CHAPTER II

LITERATURE REVIEW

2.1 Development of Membrane Technology

A membrane can be defined as semi-permeable barrier, which separates a fluid and restricts transport of various chemicals in selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge or be neutral or bipolar. Transport trough a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 100 microns to several millimeters (mm) (Srikant, 2008).

Systematic studies of membrane phenomena can be traced to the eighteenth century philosopher scientists. In 1748, Abble Nolet created the word 'osmosis' to describe permeation of water through a diaphragm. Through the nineteenth and early twentieth centuries, membranes were only used as laboratory tools to develop physical and chemical theories, not for industrial or commercial uses (Baker, 2004).

Sartorius Werke GmbH, Germany manufactured industrial scale membranes, microfiltration membranes, for the first time in 1950. In 1960, Lonsdale develop membranes in small scale for laboratory applications. However, the most fundamental breakthrough in membrane technology came in late 1950s when Loeb and Sourirajan discovered very thin membranes for reverse osmosis, the asymmetric membranes (Wenten, 2003). Table 1 shows the summary of membrane history.

TABLE 1: History of membranes (Andrej, 2005)

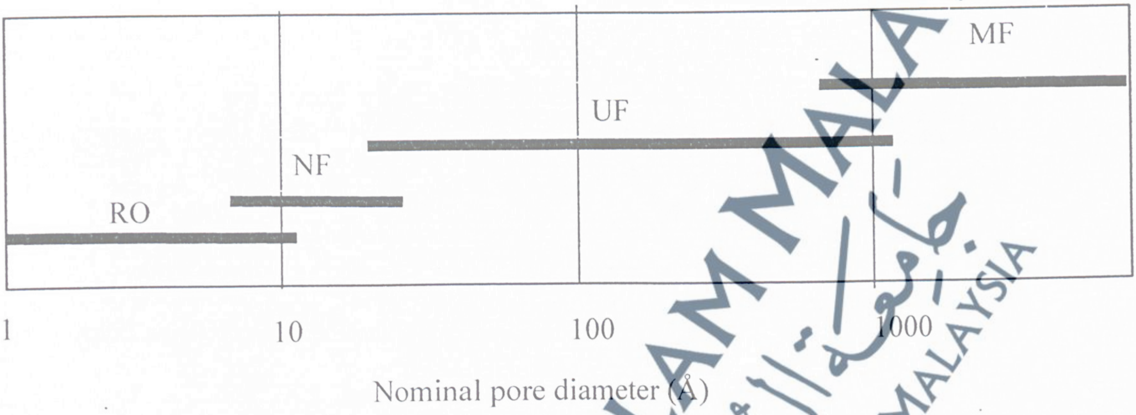
Researcher	Year	Achievement
Abbe Noilett	1748	Discovering of osmosis phenomenon in natural membranes
Matteucci	1845	Research on anisothropy of natural membranes
Fick	1865	The first synthetic membrane from nitrocellulosis
Graham	1866	Research on gas separation on rubber membranes and dialysis
Traube	1867	Research on osmosis on synthetic membranes
Pfeffer, Gibbs I van Hoff	1877	Research on osmosis on ceramic membranes and theory of osmosis phenomena
Michaels, Manegold, McBain	1926-1931	Research on reverse osmosis
Lonsdale	1960	Research on composite membranes
Loeb I Surirayan	1962	Preparation of assymetric membranes
Porter	1975	Classification of pressure-driven processes
Leblanc	1980	Membranes with immobilised carriers
Yoshikawa	1986	Membranes with active centres
Cussler, Aris, Brown	1989	The chain model of facilitated transport
Rautenbach	1990	Membrane hybrid processes

Nowadays membrane applications spread over various industries: metal industries (metal recovery, pollution control, air enriching for combustion), food and biotechnology industries (separation, purification, sterilization and byproduct recovery), leather and textile industries (sensible heat recovery, pollution control and chemicals recovery). Other industries that also use membrane technology are pulp and paper industries (replacing evaporation process, pollution control, fiber and chemicals recovery), and chemical process industries (organic material separation, gas separation, recovery and recycle chemicals). Medical sector including health-pharmaceutical-and medical industries (artificial organs, control release (pharmaceutical), blood fractionation, sterilization and water purification), and waste treatment (separation of salt or other minerals and deionization) (Wenten, 2003).

2.2 Types of Membrane

They are several types of membranes which include microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) membranes. MF membranes have the largest pore size and typically reject large particles and various microorganisms. UF membranes have smaller pores than MF membranes and, therefore, in addition to large particles and microorganisms, they can reject bacteria and soluble macromolecules such as proteins. RO membranes are effectively non-porous and, therefore, exclude particles and even many low molar mass species such as salt ions and organics. NF membranes are relatively new and are sometimes called "loose" RO membranes. They are porous membranes, but since the pores are on the order of ten angstroms (10Å) or less, they exhibit performance between that of RO and UF membranes (Sagle and Freeman, 2004). The range of nominal pore diameter sizes is shown in Figure 1.

FIGURE 1: Range of nominal pore diameter sizes



2.3 Reverse Osmosis

Reverse osmosis (RO) is a process wherein a relatively pure solvent is separated from a salt solution by using a semipermeable membrane by the application of hydrostatic pressure. The hydrostatic pressure can vary from 2 MPa to around 6 MPa depend on the salt content of the feed mixture. The solvent permeates preferentially through the membranes whereas the solutes, particularly electrolytes and low molecular weight nonelectrolytes are retained by the membranes. Figure 2 shows the illustration of reverse osmosis membrane. Reverse osmosis process is used for effectively retaining microsolutes having molecular weight less than 300 or effective size less than 10 Å. The process is used to produce relatively pure water or a concentrated solution of microsolutes from a given salt solution. A simple schematic of the process is given in

Figure 3. The most notable example of reverse osmosis process is the production of drinking water from naturally occurring saline waters (Scott, 1995).

FIGURE 2: Illustration on reverse osmosis membrane

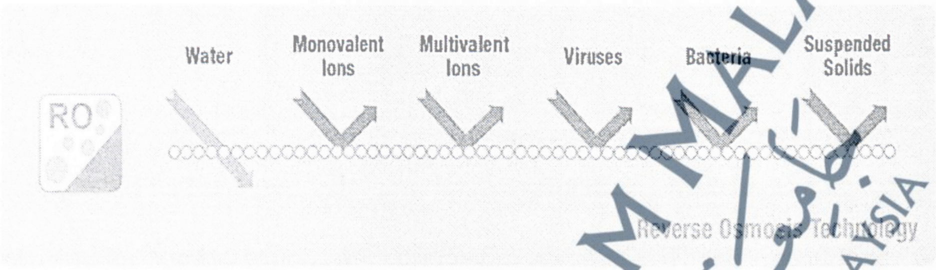
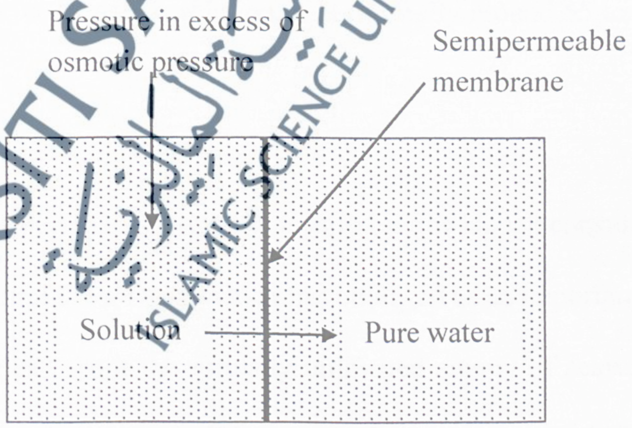


FIGURE 3: The schematic representation of a reverse osmosis process



2.4 Desalination

Basically, the desalination is a general term for the process of removing salt from water to produce fresh water (Lauren et al., 2009). Fresh water is defined as containing less than 1000 mg/L of salts or total dissolved solids (TDS). For above 1000 mg/L, properties such as taste, color, corrosion propensity, and odor can be adversely affected.

Catherine (2009) had reported that generally, desalination processes can be categorized into two major types which are phase-change thermal and membrane process separation. Phase-change thermal processes include multi-stage flash, multiple effect boiling, vapor compression, freezing, humidification or dehumidification and solar stills. Membrane process separation include reverse osmosis (RO), membrane distillation (MD) and electro dialysis (ED). The required pressure depends on the salt concentration of the resource of saline solution, it is normally around 55 to 70 bar for seawater desalination.

Akili et al. (2008) had claimed that, seawater is unsuitable for human consumption and for industrial and agricultural uses. Desalination has emerged as an important source of fresh water by removing salt from the virtually unlimited supply of seawater. Since there is many countries in the world suffer from a shortage of natural fresh water. Increasing amounts of fresh water will be required in the future as a result of the rise in population rates and enhanced living standards, together with the expansion of industrial and agricultural activities. Available fresh-water resources from rivers and groundwater are presently limited and are being increasingly depleted at an alarming rate in many places.

A variety of desalination technologies both thermally-driven and membrane based, have been increasingly employed to enhance the limited freshwater supply. Among of them, reverse osmosis (RO) is one of the most efficient requiring about 3-10 kWh of electric energy per m^3 of fresh water produced from seawater. The rate at which fresh water crosses the membrane is proportional to the pressure differential that exceeds the natural osmotic pressure differential. The membrane itself represents a major pressure differential to the flow of fresh water. The major energy requirement is for the initial pressurization of the feed water for seawater desalination from 55 to 70 bar (Catherine 2009).

There is a critical issue of fresh water shortage for the 1990s and beyond. The potable water, until recently considered to be inexpensive and plentiful is now understood to be scarce and vulnerable, and the demand for potable water is increasing. Population growth, rising living standards, industrialization, and the expansion of irrigation agriculture point out that there will be no let-up in the increasing demand for potable water in the years to come (Cerci, 2002).

Cerci had reported that, desalination has been a major source of additional potable water in many parts of the world. In 1997, a worldwide survey showed that there are about 12,500 desalination plants in the world, producing over 23 million m^3/d of fresh water. Most of these plants are in the Middle East. Saudi Arabia is the largest user of desalination with about 25% of world capacity, and the US is the second largest user with about 10% of world capacity.

2.4.1 Saline water

Saline water is water that contains a significant concentration of dissolved salts (mainly NaCl) and is commonly known as salt water. The salt concentration is usually expressed in parts per thousand (ppt) or parts per million (ppm). There are two main categories of saline water which are brackish and seawater. Brackish water is typically defined as distastefully salty but less saline than seawater which is between 2,000 to 10,000 ppm of salt concentration. In addition to certain surface water settings such as estuaries, brackish water can be found in aquifers. In some regions of the country with limited availability of freshwater, desalination of brackish groundwater is being used as an alternative supply. Meanwhile, seawater usually contains a higher salt content, about 30,000 ppm up to 50, 000 ppm of salt concentration (ngwa.org, 18 August 2015)

2.5 Polysulfone (PSF) Based Membrane

Polysulfones, PSF, consist both aliphatic and aromatic polymers that widely used as membrane since PSF has good resistant to high temperatures, good mechanical and chemically stable. Commonly, polysulfones are prepared by the reaction of disodium bisphenol A with 4, 4-dichlorodiphenylsulfone (Speight, 2002).

Polysulfones belong to a class of high-Tg polymers of high mechanical, thermal and chemical resistances. They are widely used in the manufacture of asymmetric membranes with different pore sizes in the active (skin) layer. Asymmetric polysulfone membranes are also used as a support layer for a thin film of cross-linked polyamide made by interfacial polycondensation of two bifunctional reactants dissolved in two non-miscible liquids in the preparation of reverse osmosis and nanofiltration membranes (Blanco et al., 2006). However, the polysulfones are hydrophobic and are sensitive to many organic solvents. Therefore, they cannot be used as asymmetric support-films for the pervaporation membranes, which are generally designed to work in organic solvents. Even for the applications in aqueous media, the hydrophobic nature of the membrane surface leads to an easy deposition of macromolecular solutes or particles, which have hydrophobic regions. In addition to the fouling due to deposition of large-size species on the membrane surface, the hydrophobic nature of the materials leads to a poor wetting of the pores and low water flux through the membrane pores. The lower the pore size, the larger the pressure required to induce the solvent transport (Kosutic et al., 2000).

2.6 Polymeric Additives

Structure and properties of membranes prepared by phase inversion method depend on many factors. Addition of small amount of additives into the casting solution is one of the major factors. Besides that, one role of additives is to control the membrane formation. Additives also may affect the final membrane characteristics either by changing phase separation kinetics and thermodynamic properties. Some additives have tendency and ability to suppress the formation of macrovoids improving the interconnectivity of the pores, to enlarge macrovoids and lead in higher porosity in the top sublayer and top layer. Thus, by variation of the addition of additives concentration or additives molecular weight, optimal membrane structure can be obtained through the enlargement or suppression of macrovoids of the membranes. It has been proven that the presence of even minor amounts of additives in a membrane casting solution can have an immense effect on membrane performance.

To improve the membrane morphology and properties, various inorganic (such as LiCl) and high molecular weight organic such as polyvinyl pyrrolidone (PVP) or polyethylene glycol (PEG) additives to casting solution are often used (Chuang et al., 2000). PVP and PEG are the most important polymeric additives used in study and evaluate the membranes performances. This is because they are miscible with the most of the membrane materials and are soluble in both aqueous and many organic media (Jung et al., 2004). An additive can function as a pore former, increase solution viscosity or accelerate the phase inversion process.

Fontananova et al. (2006) found that LiCl addition in the PVDF/dimethylacetamide dope increases flux of the casted membranes at low LiCl concentration of 2.5 wt.%, but it suppressed macrovoid formation at a high concentration of 7.5% LiCl and resulted in a decrease of the membrane permeation flux. The similar results were obtained by Lee et al. (2002) for poly(amic acid) (PAA) casting solutions in N-methyl-2-pyrrolidone. They found that by increasing LiCl concentration in the PAA/N-methyl-2-pyrrolidone system, the solution viscosity can be raised to the point where macrovoid formation is hindered and development of a finely porous structure is favored. The above observations were believed to be associated with the change of the thermodynamic and kinetic properties of the polymer dope system before and after LiCl addition. It was shown that LiCl addition increased the dope's thermodynamic instability in reaction with water, which facilitated a rapid phase demixing and resulted in macrovoid formation (thermodynamic effect).

On the other hand, LiCl possesses strong interactions with the polymer and solvent, which was supported by the significant increase in viscosity of LiCl added casting solutions. The strong interactions among the components of the casting solution tended to delay the dope precipitation (the kinetic effect), which partially offset the thermodynamic impact of LiCl addition. As a result, the size of the macrovoids in the fabricated membranes is reduced at high LiCl dosage in the casting solutions (Lee et al., 2002).

Wang et al. (2009) showed that the PVP-added PES membrane has a higher water flux and lower water contact angle than the neat PES membrane. The contact angle decreased by 16% when the PVP content in the casting solution was 10 wt.%. Ochoa et al. (2001) confirmed that the addition of PVP to the casting solution increases the UF PES membrane permeability without significant changes in selectivity. Marchese et al. (2003) reported that an increment in the pore density, a decrease of the effective thickness of the dense layer due to macrovoids in the support layer and an increment in the hydrophilicity of the surfaces on the membrane and inside the pores are the reasons behind the increase of membrane permeability when PVP is added. The formation phenomena of macrovoids, which are large elongated spaces below the upper surface of the membrane, have been widely discussed by Smolders et al. (1992), Wang et al. (1998), and McKelvey and Koros (1996).

Arthanareeswaran et al. (2007) concluded that the presence of low molecular weight PEG additive in the cast solution film increased porosity/permeability of the prepared membranes. Saljoughi et al. (2010) studied the effects of PEG concentration (0 wt.%, 5 wt.% and 10 wt.%) on morphology, pure water permeation flux of the prepared membranes at different coagulation bath temperatures (0 and 25 °C). Increasing PEG concentration in the cast film results in the facilitation of macrovoid formation in the membrane sub-layer, which increases flux and rejection of human serum albumin. Susanto and Ulbricht (2009) compared the effect of three different macromolecular additives PVP, PEG and poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (Pluronic) on the membrane structure and their stability in the polymer membrane matrix of the PES membrane. They found that the addition of Pluronic as a modifier agent showed the best membrane performance and stability. The authors suggest that the reason for this phenomenon would be that the hydrophobic part of Pluronic enhances the PES–additive interaction.

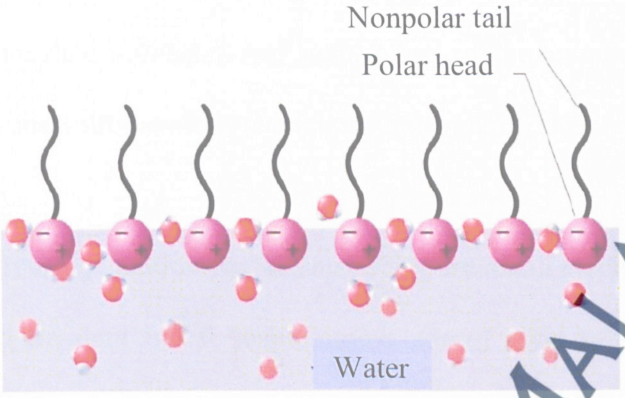
Recently the use of inorganic nanoparticles as additives to polymeric membranes has begun to attract wide interest due to the improved membrane properties, including increased strength and modulus, which result from the strong interfacial interactions the nanoparticles have with the surrounding polymer matrix (Rong et al., 2001). Zodrow et al. (2009) prepared polysulfone membrane contained Ag nanoparticles (1–70 nm) via the phase-inversion process by dispersing nanoparticles in the casting solution. It was shown that polysulfone membranes impregnated with 0.9 wt.% Ag nanoparticles possess similar permeability and surface charges compared with pure polysulfone membranes, however they were significantly more hydrophilic with 10% reduction in contact angle. It was found that the addition of Ag nanoparticles does not visibly alter the membrane structure. Similar results were obtained by Yan et al. (2006), which used nano-sized Al_2O_3 particles in dimethylacetamide casting solutions for preparation of PVDF membranes. It was found that increased Al_2O_3 concentrations from 0 to 2% in the casting solution had led to increased water permeate fluxes due to an increase in the membrane hydrophilicity. SEM images showed that the addition of nano-sized Al_2O_3particles did not affect the surface, cross-section, and inner pore membrane structures. Both pure PVDF and PVDF – Al_2O_3 membranes showed typical asymmetric morphology with finger-like pores.

2.7 Surfactant

According to Muthuprasanna et al. (2009), the term surfactant was coined by Antara Products in 1950. Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and can also lower the interfacial tension between two liquids. Surfactants are usually organic compounds that are amphipathic, as they contain both hydrophobic groups (tails) and hydrophilic groups (heads). Therefore, they are soluble in both organic solvents and water. Surfactants are indicated by the presence of both polar and non-polar region.

A surfactant molecule is formed by two parts with different affinities for the solvents. One of them has affinity for water (polar solvents) and the other for oil (non-polar solvents). A little quantity of surfactant molecules rests upon the water-air interface and decreases the water surface tension value (the force per unit area needed to make available surface). When water, oil and a surfactant are mixed, the surfactant rests at the water-oil interface. These systems depending on their stability are called emulsions or microemulsions (thermodynamically stable). Although, the properties for an emulsion and a micro emulsion are different, both obey the same principle. They try to form enough interface for preventing the polar non-polar solvent contact. In the field of pharmaceutical sciences, the surfactants are used as emulsifiers, wetting agents, solubilizers etc. Those surfactants are mostly derived from petroleum but some may be from natural fats or sugars (Muthuprasanna et.al, 2009). Figure 4 shows the head and tails orientation for surfactant.

FIGURE 4: Head and tails orientation of surfactant (Muthuprasanna et.al, 2009)



Surfactants commonly classified into four categories, according to the formal charge present in their hydrophilic head: anionic (negatively charged), cationic (positively charged), nonionic (uncharged) and amphoteric (presents both positive and negative charges at an intermediate pH). For the household industry, the most common anionic surfactants are those with a sulfate, sulfonate, or carboxylate (soap) group attached to them. For the cationic surfactants, the quartenary ammonium groups are widely used, and are by far the most common. The nonionic surfactants are mainly derived from the ethylene oxide and/or propylene oxide. Finally, the amphoteric surfactants, also known as zwitterionic surfactants, are represented mainly by acyl ethylenediamines and alkyl amino acids (Kume et al., 2008).

2.7.1 Anionic Surfactant

In solution, the head is negatively charged. These surfactants are the most widely used type of surfactant for preparing shampoos because of its excellent cleaning properties and high hair conditioning effects. Anionic surfactants are particularly effective at oil cleaning and oil/clay suspension. They still can react in the wash water with the positively charged water hardness ions (calcium and magnesium), which can lead to partial deactivation. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soap. Most of the anionic surfactants are carboxylate, sulfate and sulfonate ions (Muthuprasanna et al., 2009).

There are five subgroups of anionic surfactants. They are alkali metal and ammonium soaps, divalent and trivalent metal soaps, amine soaps, alkyl sulphates and alkyl phosphate anionic surfactants. Alkali metal soaps are sodium, potassium or ammonium slats of long chain fatty acids such as oleic, stearic and ricinoleic acid and they produce oil in water emulsion. They are stable above pH 10 but are very sensitive to acids and the emulsion to break. Divalent and trivalent surfactants are water in oil emulsifying surfactant. They are less alkali and less sensitive to acids. In the case of amine surfactants triethanolamine surfactant is preferentially used for pharmaceutical applications. They form oil in water emulsion. Alkyl sulphate anionic surfactants are the esters of fatty alcohols and sulphuric acids. Most widely used surfactants are sodium lauryl sulphate. They are oil in water emulsifying agents. Alkyl phosphates are similar to that of alkyl sulphates but they have their alcohols phosphate instead of sulphate. They are mostly used to prepare oil in water emulsion creams. Sodium Dodecyl Sulphate (SDS) is one of the example of surfactants that represent linear alkyl sulphate (Muthuprasanna et al., 2009).

2.7.2 Cationic Surfactant

The head of cationic surfactant is positively charged in solution. Cationic surfactants are quartenary ammonium compounds and they are mostly used for their disinfectant and preservative properties as they have good bactericidal properties. They are usually used on skin for cleansing wounds or burns (Muthuprasanna et al., 2009). They are also useful as fabric softeners and corrosion inhibitors. As they do not provide effective cleaning at neutral pH, they are not used in general purpose detergents. 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 (Schmitt, 2001). Cetyl trimethylammonium bromide (CTAB) is one of the examples of cationic surfactant.

2.7.3 Nonionic Surfactant

Nonionic surfactants do not have any electrical charge, which makes them resistant to water hardness deactivation. They are less irritant compared to other anionic and cationic surfactants. The hydrophilic part contains the polyoxythylene, polyoxypropylene or polyol derivatives. The hydrophobic part contains saturated or unsaturated fatty acids or fatty alcohols (Muthuprasanna et al, 2009).

They tend to be more effective than other surfactants for removal of oily soil from synthetic fabrics. Most of the nonionic surfactants are considered as low-foaming products, 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 surfactant in certain formulations (Schmitt, 2001). The nonionic surfactant can be classified as Poly esters, polyoxyethylene esters, polyoxamers. The polyol esters include glycol and glycerol esters and sorbitan derivatives. Polyoxyehylene esters include polyethylene glycol (PEG-40, PEG-50, PEG-55). The most commonly used nonionic surfactants are ethers of fatty alcohols. Triton X-100 is an example of nonionic surfactant from polyoxyethylene.

2.7.4 Amphoteric/Zwitterionic Surfactant

Amphoteric/Zwitterionic surfactants are very mild, making them particularly suited for use in personal care preparations over sensitive skins. They can be anionic (negatively charged), cationic (positively charged) or nonionic (no charge) in solution, depending on the acidity or pH of the water. Those surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium but the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties (Muthuprasanna et al., 2009).

2.8 Membrane Based Surfactant

Many researchers had reported on the role of surfactants in the membrane structure. Yamasaki et al. (2000) and Alsari et al. (2001) were used sodium dodecyl sulphate (SDS) as surfactant additive in the polysulfone (PSF) casting solution for gas separation and as gelatin media on the formation of polyethersulfone (PES) membranes, respectively. Mulijani et al. (2010) had reported the effect of the effects of temperature and concentration of cationic surfactant, which is Cetyl trimethylammonium bromide (CTAB) in the formation of asymmetric nanofiltration membrane. The result indicated that the formation of membrane pore increases as the addition of CTAB increases. Saedi et al. (2012) investigated the effect of three types of surfactant including SDS, CTAB and Triton X-100 on structure and performance of PES membrane for carbon dioxide separation from methane. The result demonstrated that the addition of surfactants in the casting solution increases the formation of macrovoids and large finger-like pores in the sub-layer of PES membranes. Rahimpour et al. (2007) reported that the small addition of SDS, CTAB, and Triton X-100 as additives in casting solution increases the porosity of the membrane support pure solution layer enhances pure water flux and milk concentration.

Amirilargani et al. (2010) found out that addition of Tween 80 increases water content and porosity of the membrane support layer and enhance pure water permeability and also for PES ultrafiltration membranes the rejection ratio of bovine serum decreases while the flux recovery ratio of bovine serum albumin decreases, while the flux recovery ratio remarkably increases and the degree of irreversible fouling decreases .The effect of addition of Span 80 on the morphology and pervaporation performance of asymmetric PSF membranes is reported by Tsai et al. (2000). It was found that the addition of Span-80 in the casting solution can suppress macrovoids in the asymmetric PSF membrane. Also, the influence of CTAB and Triton X-100 on morphology and separation nitrophenols using CA nanofiltration membrane was investigated by Ghaemi et al. (2012). Addition of surfactants as additive resulted in membranes with superior pure water flux, permeation and rejection in comparison to CA membrane.