the Feed Flow



Source: Baker, 2005

The cross flow velocity plays a significant part in membrane filtration as it directly influences concentration polarization. If increasing in cross flow velocity, hence the concentration polarization will decrease. It is vital that concentration polarization is reduced as much as possible as it has a very strong impact on permeate flux, operating costs and also the overall performance of the process (Chollangi, 2009).

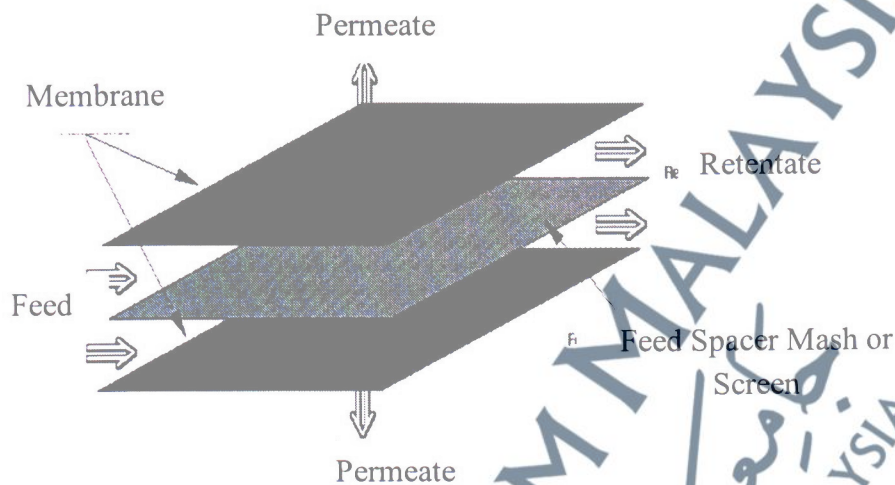
2.2.2 Module Types of Membranes and Characteristics

Before a membrane separation can be performed industrially, therefore methods of economically and efficiently packaging large areas of membrane are required. These packages are called membrane modules. There are four types of tangential flow filtration modules used widely which are plate-and-frame membrane module, tubular, spiral-wound and hollow fiber module.

2.2.2.1 Plate-and-frame Membrane Modules

The plate-and-frame membrane module system was among the first introduced on a large scale and earliest configurations in the market. Plate-and-frame devices use flat sheet membranes and constitute another early form of practical membrane device and are modelled after plate-and-frame filter presses. The major use of plate-and-frame devices is to concentrate liquids containing high suspended solids or highly viscous liquids in the food, beverage, and pharmaceutical industries and in the treatment of waste waters. These configurations are, however, widely used in electrolytic membrane applications such as electrodialysis (Cheryan, 1998; Brandt et al., 1993).

The simplest stack design consists of several sets of alternating frames, which support the membrane on the permeate side and separate the membranes on the feed side. The entire assembly is pressed between two end plates and held together with tie rods. The frames, in addition to support the membranes, have flow channels that collect the permeate and direct it to a permeate manifold. The feed frames are connected in parallel by a feed manifold and contain a spacer material to separate adjacent membrane sheets and provide flow channels (Brandt et al., 1993). The assembled plate-and-frame module is shown in Figure 8 (Humphrey, 1997).

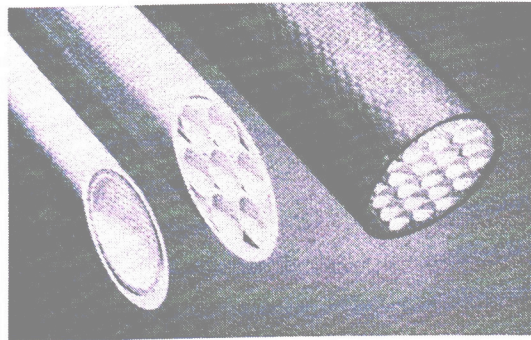
FIGURE 8: Plate-and-Frame Membrane Module

Source: Pelligrino and Sirdar, 2004

2.2.2.2 Tubular Membrane Modules

Tubular membranes (Figure 9) are essentially a larger, more rigid version of hollow-fiber membranes. With diameter as large as 1 to 2 inches, the tubes are not prone to clogging and the membrane material (the tube wall) is comparatively easy to clean. However, the large tubes also result in a very inefficient amount of membrane surface area per unit volume in the pressure vessel. Both porous (for MF/UF) and semi-permeable (for NF/RO) membranes have been manufactured in tubular configurations (Cheryan, 1998; Pirnie, 2005).

FIGURE 9: Tubular UF/MF Module Available from Koch



Source: Cheryan, 1998

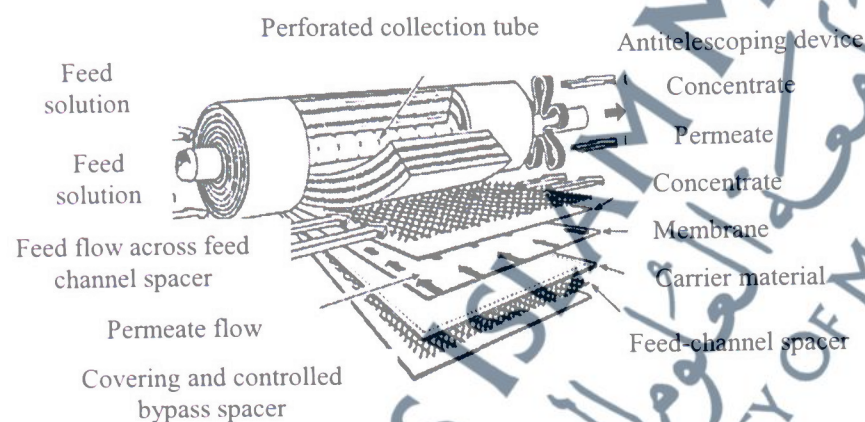
High pressure feed streams enter the tube bore, and the permeate passes through the membrane and supporting structure into the jacket, where it is removed through permeate ports. The feed, continually concentrated as it flows through the tube, exits the tube sheet on the opposite end where its flow is reversed by the U-connection and is passed through additional tubes to achieve the desired overall recovery (Brandt et al., 1993).

2.2.2.3 Spiral-wound Membrane Modules

Spiral wound modules represent a very different approach to creating high amounts of surface area per unit volume (Humphrey, 1997). This module is one of the most compact and inexpensive designs that are available. These membrane elements are designed around flat sheets. Two flat sheets are placed together with their active sides facing away from each other. Each flat sheet membrane has one active side through which the smaller molecules permeate through. A feed spacer, which is a thin and mesh-like material, is placed between the two flat sheet membranes. The two flat sheet membranes with the feed spacer separating them are rolled around a perforated tube

(Cheryan, 1998; Nielsen, 2000). In all spiral wound membrane modules, the membrane surface per unit volume is very high and operating costs are low. Figure 10 shows the schematic of a spiral wound membrane.

FIGURE 10: Spiral Wound Module Showing the Direction of the Feed Flow and the Set-Up of the Spiral Wound Membrane



Source: Cheryan, 1998

2.2.2.4 Hollow-fiber Membrane Modules

As the name suggests, these modules are comprised of hollow-fiber membranes, which are long and very narrow tubes that may be constructed of any of the various membrane materials. The fibers may be bundled in one of several different arrangements. In one common configuration used by manufacturers, the fibers are bundle together longitudinally, potted in a resin on both ends, and encased in a pressure vessel that is included as a part of hollow-fiber module. These modules are typically mounted vertically, although horizontal mounting may also be utilized. A typical commercially available hollow-fiber module may consist of several hundred to over 10,000 fibers (Pirnie, 2005). Figure 11 shows the cross section of a hollow-fibers

membrane. Bundles of the individual fibers are sealed into a hydraulically symmetrical housing to make one module (Kuriyel, 2000).

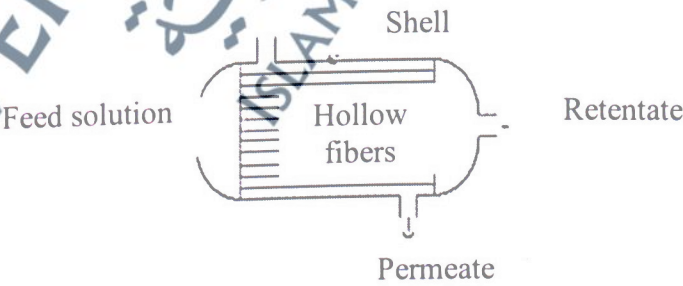
FIGURE 11: Cross Sectional View of an Individual Hollow-Fiber, the Pores are Clearly Visible on the Fiber



Source: Cheryan, 1998

The bundles are arranged in a shell and tube arrangement as shown in Figure 12. The feed enters and exits the shell whereas the permeate that has passed through each individual hollow-fiber is collected on the tube side (Yeh et al., 2003).

FIGURE 12: Schematic of the Shell, Tube Arrangement and the Flow Directions of the Hollow-Fiber Module



Source: Yet et al., 2003

2.3 Membrane Separation Process

The membrane separation process was categorized based on size exclusion membrane. Size exclusion membrane is a porous barrier, by which filtration can be performed to separate suspended or dissolved materials in solution based on size or molecular weight. Each of them has different character such as mechanisms of separation, physical morphology and chemical nature. There are four main classifications of separation process which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Nielsen, 2000). The important membrane processes with the general classification and their operating principles are listed in Table 1.

TABLE 1: Technically relevant membrane separation processes, operating principles, and application

Separation Process	Membrane Type Used	Applied Driving Force	Mode of Separation	Applications
Microfiltration	Symmetric porous structure, pore radius 0.05-5 μm	Hydrostatic pressure 0.5-4 bar	Filtration (size exclusion)	Water purification, Sterilization
Ultrafiltration	Asymmetric porous structure, pore radius 2-10 nm	Hydrostatic pressure 1-10 bar	Filtration (size exclusion)	Separation and fractionation of molecular mixtures
Nanofiltration	Asymmetric porous structure	Hydrostatic pressure	Filtration (size exclusion)	Separation of small organic compounds and selected salts from solutions
Reverse Osmosis	Asymmetric skin-type	Hydrostatic pressure 10-100 bar	Solution-diffusion mechanism	Sea and brackish water desalination

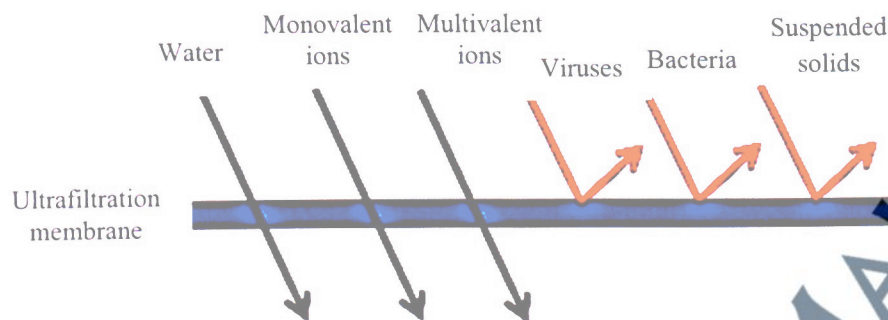
Source: Membrane Technology, 2005

2.3.1 Ultrafiltration

Ultrafiltration (UF) is one of the pressure driven processes that are most often associated with the term of membrane filtration with pore size ranging from 5 to 50 nm. It is characterized by its ability to remove suspended or colloidal particles via a sieving mechanism based on the size of the membrane pores relative to that of the particulate matter. The term molecular weight cut-off (MWCO) is used to describe the sizes of particles separate by an ultrafilter. This is because some of UF membranes have the ability to retain larger organic macromolecules as well as they have been historically characterized by MWCO rather than by a particular pore size. Typical MWCO levels for UF membranes range from 10,000 to 500,000 Daltons. The shape of the solute, its association with water and its charge also affect its permeability through an UF membrane (Cheryan, 1998; Cynthia, 2000).

Generally, UF membrane is typically used to retain macromolecules and colloids from a solution, the lowest limit being solutes with molecular weights of a few thousand Daltons. The finely porous surface layer performs the separation while the microporous substrate provides mechanical strength. The membranes discriminate between dissolved macromolecules of differences sizes and are usually characterized by their molecular weight of the globular protein molecules that is 90% rejected by the membranes as shown in Figure 13 (Membrane Technology, 2005).

FIGURE 13: Example of Ultrafiltration Membrane Process



Source: Membrane Technology, 2005

2.3.2 Factors Affecting Retentivity of Ultrafiltration Membranes

There are six factors that will affect the retentivity of UF membranes, namely as below: (Cheryan, 1998).

a) Size of the molecules

UF membranes have very broad pore size or MWCO distributions which covering more than one order of magnitude. The water and low molecular weight solutes will pass through the membrane while the suspended solids and solutes of high molecular weight will be retained on the membrane (Cheryan, 1998).

b) Shape of molecules

The shape and conformation of macromolecules are also affected by ionic strength, temperature, and interactions with other components. Differences in shape could also be a reason why the MWCO for proteins and others are different (Cheryan, 1998).

c) Membrane configuration

The different types of membrane are affected the rejection coefficient and also flux of permeate. Therefore, rejections coefficient and flux for the same membrane could be different in different module designs. For example, the flat-sheet rejections are different with hollow fiber configurations (Cheryan, 1998).

d) Type of membrane materials

Different membrane materials with the same nominal MWCO will appear to give different solute rejection. For example, regenerated cellulose (RC) membranes have broader pore size distributions compared to polyethersulfone (PES) membranes. RC membranes have higher rejections and show less deviation between observed and true rejections and less effect of transmembrane pressure on rejection. These phenomena are probably related to fouling effects, hydrophobicity, charge, and surface roughness (Cheryan, 1998).

e) Presence of other solutes

In general, low molecular weight solutes (such as sugars and salts) whose molecular size is smaller than the smallest pore on the membrane will be freely permeable means that they will have no rejection. The permeability of individual components in a mixture depends on the relative sizes of these components and the pores. Their presence in the feed solution will not usually affect the permeability of large molecules, such as protein, unless they interact with the large molecules and cause molecular changes (Cheryan, 1998).

f) Absorption of solutes by the membrane

Solute-membrane interactions that result in the physical adsorption of the solute by the membrane, whether on the surface or in the pores will decrease the yield of the solute. The adsorption of solutes depends on the nature of solutes and type of membrane. This adsorption phenomenon can also affect apparent rejection coefficient values, since the solute will not appear in the permeate in its full concentration until the adsorption sites are completely saturated (Cheryan, 1998).

2.4 Membrane Preparation

Most membranes used in industries have an asymmetric structure. Therefore, during the three decades of intensive membrane preparation research, there are various methods for the preparation of asymmetric membranes that have been proposed to generate selective, permeable films, which are describes in the section that follow. Asymmetric membranes are mostly fabricated by a process called phase inversion. In the techniques, an initially homogeneous polymer solution thermodynamically becomes unstable due to different external effects and phase separates into polymer lean and polymer rich phases. The polymer-rich phase forms the matrix of the membrane while the polymer-lean phase rich in solvents and non-solvents, fills the pores.

2.4.1 Phase Inversion Technique

The most commercially used and thus important class of techniques is called phase inversion techniques. The phase inversion method is widely used to prepare a variety of polymeric membranes from microfiltration to gas separation. In the phase inversion process, the homogeneous polymer solution decomposes into two phases which are one with a high polymer concentration, and one with a low polymer concentration. The concentrated phase solidifies shortly after phase separation, and forms the membrane.

This process is based on the phenomenon of liquid-liquid phase separation and is also known as solution precipitation or polymer precipitation. Phase inversion is a

process where a polymer solution is transformed in a controlled manner from a liquid to a solid state. A homogeneous casting solution is cast into a thin film membrane or spun as a hollow fiber and immersed in a non-solvent bath. The membrane is formed by demixing of the solution and the precipitation of the polymer (Baker, 2004).

In this process, a homogeneous polymer solution is cast onto a suitable support as a thin film and then immersed into a coagulation bath containing a suitable non-solvent. The polymer film solidifies to form a membrane with a symmetric or asymmetric structure through the exchange between the solvent inside the cast film and the non-solvent outside the cast film in the coagulation bath. In this process of solidification, the film goes through complicated phase changes which include liquid-liquid phase separation, solid-liquid phase separation or both, depending on polymer properties and coagulation conditions.

There are two types of demixing taking place during the phase inversion process which are instantaneous and delayed demixing. Membranes formed by instantaneous demixing generally show a highly porous substructure (with macrovoids) and a finely porous, thin skin layer. Besides, membranes formed by a delayed demixing mechanism show a porous (often closed-cell, macrovoid-free) substructure with a dense, relatively thick skin layer (Chakrabarty et al., 2008).

In addition, phase inversion can be described as a demixing process whereby the initially homogeneous polymer solution is transformed in a controlled manner from a liquid to a solid state. This transformation can be accomplished in several ways (Lalia et al., 2013), namely:

- a) Immersion precipitation. The polymer solution is immersed in a non-solvent coagulation bath (typically water). Demixing and precipitation occur due to the exchange of solvent (from polymer solution) and non-solvent (from coagulation bath), that is the solvent and non-solvent must be miscible.
- b) Thermally induced phase separation. This method is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying.
- c) Evaporation-induced phase separation. The polymer solution is made in a solvent or in a mixture of a volatile non-solvent, and the solvent is allowed to evaporate, leading to precipitation or demixing/precipitation. This technique is also known as a solution casting method.
- d) Vapor-induced phase separation. The polymer solution is exposed to an atmosphere containing a non-solvent (typically water); absorption of non-solvent causes demixing/precipitation.

2.4.1.1 Immersion Precipitation

Among these techniques, the immersion precipitation is the most efficient one because it is operated in the room temperature and it does not have to deal with vapor phase. The preparation of asymmetric polymeric membranes by means of immersion precipitation of a casting solution started with the development of reverse osmosis membranes by Loeb and Sourirajan in 1962. Since then different kinds of asymmetric membranes have been prepared by means of immersion precipitation. In the other

hand, the immersion precipitation process is also used to prepare the supporting layer of composite membranes. By using this method, they achieved high-flux cellulose acetate membrane with a dense skin, having desalination properties (Lalia et al., 2013).

The basic process of immersion precipitation can be carried out with three components. Solvent and polymer are used to prepare the casting solution and non-solvent is used as the coagulation bath. The formation process of the membrane can be split up into three parts which are as follows:

- a) Composition changes in the polymer solution before immersion into a coagulation bath, by evaporation.
- b) Composition changes in the polymer solution after immersion into a coagulation bath prior to possible demixing processes.
- c) Demixing processes which take place when the composition of the polymer solution becomes thermodynamically unstable.

Binary diffusion during the time in between casting and immersion of the polymer solution (evaporation step) has been investigated by a number of authors (Anderson and Ullman, 1973; Krantz et al., 1986). The duration of the evaporation step influences the membrane structure when volatile solvents are used. However, when nonvolatile solvents are used or when no evaporation step is carried out, asymmetric membranes can also be obtained. Hence, this means that the ternary diffusion process which starts after immersion of the polymer solution into a non-solvent bath mainly determines the asymmetric structure of the membrane. In addition, the important feature of the membrane formation process is the type of

demixing processes that can occur in the immersed polymer solution after diffusion has led to a metastable composition. These demixing processes create the pores in the sublayer and determine the structure of the top layer of the membrane (Reuvers et al., 1987).

Most of the commercial membranes available are being prepared by immersion precipitation, sometimes with modified steps (Tan, 1999). The modification methods include changing composition in the casting solution or in the coagulation bath and introducing additional steps such as evaporation or annealing (Lai et al., 1996). The schematic representations of membrane formation by immersion precipitation in the lab scale and industrial continuous scale are presented in Figure 14 and Figure 15, respectively.

FIGURE 14: Schematic Depiction of the Immersion Precipitation Process:
P=Polymer; S=Solvent; NS=Non-solvent

- Substrate
- Polymer solution: P (polymer) + S (solvent)
- Coagulation bath: NS (non-solvent)

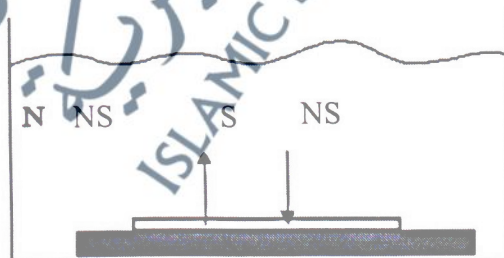
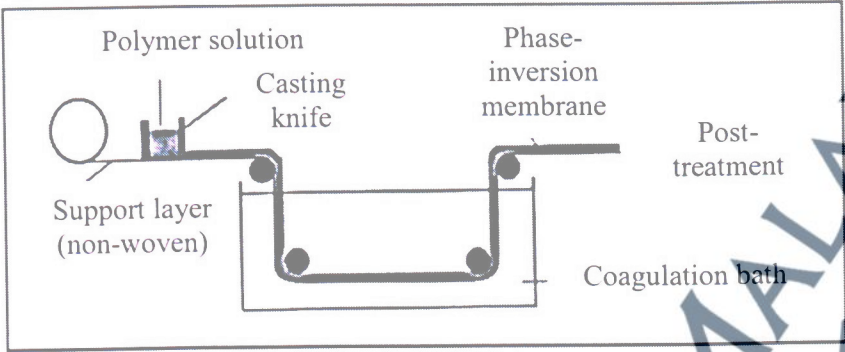
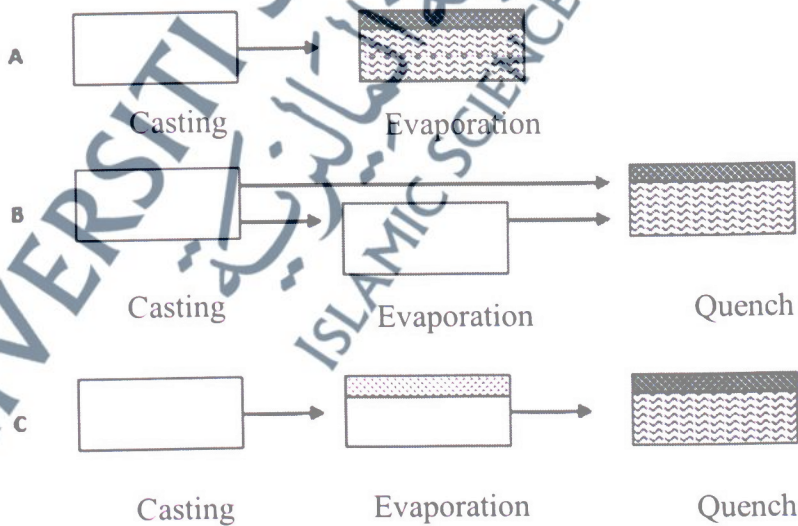


FIGURE 15: Schematic Depiction of the Industrial Immersion Precipitation Process



Phase inversion based immersion precipitation technique is divided into three categories: wet phase inversion technique, dry phase inversion technique and dry/wet phase inversion technique. Comparisons bet wet, dry and dry/wet phase processes are appropriate and shown in Figure 16.

FIGURE 16: Schematic Representation of Phase Inversion Processes: (A) Dry Phase Inversion, (B) Wet Phase Inversion, and (C) Dry/Wet Phase Inversion

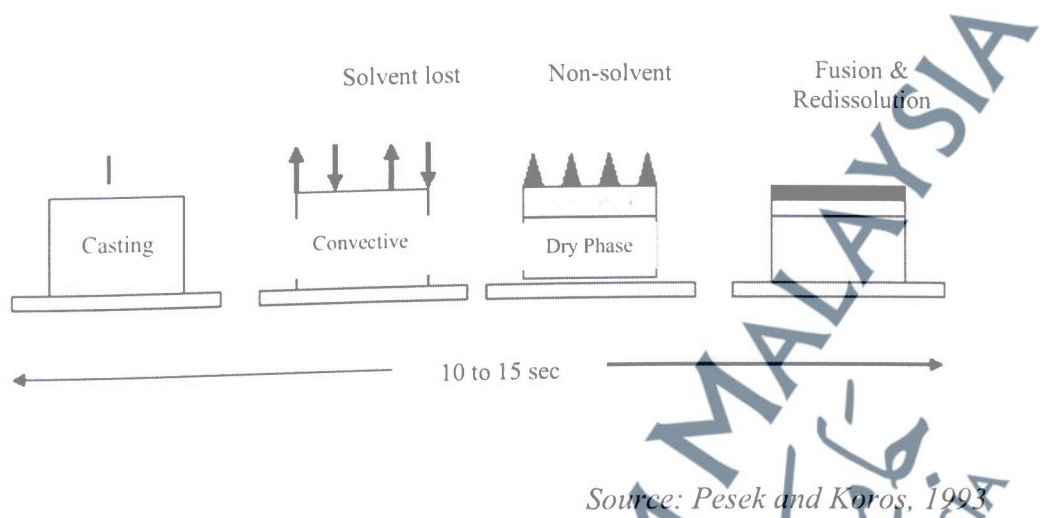


2.4.1.2 Dry Phase Inversion

The dry-casting method is one of the major phase inversion techniques in which a homogeneous polymer solution consisting of solvent and non-solvent is cast on a support and then evaporation of the casting solution takes place under convective conditions (Alinkaya and Ozbas, 2004). In dry phase inversion, the phase separation is introduced by evaporation of volatile solvent and/or by absorption of water as non-solvent from the air moisture (Madaeni et al., 2004). The membrane formation process in the dry-casting technique is relatively simple in the sense that there is no exchange of non-solvent. This dry phase inversion process differs from the more common wet or dry/wet procedure by the absence of the immersion coagulation step (Macchionea et al., 2005).

Dry phase inversion process could be defined when the solvent and the non-solvent is absolutely removed by evaporation as shown in Figure 17. Generally, the pores at the film surface where precipitation occur first and most rapidly are much smaller than those in the interior or the bottom side of the film, and this leads to asymmetric membrane structure. According to Pinnau and Koros, large macrovoids are present in the bulk structure (methanol quench membranes), similar to those seen in the membranes made by dry/wet phase inversion using force convective evaporation with smaller macrovoids occurring directly underneath the top surface. Thus, force convective evaporation step could make the membrane with smaller macrovoids (Pinnau and Koros, 1992). Recently, Zeman and Fraser found the macrovoid formation by the dry cast process (Matsuyama et al., 1997).

FIGURE 17: Dry Phase Inversion Process Mechanism



2.4.1.3 Wet Phase Inversion

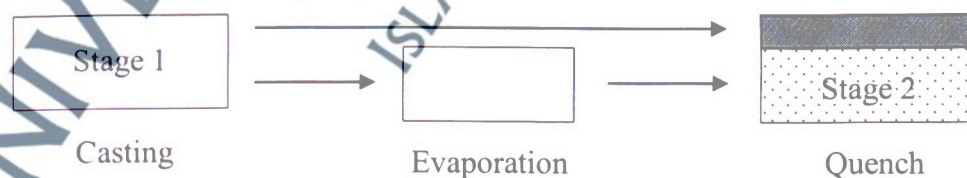
The wet phase separation process was successfully implemented in the 1960 by Loeb and Sourirajan for the desalination of brackish sea water (Loeb and Sourirajan, 1963). Their technique include casting a homogeneous solution consisting of cellulose acetate along with other solvents and non-solvents onto a glass plate, partial evaporation of solvents from the surface of the membrane and immersion of the nascent membrane into a coagulation water. This wet phase separation process is characterized by the demixing of a stable, homogeneous polymer solution in a non-solvent precipitation bath. The casting solution generally consists of either a binary mixture of polymer and solvent or a combination of polymers, solvents and non-solvents. A brief evaporation period is often used to concentrate the outermost region of the nascent membrane prior to coagulation. Phase separation, however, takes place

by the diffusional exchange of solvents and non-solvents in the coagulation bath (Pesek and Koros, 1993).

In addition, the basic procedure of wet phase inversion method contains two stages as shown in Figure 18. First, the polymer solution is cast over a suitable substrate to form a thin film. Then the thin polymer film is immersed in a coagulation bath where the replacement of solvent by coagulant and the precipitation of polymer take place. By using the wet phase inversion method alone, smooth membranes could not be obtained because of the serious shrinkage of membranes during the immersion process. This could be prevented by introducing an evaporation step before immersion (Lai et al., 1996; Lin et al., 2008).

According to Stropnik and Kaiser have been studied regarding the formation of polymeric asymmetric porous membranes by wet phase separation when a thin cast layer of the polymer solution is transformed into a protomembrane after its immersion into the coagulation bath which in general mostly consists of non-solvent for polymer (Stropnik et al., 2002).

FIGURE 18: Schematic Representation of Wet Phase Inversion Process



Source: Lai et al., 1996; Lin et al., 2008

2.4.1.4 Dry/Wet Phase Inversion

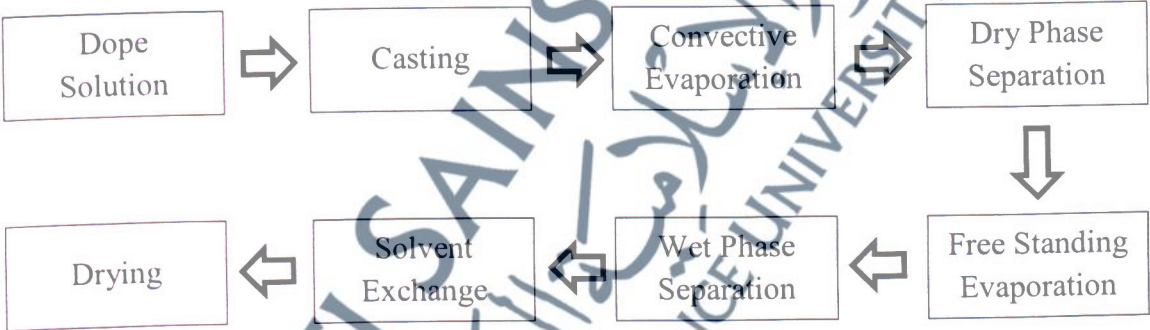
A number of methods can be used to achieve phase inversion. This dry/wet phase inversion technique is the most commonly used in membrane manufacturing. This technique is also called the Loeb-Sourirajan technique, was used by Loeb and Sourirajan in their development of the first cellulose acetate membrane for seawater desalination.

According to earlier studies, dry/wet phase inversion process is one of the most versatile methods to produce high performance asymmetric membranes for gas separation (Ismail and Lai, 2004). Dry/wet phase inversion method was developed from the immersion precipitation method. In this method, a homogeneous polymer solution is prepared by mixing polymer and solvent (sometimes even non-solvent). The solution is then cast on a suitable surface or a piece of nascent film by a blade to a precalculated thickness. After a partial evaporation of the solvent, the cast film is then immersed into a non-solvent medium called coagulation bath, where phase separation and polymer precipitation occurs (Cheng et al., 1999). The essence of this method is to obtain a porous solid from a homogeneous solution in a controlled manner. The process of solidification is initiated by a phase transition of the solution into a polymer-lean phase and a polymer-rich phase, which densifies to form a solid matrix at a certain stage. The membrane porous structure can be tuned by controlling the initial stage of phase transition (Mulder, 1991; Cheng et al., 1999).

Due to a sequence of two desolvation steps which are evaporation of the solvent and solvent-non-solvent exchange in the coagulation bath, solidification of the

polymer film takes place. It is desirable to choose a solvent of strong dissolving power with a high volatility. During the first step of desolvation by solvent evaporation, a thin skin layer of solid polymer is formed instantly at the top of the cast film due to the loss of solvent. In the solvent-non-solvent exchange process that follows, the non-solvent diffuses into the polymer solution film through the thin solid layer while the solvent diffuses out. The change in the composition of the polymer solution film during the solvent-non-solvent exchange process, often called a composition path. The dry/wet phase inversion process is being shown in Figure 19.

FIGURE19: Steps Involved in the Preparation of Integrally Skinned Asymmetric Membrane



2.5 Membrane Formation by Phase Inversion

Generally, phase inversion is one of the most important processes for preparing asymmetric polymer porous membranes such as MF, UF, NF, RO and supports for composite membrane. It is not only a thermodynamic but also a kinetic process and plays an important role in membranes' structure formation. The exchange process between non-solvent in coagulation bath and solvent in polymer dope which is

determined by their concentrations governs the ultimate membrane structure (Ma et al., 2011).

Structure and properties of membranes prepared by phase inversion method depend upon many factors. Additives are one of the major factors and play vital role in the formation of membrane structure by enlarging or preventing of macrovoid formation, enhancing pore formation, improving pore interconnectivity, and/or introducing hydrophilicity. Besides, there are several variables can be adjusted to control membrane properties in the preparation of asymmetric membranes by phase inversion. The main factors are the solvent evaporation temperature and evaporation time, and the composition of the polymer solution (additives) (Jimenez et al., 2004).

2.5.1 Polymeric Materials for Ultrafiltration Membranes

Membrane is an interphase between two phases that act as selective barrier and regulating the transport of substances between two compartments. The membrane is added with polymer in order to enhance the permeability and selectivity process. The word polymer comes from Greek word "polimeres" means having many parts. A polymer consists of many small molecules of plastic refer to as monomers which have undergone a chemical reaction to form large molecules consisting of repeating sequence of monomer. Example of commonly polymer use in the UF membrane are poly(vinylidene fluoride) (PVDF), polysulfone (PSF), poly(acrylonitrile) (PAN), and poly(ether sulfone) (PES) (Baker, 2000).

Polymeric UF membranes have become a kind of high performance separation materials widely applied in the fields such as food manufacturing, effluent treatment and pharmaceuticals synthesis (Liu et al., 2013). At the same time, blending of two different polymers offers attractive opportunity for the development of novel materials with valuable combination of properties. In recent years, several polymer blends have been developed for successful application in UF separation. Besides, the addition of organic or inorganic additives as the third component to the blend polymers has been one of the important procedures used in membrane preparation to control the morphology and performance of membranes (Arthanareeswaran, 2010).

2.5.2 PVDF based Membranes

PVDF is one of the most popular hydrophobic membrane materials. PVDF based membranes are widely used in MF and UF as it offers many advantages as a separation membrane material due to their high mechanical strength, excellent thermal and chemical stability. These membranes remain popular in many applications such as in various industries, waste water treatment and reverse osmosis pretreatment due to their well-controlled porosity. However, the higher hydrophobic nature of its surface limits its application. For instance, the hydrophobicity of PVDF based membranes will results in membrane fouling by biomolecules and other organic matter. Therefore, it often causes severe decrease of the flux and as a result, a decrease in membrane efficiency (Sui et al., 2012).

By comparing with other materials such as polysulfone (PS), polyethersulfone (PES) and polyimide (PI), PVDF is relatively more hydrophobic, although the

hydrophobicity may not be as high as polypropylene (PP) and polytetrafluoroethylene (PTFE). The hydrophobicity of materials is often associated with their surface tensions. The critical surface tensions of major polymeric membrane materials are listed in Table 2 (Nohmi and Yamada, 1983). Since the fabrication of PP and PTFE membranes via phase inversion process is limited due to the complexity in solvent selection, PVDF remains the best option of membrane material for the applications (Bottino et al., 2005).

TABLE 2: Critical surface tensions of major polymeric membrane materials

Polymer	Critical surface tension (dynes/cm)
Polyacrylonitrile (PAN)	44
Polysulfone (PS)	41
Polyphenylene oxide (PPO)	41
Polyethylene (PE)	31
Polypropylene (PP)	29
Polyvinylidene fluoride (PVDF)	25-28.5
Polyfluoroethylene (PFE)	22
Polytetrafluoroethylene (PTFE)	18.5
Fluorinated ethylene propylene (FEP)	16
Ethylentetrafluoroethylene (ETFE)	17

Source: Nohmi and Yamada, 1983

Common methods of improving the hydrophilicity and antifouling property of PVDF membranes generally include surface modification and blending. Surface modification of PVDF membranes retaining the bulk membrane properties, can be classified into coating, surface graft polymerization, and hydrophilic chemical modification of bulk membrane materials (Barona et al., 2007). Surface modification,

especially grafting or adsorption of hydrophilic polymers, often leads to decrease flux due to narrowing and blocking of surface pores (Kang et al., 2007).

Generally, polymer crystallinity and the resultant membrane morphology are among important factors in determining the mechanical strength properties, as well as the impact resistance of the membranes. The degree of the crystallinity of PVDF can range between 35% and 70%, and can be determined by measuring the specific volume of crystalline and amorphous phases. Crystallisation of PVDF is controlled by a number of variables including molecular weight, molecular weight distribution, polymerization method, thermal history and cooling rates. It is important to understand the effects of fabrication conditions on the crystalline phase formed in order to have a proper control on the properties of the resultant membrane (Liu et al., 2011).

In addition, solubility in common organic solvents such as N,N-dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidone (NMP) makes it a strong candidate for membrane production via the inexpensive method of immersion precipitation (IP). These desirable properties have generated a great deal of research on the PVDF membrane production and applications. Despite the above mentioned desirable properties, the hydrophobic nature of the PVDF makes it susceptible to fouling when applied in filtration or separation processes. Hence, considerable effort has been devoted to improve the hydrophilicity and fouling resistant properties of the PVDF membranes, including the use of additives, for examples hydrophilic polymers such as poly(ethylene glycol (PEG) and polyvinylpyrrolidone (PVP) (Moghareh et al., 2013).

2.5.3 Polymeric Additives

For the past several decades, synthetic polymeric membranes are used for a wide variety of liquid separations such as MF, UF, RO and NF. Alongside, the addition of organic or inorganic additives as the third component to the blend polymers has been one of the important procedures used in membrane preparation to control the morphology and performance of membranes (Arthanareeswaran et al., 2010). The role of organic and inorganic additives, such as polymeric additives, alcohols, surfactants, and salts was mainly reported as pore forming agents enhancing permeation properties. However, additives do not always act as pore formers (Sadrzadeh and Bhattacharjee, 2013).

Generally, additives work as non-solvent materials to reduce solvent power in the solution. They are leached out of the cast film into the non-solvent bath during solidification process. The additive leaching rate affects the final morphology and is primarily dependent on the molecular weight (MW) of additive and its affinity with the non-solvent. In addition, water soluble polymers such as PVP and PEG have been frequently used as additives in the casting solution to improve the membrane performances (Lee et al., 2003). Key features of previous studies are listed in Table 3. According to this table, wide MW ranges of several additives were used to modify the synthesized membranes.

TABLE 3: Overview of previous studies on the effect of additives on membrane properties

Additive (s)	Polymer	Solvent (s)	Significant Results	Reference (s)
PVP	PVDF	DMAC	- Lower MW additives increase both the PWF and dextran rejection. - Low PVP tends to form small pores and easily leaches out from the membrane. - Decrease PVP concentration results in the membranes with low water solution flux and high rejection	Wang et al., 1999
PVP	PSF	NMP	- At lower concentration of additive, membranes with enlarged macrovoids and higher PWF are formed.	Han and Nam, 2002
PVP	PSF	NMP, DMAC	- Increase PVP : • pore number found to be increased • PWF decreased • significant increase in rejection • decrease in flux	Chakrabarty et al., 2008
PVP	PES	NMP	- Increasing the PVP concentration increased the PWF and pore diameter and decreased salt rejection. - Number of membranes pore has been increasing while the macrovoids have been disappearing.	Ismail and Hassan, 2007

TABLE 3: Continued

PVP	PES	NMP	- The additive increased both MWCO and the PWF of the membranes. - The mean pore size and MWCO of the membranes were decreased either by increasing the PES concentration in the casting solution or by increasing the solvent evaporation time.	Jimenez et al., 2004
PVP	CA	NMP	- Initial addition PVP (0-3 wt%) results in increasing macrovoids formation and PWF. - Further addition of PVP (3-6 wt%) results in suppression of macrovoids and reduction of PWF. - Increase CBT (0-25C) will increase PWF whereas further increasing CBT (25-50C) results in reduction of PWF.	Saljoughi and Mohammadi, 2009
PVP	PI	NMP	- A macrovoid free, porous membrane with a sponge-like structure was obtained by phase inversion of a PI/GBL/water system without PVP. - A membrane with a finger-like structure was obtained from a PI/NMP/water system without PVP.	Yoo et al., 2004
PVP	PAN	DMSO	- The higher molecular weight of PVP is added, the thicker top layer of the asymmetric membrane is. - The thickness of top layer increase as higher molecular weight of PVP is added.	Jung et al., 2004

TABLE 3: Continued

PVP	RES	DMF, THF	-	The presence of PVP acts preventing to some extent pore blockage due to its hydrophilic action.	Marchese et al., 2003
PEG	PVDF	DMAC	-	Higher MW PEG enhanced the PWF and reduced solute rejection of membranes, but low MW PEG act as pore-reducing agent.	Zuo et al., 2008
PEG	PSF	NMP	-	The PWF increased and PEG rejection decreased by increasing both MW and concentration of PEG.	Kim and Lee, 1998
PEG	PEI	NMP	-	The PWF increased and PEG rejection rate decreased by increasing PEG MW from 200 to 600 Da.	Kim and Lee, 2004
PEG	PSF	DMAC, NMP	-	Porosity and the PWF increased by increasing PEG concentration up to 12 wt% then decreased.	Zheng et al, 2006
PEG	PSF	DMAC	-	PEG additive as pore-former. Improves the hydrophilicity of membranes. PWF and porosity of membranes increase with increase in MW of PEG. The PSD of membrane skin layer becomes narrower.	Ma et al., 2011

TABLE 3: Continued

PEG	PAN	DMSO	- PEG with different Mw acts as pore former, which inhibits DMSO₂ from crystallization and then facilitates the L-L phase separation of the ternary system. - The water flux and porosity of PAN membranes increase as the Mw of PEG increases or the cooling rate decreases.	Yun Wu et al., 2013
PEG (400 Da, 6000 Da and 20000 Da)	PSF	NMP, DMAc	- PEG 6000 can be a suitable additive for making asymmetric membranes having a dense skin layer and a relatively macrovoid free sponge-type support layer. - With increase in molecular weight of PEG, the pore number as well as pore area in membranes increases. - Membranes with PEG of higher molecular weights have higher PWF and higher hydraulic permeability due to high porosity.	Chakrabarty et al., 2008
PEG 600	CA	DMF	Increase in additive concentration has a direct influence on the permeate flux as well as percentage rejection values. The presence of hydrophilic additives (PEG 600) and their concentration play a key role in changing the membrane characteristics since the membranes possess changes in porosity and pore size.	Arthanareeswaran et al., 2004

TABLE 3: Continued

PEG (200, 400, 600 Da)	PES	DMF	- Addition of different polyethylene glycol as additives in casting solution improves the viscosity and influences the performance of pure water permeation rate. - UF membrane with PEG 200 as additive exhibits the lowest value of MWCO and mean pore size compared to other membranes. - As concentration of PEG 400 and PEG 600 in the casting solution is increased solute separation decreased while flux increased. - Addition of PEG 400 and PEG 600 in the casting solution increased the number and size of macrovoids while PEG 200 decreased the size of macrovoids in the intermediate. - The membrane surface becomes rougher with increased molecular weight of additives and tends to have higher flux.	Idris et al., 2007
PEG	PSF	DMF	- The addition, of PEG increases the exchange rate of additive and non-solvent, resulting in the enhancement of the macrovoids formation. - With increase in concentration of PEG, the pore size as well porosity was increased. - The pure water flux and equilibrium water content of the blend membranes were increased while hydraulic permeability was decreased.	Arthanareeswaran et al., 2010

TABLE 3: Continued

PEG (200kDa, 600kDa, 6000kDa)	PVDF-HFP	NMP	- The addition of PEG resulted in the system thermodynamically less stable in reaction with water, promoting rapid phase demixing in the phase inversion process. - The dimension of finger-like macrovoids in the sublayer of the resultant membrane increased in parallel with the increase of PEG molecular weight from 200 to 600 and 6000kDa, and PWP also increased.	Wongchitphimon et al., 2011
LiCl	PVDF	NMP	- Increase LiCl concentration, the membrane structure changed from finger-like to sponge-like.	Mansourizadeh and Ismail, 2010
Pluronic, LiCl	PVDF	NMP	- The addition of Pluronic F127 increased the PWP of as-spun fibers, while the membrane contact angle was reduced. - LiCl and higher coagulant temperature were also found to suppress the macrovoids formation, enhance the water permeability, and increase the surface pore size.	Loh and Wang, 2012
PVP, LiCl	PVDF	DMAc	- PVP is the better additive for preparation of membranes with a higher permeates flux. - LiCl used to reduce macrovoid formation.	Fontananova et al., 2006

TABLE 3: Continued

PEG, PVP, Pluronic	PES	NMP	- The addition of Pluronic (PES-Plu) showed the highest hydraulic permeability among the membranes prepared with macromolecular additives. - The PWF increased and protein rejection decreased.	Susanto and Ullbricht, 2009
PVP, PANI	PSf	NMP	- PSf/PVP/NMP casting film had obvious macrovoids while PSf/PANI nanofibers/NMP casting film had finger-like pores. - PSf/PANI nanocomposite membranes had larger surface pore size and higher porosity than PSf/PVP membranes. PSf/PVP membranes had loose and thick skinlayer, large acicular pores and fully developed macrovoids. - The addition of both PVP and PANI nanofibers increased membrane pure water flux and antifouling property.	Zhou et al., 2011
PVP, Dextran	PVA	-	- The addition of dextran additives in the system could induce pores in the top layer. - The addition of dextran additives can enhance the phase separation and induce pores in the top layer.	Chuang et al., 2000

TABLE 3: Continued

PVP, PMMA	PVDF	DEP	- PVDF/PMMA blend membranes showed similar surface and cross-section structures to those of PVDF membranes. - Addition of PVP, the membrane outer surface became denser and the spherulitic structure was eliminated. - Addition of PMMA, membrane water permeability decreases slowly.	Rajabzadeh et al., 2012
PVP, Hydrophilic monomer (AA and HEMA)	PES	DMAc	- Sizes of membrane pores in surface and sub-layer were reduced with addition of AA and HEMA. - Surface porosity was increased. - The pure water fluxes of membranes were declined at the presence of AA and HEMA. - The milk water permeation, protein rejections and antifouling properties of the membranes were improved	Rahimpour, Madaeni, 2010
Glycol additives (PEG 600, PG, and EG)	CA	DMF	- PEG 600 had a significant role in altering thermal properties, especially the thermal stability of the developed blend membranes. - The presence of PEG 600 in the blend membrane enhanced the membrane pervaporation performance. - The separation factor and permeation flux were increased by the addition of the PEG 600.	Ali et al., 2011

TABLE 3: Continued

PEG-600, EG, PG	CA	Acetic acid	- The additives responsible for improving the performance and proper-ties of plain CA membrane. - The permeation flux increased with the increase in the additive contents	Zafar et al., 2012
PEO	PES	DMF	- The appearance of PEO segments on the polyamide thin film plays major role of fouling resistance. - The water permeability and rejection property were improved.	Zhang et al., 2011
DGDE	PSF	NMP	- The addition of DGDE decreases the ex-change rate of solvent and non-solvent, resulting in the suppression of the macrovoids formation.	Tsai et al., 2002
LiCl, Glycerol	PVDF-HFP	NMP	- The addition of LiCl or glycerol reduced the thermodynamic stability of the dope solution in reaction with water, similarly to the case of PVP as an additive. The LiCl or glycerol addition into the polymer dope solution also made the resultant membranes exhibit an arrow pore size distribution compared to the effect of PVP addition. - The addition of 4wt.% LiCl into the dope solution could form the membrane with almost four times stronger strain strength than the PVDF commercial membrane while keeping the similar rigidity.	Shi et al., 2008

2.5.4 PVDF/NMP Blend Ultrafiltration

Polyvinylidene fluoride (PVDF) has a superior thermal, chemical resistance and oxidation resistance among polymeric membrane materials. Therefore, all the above advantages make it one of the most popular choices as a membrane material and widely used for pervaporation, membrane distillation, UF and other fields (Tavares et al., 2002). However, PVDF UF membrane is easily contaminated by protein and biomolecules because of its hydrophobic property. Usually, the antifouling property of hydrophobic membrane can be improved by creating a hydrophilic surface through chemical bonding and physical blending method. Physical blending method is simple and sometimes they are using two or more polymers. Up to now, PVDF polymer has been used in dope solution to prepare blend membranes with favorable performances for applications of UF (Lang et al., 2007).

The blend solutions based on PVDF polymers can be prepared by dissolving the polymers in different compositions, in presence of additive and also in different solvents (Wu et al., 2006). As a result, the final membrane structure is influenced by the composition (concentration, solvent, additives), temperature of solution, the non-solvent or the mixture of non-solvent and the coagulation bath. In addition, among the common hydrophobic polymers, PVDF has a higher processing ability compared to polytetrafluoroethylene (PTFE) and polypropylene (PP) as the former can be easily dissolved in common solvents including 1-methyl-2-pyrrolidone (NMP), dimethyl acetamide (DMAc), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and others. However, it has been found that the penetration of coagulant (water) into the

polymer dope solution is restricted during the phase inversion process due to the hydrophobic nature of PVDF material (Wang et al., 2000).

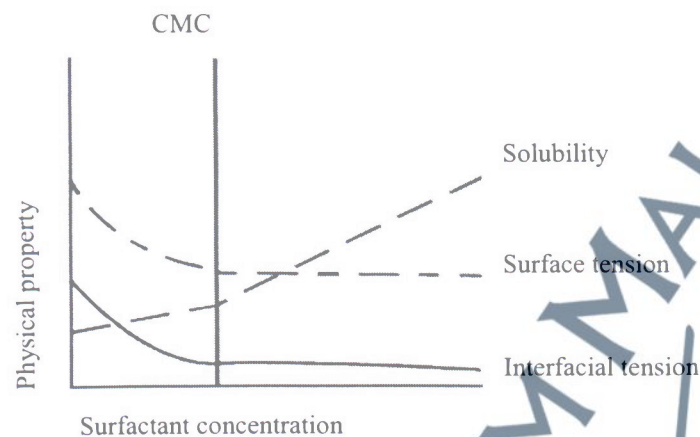
Blending is often used in the preparation of UF membranes to change the properties of polymeric materials (Li et al., 2010). In order to develop a new polymer membrane with high flux, good mechanical strength and hydrophilicity, PVDF polymer is usually used as interest materials for the membrane formation. In preparing dope solution of PVDF based membrane, NMP is commonly used as solvents to dissolve polymer under constant mechanical stirring at a moderate speed of rotation in a round bottom flask (Arthanareeswaran et al., 2004). By using the immersion phase inversion process, PVDF and NMP were dissolved and mixed homogeneously to prepare blended PVDF UF membrane (Wang et al., 2012).

2.6 Surfactant

The term surfactant is defined as contraction of “surface active agent” which literally means active at a surface. Surfactants are from organic compound which are amphiphilic, meaning they contain both hydrophobic groups (their “tails”) and hydrophilic groups (their “heads”). The hydrophobic portion has little affinity for the bulk medium, less soluble in water, and is a long chain of fatty acids, hydroxyl fatty acids, hydroxyl fatty acids or α -alkyl- β -hydroxy fatty acids. Additionally, this hydrophobic moiety is usually a C8 to C22 alkyl chain or alkylaryl that may be linear or branched (Ginkel, 1989). The other part is a hydrophilic end is water soluble, attracted to the bulk medium and it can be a carbohydrate, cyclic peptide, phosphate, amino acid, alcohol or carboxylic acid (Pattanathu et al., 2008).

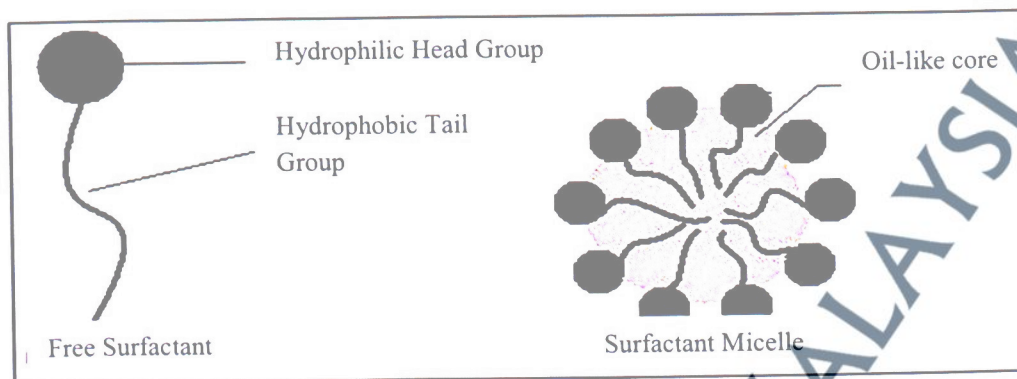
The effectiveness of a surfactant is determined by its ability to lower the surface tension, which is a measure of the surface free energy per unit area required to bring a molecule from the bulk phase to the surface. Since the surfactant is present, so that less work is required to bring a molecule to the surface and also the surface tension is reduced. As an example, a good surfactant can lower the surface tension of water from 72 to 35mN/m and the interfacial tension of water (tension between polar and non-polar liquids). It is reduced the surface tension of water by adsorbing at the air-water interface and also reduced the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. In addition, the surface tension is correlated with the concentration of the surface-active compound until the critical micelle concentration (CMC) is reached as shown in Figure 20 (Mulligan, 2005).

FIGURE 20: Surface Tension, Interfacial Tension and Solubilization as a Function of Surfactant Concentration



Source: Mulligan, 2005

An effective surfactant can be referred to which has a low CMC therefore, less surfactant is necessary to decrease the surface tension. The CMC can be defined as the minimum concentration that is necessary to initiate the micelle formation. On the other hand, CMC is also the maximum concentration of surfactant monomers in water. This is influenced by three factors which are pH, temperature and ionic strength. When micelles form in water, their tails form a core that can encapsulate an oil droplet, while their (ionic/polar) heads form an outer shell that maintains favorable contact with water. Otherwise, when surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil as shown in Figure 21 (Kline et al., 2001).

FIGURE 21: Surfactant Molecules and Its Micelle

Source: Kline *et al.*, 2001

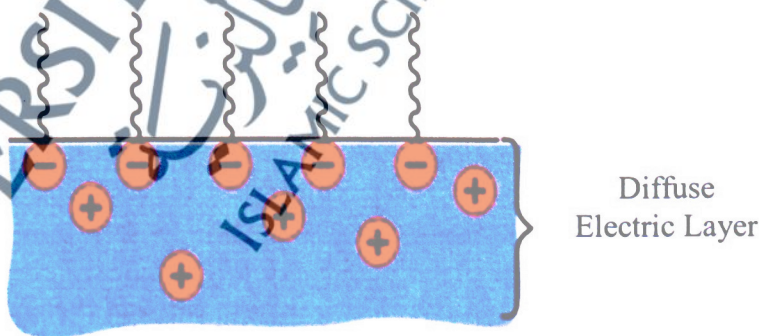
There is an important application of surfactants and also protein at the air-water interface which is as foam stabilizers. The competitive adsorption at this interface involved in surfactant displacement and solubilisation of proteins at interfaces. However, at this interface it is also interesting to evaluate the cleaning potential. The protein and surfactants behavior are different at the interfaces because of their structures differ greatly. These two species work at different mechanism to stabilize interfaces, which are incompatible (Frazier *et al.*, 2011).

In addition, proteins will form a viscoelastic network as referring to two-dimensional gel (Murray, 2002). The strength to maintain its coherence depends on the intermolecular interactions between the protein molecules. In contrast, surfactants rely on a high degree of surface mobility to counter deformation. Generally, the surfactants form weaker interfacial interactions between its molecules than proteins (Mackie and Wilde, 2005).

2.6.1 Anionic Surfactant

Anionic Surfactants are dissociated in water in an amphiphilic anion and a cation, which is in general an alkaline metal (Na^+ , K^+) or a quaternary ammonium (Louis, 2002). Anionic surfactants are usually based on sulfate, sulfonate or sulphur group. The hydrophilic head is negatively charged. This is the most widely used because it is good for cleaning applications from household tasks, dry cleaning, shampoos and other personal cleaning products. They are also used to specialty industrial uses such as dispersing agent in dyes for instance are soaps, or fatty acid salts, and sodium lauryl sulfate, also known as sodium lauryl ether sulfate (SLES). Most of anionic surfactants are high foaming but sensitive to hard water and therefore require the addition of substances to complex calcium and magnesium ions (detergent builders). They are more effective than other surfactants in particulate soil removal, especially from natural fabrics. Anionic surfactants account for about 50% of the world production (Rosen, 2004). Figure 22 shows the movement of anionic particles.

FIGURE 22: Movement of Anionic Particles

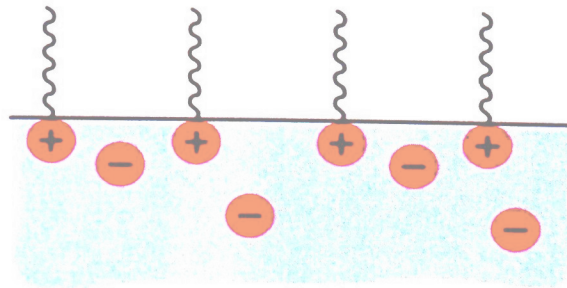


2.6.2 Cationic Surfactant

Cationic surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. They are characterized by a quaternary ammonium group which is positively charged. They are adhere to modify solid surfaces and used as ingredients in fabric softeners, fuel and lubricant additives and corrosion inhibitor. For example, cetyl trimethyl ammonium bromide (CTAB) and others alkyl trimethyl ammonium salts (Ginkel, 1989). These surfactants are in general more expensive than anionic surfactants, because of high pressure hydrogenation reaction to be carried out during their synthesis (Louis, 2002).

For the applications, the cationic surfactants are useful as fabric softeners, corrosion inhibitors, and antimicrobial agents. They are not used in general purpose detergents because they do not provide effective cleaning at neutral pH. They are adsorbed rapidly to textiles so that their solution concentration drops very quickly to low levels, making them unsuitable for industrial processing baths, although they see some specialty use in connection with anionic dyes. However, except for applications where biological activity is critical, as in pesticides and pharmaceuticals, only nitrogen-based compounds are used as cationic surfactants (Thomas, 2001). Figure 23 shows the movement of cationic particles.

FIGURE 23: Movement of Cationic Particles



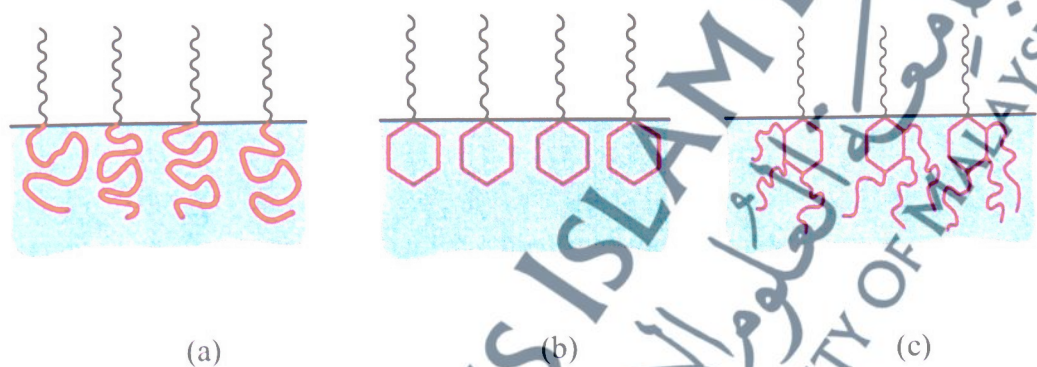
2.6.3 Nonionic Surfactant

Nonionic surfactants come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type such as alcohol, phenol, ether, ester, or amide (Louis, 2002). The hydrophilic head of nonionic surfactants is polar but not fully charged. They lack ionic constituent and the majority of all nonionic surfactants are polymerization products of 1,2-epoxyethane. In addition, they are low foaming and good for dishwasher detergents, textile applications and in combination with anionic surfactants for cleaning applications. For instance are ethylene oxide and polyethylene glycol (Rosen, 2004).

In addition, nonionic surfactants are generally more tolerant than anionic surfactants of water hardness, which makes the requirements for "builders" in laundry detergents. Besides, for removal of oily soil from synthetic fabrics, they tend to be more effective than other surfactants. Most nonionic surfactants have good cold water solubility and have a low critical micelle concentration, making them effective at low

concentration. Their compatibility with cationic fabric softeners makes them preferable to anionic surfactants in certain formulations. They are more common in industrial applications than are anionic surfactants (Thomas, 2001). Figure 24 show the examples of nonionic surfactants.

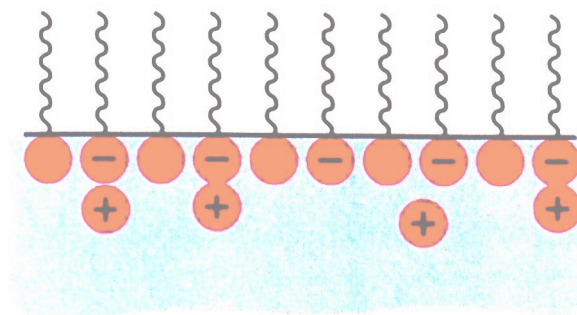
FIGURE 24: Examples of Nonionic Surfactants (a) Alkypolyoxyethylenes, (b) Spans and (c) Tweens



2.6.4 Amphoteric Surfactant

Amphoteric surfactants are also known as zwitterionic surfactants. They have both positively and negatively charged moieties in the same molecule depending on the pH of the solution. These zwitterionic surfactants are used in dermatological and cosmeceutical applications and in combination with the other surfactants such as dodecyl betaine and dodecyl dimethylamine oxide (Ginkel, 1989). More costly to produce than ionic surfactants, amphoteric surfactants represent only about 3% of surfactant volume in Europe and less than 1% in the United States (Thomas, 2001).

Figure 25 shows the movement of amphoteric particles.

FIGURE 25: Movement of Amphoteric Particles

Source: Kosaic, 2001

2.7 Membrane based Surfactant

Surfactant is secondary additive which added into the polymer solution as one of the effective strategies to produce membranes with optimal and specific properties. The membrane structure would be influenced by the addition of surfactants, which can affect the interfacial properties, also towards performance, physical characteristics and morphology of the membranes. Many researchers indicate that the addition of surfactant in the casting solution can suppress macrovoids in polymeric membrane. Thus, addition of surfactant and others additives will give significance different in morphological study of the membrane. The interactions between surfactant and membrane were investigated because of their effect upon flux and rejection.

2.7.1 Ultrafiltration-Surfactant Membrane

Ultrafiltration-surfactant membranes allow almost complete passage of surfactant monomers is therefore mainly influenced by the presence of micelles. Surfactants are

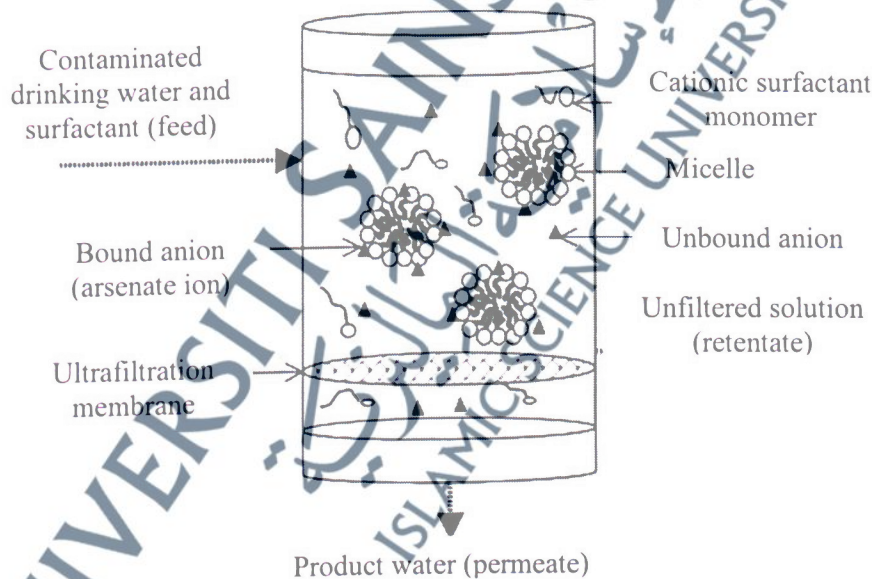
present in almost all aqueous solutions as additives for different purposes. Therefore, because of the common occurrence of surfactants in the process it is important to know how they behave in membrane processes. However, concentration polarization during UF of surfactant solutions is therefore mainly influenced by the presence of micelles. In some surfactants, micelles are generated already at a very low surfactant concentration in water. The concentration at which micelles start to form is called the critical micelle concentration (CMC) and is an important characteristic of a surfactant. When the concentration is further increased, the surfactants can associate in a range of different formations (Byhlin and Jonsson, 2002).

Micellar enhanced ultrafiltration (MEUF) has attracted considerable attention during the recent years. In MEUF, the surfactant is added to the solution to solubilize a compounds which for some reason, is undesirable in the permeate and too small to be retained by the membrane. The undesirable compound is enclosed in the interior of the micelles formed by the surfactant. The micelles are large enough to be retained by the membrane and in this way the undesirable, low molecular weight compound is retained (Byhlin and Jonsson, 2002). The adsorption of surfactant onto UF membranes surfaces is an important issue and plays an important role in the characterization of membranes, their removal from solutions streams and their cleaning processes. The characterization of membranes by determination of interactions involved in a specific system has been studied with the aid of surfactants solutions (Xiarchos and Doulia, 2006).

In additions, the role of interactions in UF processes, where surfactants are present in order to extend membrane life, optimize processes, and enhance UF

effectiveness. Therefore, the main factors such as surfactant concentration, chemical nature of surfactants and membranes, pH, ionic strength and additives that would affect adsorption behavior of a solution-membrane system have been examined. Gecol et al. were investigated the removal of arsenic from water via surfactant micelles and UF membrane by using stimulated water and stirred cell UF unit. It showed that low molecular weight inorganic arsenic species can be removed from water using UF membranes with high rejection if surfactants are added to the contaminated water stream (Gecol et al., 2004). Figure 26 shows experimental water treatment process using cationic surfactant and UF membrane.

FIGURE 26: Schematic of Experimental Water Treatment Process using Cationic Surfactant and Ultrafiltration Membrane



Sorce: Gecol et al., 2004