Phase Diagram and Membrane Desalination

Ayman Taha Abd El-aziem El-gendi

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/60419

Abstract

Desalination technologies have made a significant impact in seawater and brackish water desalination. Recently, the evolution of membrane development has improved performance to lower operating costs and membranes have become the preferred technology for water desalination. Fortunately, different raw materials can be used for preparing membrane sheets which include either organic or inorganic materials, such as cellulose acetate, polyamide, polyimide, ceramic, natural, or artificial polymers. On the one hand, as a result of the variety of the raw materials which already exist in the entire world, different membrane separation processes might be applied dependent on the nature of the membrane sheet and the requirements of treatment process. On the other hand, there are different types of membranes can be used for membrane desalination by using different technologies such as reverse osmosis (RO), membrane distillation (MD), and forward osmosis (FO). The ternary phase diagram for membrane casting solution has an important role to get the required membranes.

Keywords: Desalination technologies, membrane, phase diagram, membrane separation processes

1. Introduction

This chapter intends to focus on using membrane separation processes for desalination based on the selectivity of the membrane, such as the preferential permeation of water (classical selectivity) or the solute (reverse selectivity). Phase inversion process is the most important technique used to prepare asymmetric polymeric membranes. In addition, the morphology

and performance of membranes depend on their effects, which also depend on the membrane preparation process parameters. From a thermodynamic point of view, study on polymer–solvent– nonsolvent system can be well depicted in a ternary phase diagram. The Flory-Huggins theory was found to be a convenient and useful framework for the thermodynamic analysis of component mixing in a membrane preparation system. As a result of the variety of the raw materials which already exist in the entire world, different membrane separation processes might be applied dependent on the nature of the membrane sheet and the requirements of treatment process. In addition, there are different engineering forms which have been established for membranes that include flat, tubular, spiral wound or hollow fiber. Generally, the membrane preparation techniques are classified as a function of the raw materials used, the engineering forms and the characteristics of the required separation process. Over the past decades, the polymeric membranes have achieved commercial importance in a variety of separations applications in the chemical, food, pharmaceutical, and biotechnology industries. Today, the membrane industry is faced with the challenge of inventing new membrane materials.

In this chapter, we will focus particularly on membrane desalination techniques, such as reverse osmosis (RO), forward osmosis (RO) and membrane distillation for desalination. For these methods, as with any membrane process, the membrane is one of the most important characteristics which determines the usefulness and effectiveness of the entire process. For this reason, several targets of research have shifted in recent years towards developing new and more efficient materials that allow for a compromise between two fundamental properties of the separation, often antagonistic, namely the selectivity and permeability.

However, membrane processes are becoming economically competitive after the development of highly permeable polymer membranes. These membranes are less expensive than inorganic membranes and their implementation is much easier. Several types of polymers can be used such as cellulose acetate, polysulfones, polyamides and polyimides.

This chapter aims at preparing desalination membranes in order to get water selective membranes suitable for the retention of salts water mixtures. Hence two objectives must be reached: first, the selection of water selective materials well resistant in almost pure water and second, the preparation of high flux membranes needed for the recovery of water.

As a matter of fact, the preparation of polymeric membranes usually involves the phase inversion process, in which a homogeneous casting solution induces phase separation into a polymer-rich phase and a polymer-poor phase by the exchange of solvent with nonsolvent in an immersion bath (i.e: as water bath). Phase separation would continue to form the membrane structure until the polymer rich phase is solidified. Solidification during phase inversion could be induced by gelation and/or crystallization of the casted polymer solution. The equilibrium ternary phase diagram system is still a good tool for controlling the morphology and interpreting the membrane structure. Significantly, knowledge of phase equilibria (cloud points, binodals, spinodals, and critical compositions) enables one to change the conditions for the preparation of membranes such as the compositions of the casting solution, the temperature and of the coagulation bath type to obtain an optimum membrane structure.

The phase diagram has an important role to report the agreement between experimental work in order to get the required membranes, and the ternary phase diagram miscibility gaps for the evaluations of membrane-forming system. In the ternary phase diagram (polymer (p)/ solvent (s)/nonsolvent (ns)) a miscibility gap with metastable regions exists. According to the theory of phase separation three modes of phase separation can take place in such ternary system: nucleation and growth of the polymer lean phase, spinodal phase separation and nucleation and growth of the polymer rich phase. Since polymer is one of the components of the ternary system, solidification of a part of the system can take place.

2. General introduction on membrane science and technology

A general introduction on membrane science and technology is given in this section. It begins with the definition of terms and provides a description of membranes structures and membrane separation process. A short overview over the developments of membrane science and technology is given.

2.1. Membrane definition

A. Zydney et.al [1] defined membrane as a flexible layer surrounding a cell, organelle (such as the nucleus), or other bodily structure. The movement of molecules across a membrane is strictly regulated in both directions. Therefore, a membrane is a layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, molecules, or substances when exposed to the action of a driving force. Some components are allowed to pass through the membrane into a permeate stream, whereas others are retained by it and accumulated in the retentate stream (Fig. 1).

C.P Mark [2] defined a membrane as follows: What is a membrane? Possibly the broadest definition is a region of discontinuity interposed between two phases. This statement implies that membranes can be gaseous, liquid, or solid, or combinations of these phases. The term "region" in the definition is used to eliminate ordinary interfaces. Thus, the interfaces of two immiscible liquids, of a gas and a liquid, or of a gas and a solid, would not ordinarily be considered as membrane structures.

From Wikipedia [3]: membranes can be of various thicknesses, with homogeneous or heterogeneous structure. Membranes can also be classified according to their pore diameter. There are three different types of pore size classifications: microporous (dp < 2 nm), mesoporous (2 nm < dp < 50 nm), and macroporous (dp > 50 nm). Membranes can be neutral or charged, and particles transport can be active or passive. The latter can be facilitated by pressure, concentration, chemical, or electrical gradients of the membrane process. Membranes can be generally classified into three groups: inorganic, polymeric, or biological membranes. These three types of membranes differ significantly in their structure and functionality.
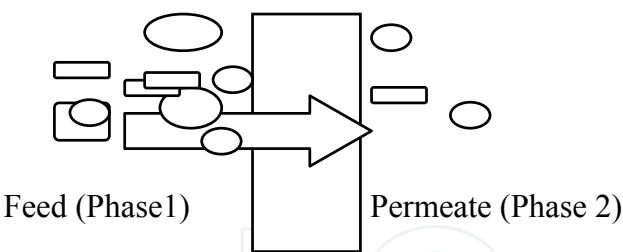
Figure 1. Membrane module.

2.2. Classification of membranes [1, 2, 6]

The membranes can be classified as follows:

a.   Classification by nature of membrane

b.   Classification by structure of membrane (Fig. 2)

c.   Classification by application of membrane

d.   Classification by mechanism of membrane function

Symmetrical membranes

\-   Isotropic microporous membrane   -   Dense (compact) membrane

Anisotropic membranes

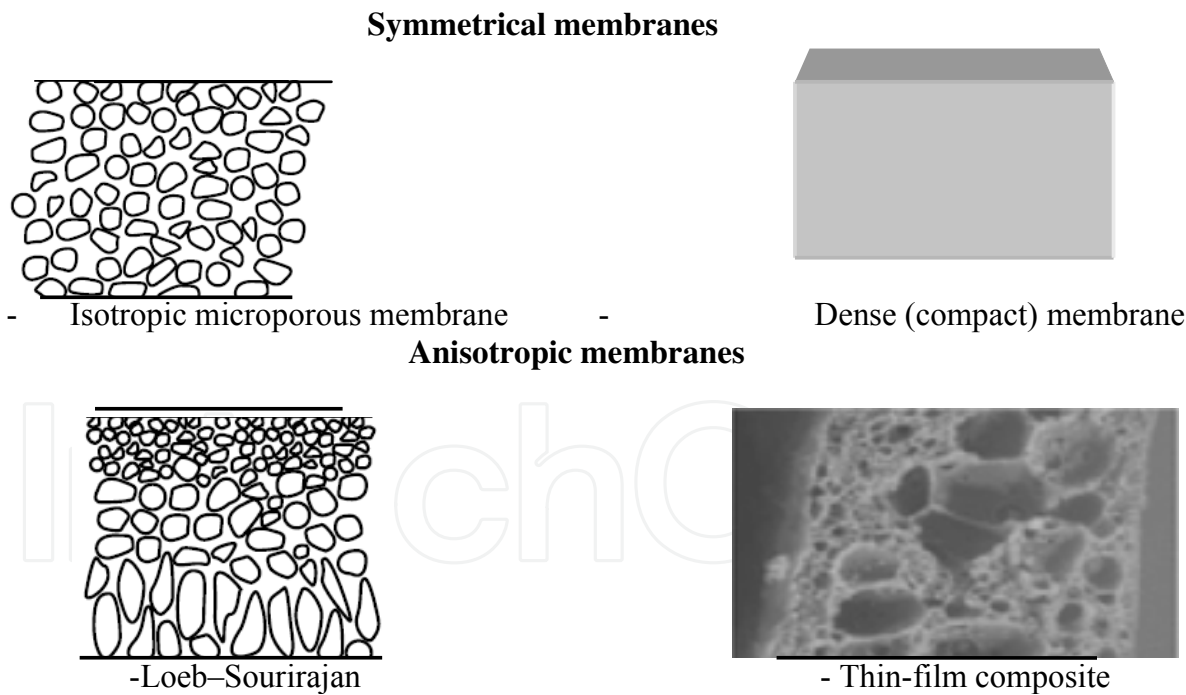-Loeb–Sourirajan   - Thin-film composite

Figure 2. The main types of membranes based on structure [4].

2.3. Membrane types based on morphology [1, 2, 6]

The membrane types can be divided into isotropic membranes, anisotropic membranes (polymeric, ceramic, metal), and liquid membranes. These types will be outlined below.

2.3.1. Isotropic membranes

An isotropic membrane is divided into three types: Microporous membranes, nonporous membranes, and electrically charged membranes.

2.3.1.1. Microporous membranes (ultrafiltration, microfiltration)

In fact, the microporous membrane is very similar in function and morphology to a traditional liquid filtration. In addition, it has a rigid, highly voided structure with unorganized, distributed, and interconnected pores. Moreover, these pores differ from those in a conventional filter by being smaller, on the order of 0.01–10 μm in diameter. Therefore, all particles larger than the largest pores will be completely rejected by the membrane. While particles smaller than the largest pores, but larger than the smallest pores could be partially rejected, according to the pore size distribution of the membrane. However, particles much smaller than the smallest pores could pass through the membrane. Thus, the separation of solutes by microporous membranes is mainly dependent on the molecular size and pore size distribution. In general, only molecules that differ considerably in size could be rejected effectively by microporous membranes, for example, in ultrafiltration and microfiltration.

2.3.1.2. Nonporous, dense membranes

Nonporous, dense membranes composed of a dense film through which material can pass on by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. However, the separation efficiency of various solutes of a mixture is dependent on their transport rate through the membrane, which is determined by their solubility and diffusivity in the membrane material. In addition, nonporous, dense membranes could reject charged or uncharged solutes of similar size if their concentration in the membrane material differs significantly. Typically, pervaporation, most gas separation, and reverse osmosis membranes use nonporous membranes to do the separation process.

2.3.1.3. Electrically charged membranes

Electrically charged membranes are dense or microporous. A membrane with fixed positively charged ions is called an anion-exchange membrane. Similarly, a membrane containing fixed negatively charged ions is referred to as a cation-exchange membrane. Separation with charged membranes is achieved mainly by the exclusion of ions of the same charge as the fixed ions of the membrane structure. The separation is affected by the charge and concentration of the ions in solution. For example, monovalent ions are excluded less effectively than divalent ions and, in solutions of high ionic strength, selectivity decreases. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis.

2.3.2. Anisotropic membranes (asymmetric membrane)

The permeate flux through a membrane is inversely proportional to the membrane thickness. Really, high permeability is desirable in membrane separation processes for economic reasons; therefore, the membrane thickness should be as thin as possible. Conventional film fabrication

technology limits the manufacture of mechanically strong, defect-free films to about 20 µm thickness. Moreover, the development of a new membrane fabrication technique to produce asymmetric membrane was one of the major breakthroughs of membrane fabrication technology during the last years. Asymmetric membranes consist of an extremely thin surface layer supported on a much thicker surface layer, porous substructure. The surface layer and its substructure may be formed in a single operation or separately. In composite membranes, the layers are usually made from different polymers. The rejection properties and flow rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such membranes.

2.3.3. Ceramic, metal, and liquid membranes

Ceramic membranes are a special class of microporous membranes. They are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required.

3. The basic membrane separation processes [5]

The membrane separation processes have been used in several applications for biological, industrial, drinking water, and wastewater treatment purposes. Moreover, the advantages of this separation system are their powerful separation capacity of small and large molecules and compounds from mixtures, organic and inorganic solutions. In addition, they are characterized by their low-power consumption and area required comparing to other separation techniques. Furthermore, membrane separation technologies have some advantages over other mass transfer processes, including high rejection, low-energy consumption, low cost-to-performance ratio, and compact and modular designs. Thus, they are generally considered to be "clean technologies." Fig. 3. shows the basic membrane separation process.
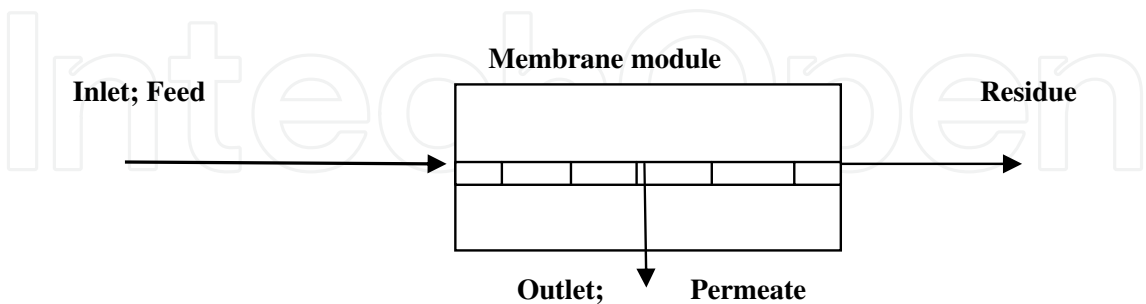

Figure 3. The basic membrane separation process.

Membrane separation processes are often used since these applications realize high removal of constituents such as charged solutes, uncharged solutes, and organic molecules. In the recent years, membrane separation techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact. Really, membrane

separation processes are easier, more efficient, and more economical than conventional separation techniques. The separation is usually performed at ambient temperature by using membrane process; this allows temperature-sensitive solutions to be produced without the constituents being damaged [2]. In fact, this is very important where temperature-sensitive products have to be processed (i.e., food, drug industry, biotechnology). The main membrane separation processes are membrane distillation, pervaporation, and pressure-driven membrane processes, and these processes are outlined below in detail.

3.1. Pressure-driven membrane process

Pressure-driven membrane process techniques have become an alternative to conventional water treatment methods, as well as in the treatment and concentration of wastewater of both industrial and municipal origin [6]. The occurrence and prevalence of organic micro-pollutants, such as pesticides, and other organic micro-pollutants are becoming a concern in drinking water, wastewater, and water reuse applications due to potential adverse health effects associated with these compounds. Thus, membrane processes are becoming increasingly widespread in water treatment and wastewater reclamation/reuse applications where a high product quality is desired [7, 8, 9].

3.1.1. Pressure-driven membrane separation processes [1, 2, 10]

The pressure-driven membrane separation processes are as follows:

- Microfiltration (MF)

- Ultrafiltration (UF)

- Nanofiltration (NF)

- Reverse osmosis (RO)

Literally, all RO, NF, and UF membranes are asymmetric. This differentiates easily most membranes from traditional filters, which are symmetric or, in other words, identical on the both sides of the common filter. In addition, membrane has a tight top layer facing the pollutant solution to be treated. This layer, also called the skin layer, is thin typically <<0.1 μm. The membrane thickness is about 150–250 μm, and the bulk of the membrane simply provides structural support for the skin layer. The asymmetric structure means that the pores are wider, which prevents the pores from being plugged. This provides good fouling resistance, since foulants have a tendency to either be totally rejected or pass all the way through a membrane. Pressure-driven membrane filtration processes are classified by pressure into two categories:

- High-pressure membrane processes, such as reverse osmosis (RO) and nanofiltration (NF), normally have a relatively small pore size compared to low-pressure membranes, since small pore size membranes require high-driving force to drive fluid through the membrane compared to big pore size membranes. Further, these types of membranes normally require a relatively high pressure from 4 to 70 bar. In addition, these high-pressure processes primarily remove contaminants through chemical diffusion.

- And low-driven pressure membrane, such as microfiltration (MF) and ultrafiltration (UF), normally requires a low pressure from 0.4 to 7 bar. These membranes primarily remove contaminants through physical sieving. More details about these types are outlined below.

i.   Microfiltration (MF)

Microfiltration (MF) is characterized by a membrane pore size between 0.05 and 10 μm and operating pressures below 2 bar. MF is primarily used to separate particles and bacteria from other smaller solutes. Further, MF is a low-pressure technique that removes particles with a molecular weight above 50, 000 or a particle size over 0.05 μm. In addition, MF is a process where ideally only suspended solids are rejected, while even proteins pass the membrane freely.

ii.   Ultrafiltration (UF)

Ultrafiltration (UF) refers to membranes having smaller pore size compared to microfiltration membranes. UF is characterized by a membrane pore size between 2 nm and 0.05 μm and operating pressures between 1 and 10 bar. UF is a low-pressure technique where protein and suspended solids are rejected freely. There is consequently no rejection of mono- and disaccharides, salts, amino acids, organics, inorganic acids, or sodium hydroxide.

iii.   Nanofiltration (NF)

Nanofiltration (NF) is characterized by a membrane pore size between 0.5 and 2 nm and operating pressures between 5 and 40 bar. NF is used to achieve a separation between sugars, other organic molecules, and multivalent salts on one hand, and monovalent salts and water on the other. True NF rejects only ions with more than one negative charge, such as phosphate, while passing single charged ions. NF also rejects uncharged, dissolved materials and positively charged ions according to the size and shape of the molecule in question.

iv.   Reverse Osmosis (RO)

Reverse osmosis (RO) is the tightest possible membrane process. Water the only material passing through it while all the dissolved and suspended materials are rejected. RO as a desalination technology has led to a reduction in the desalinate cost in the last decade. RO is now the potential competitor to the world-leading desalination technology, multistage flash desalination (MSF). Desalination by RO uses less energy than the other desalination technologies, which makes RO more attractive, as RO uses a semipermeable membrane under high pressure to separate salts. In principle, the performance of the RO desalination depends on the used membrane. Table 1 represents cost for desalting m^3 of potable water using different desalination technology.

It clearly illustrates that RO has a significant economic advantage for treating brackish water, while price quotes for ED are not readily available. For desalination of seawater, RO has an economic advantage over other thermal technology. The comparison between the four membrane processes is summarized in Fig. 4. Table 2 illustrates some of the characteristics with NF and RO membranes. Total worldwide use of membranes, based on membrane surface area, is approximately presented in Fig. 5.

MSF	MEE	VC	Seawater RO	Brackish RO	Brackish ED	Reference
1.10–1.50	0.46–85	0.87–0.92	0.45–0.92	0.20–0.35		[11]
0.80	0.45		0.72–0.93			[12]
0.89	0.27–0.56		0.68			[13]
			1.50	0.37–0.70	0.58	[14]

Table 1. Desalination costs ($/m^3 fresh water – multiply by 3.8 for $/1000 gal).

Membrane type	RO (Dow Filmtec BW30-4040)	NF (Dow Filmtec NF90-4040)
Operating pressure, bar	9.04	5
Power consumption, kW	0.37	0.22
Specific energy costs, kWh m^{-3}	1.47	0.89
Permeate TDS, ppm	65	318

Table 2. Operating pressures, power consumption, and permeate quality with NF and RO membranes [15].
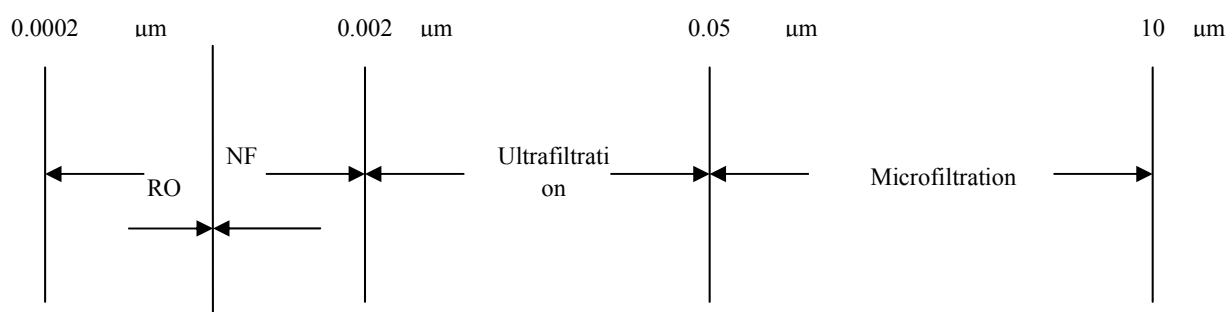

Figure 4. Pressure-driven membrane processes based on the smallest particle [2, 16].
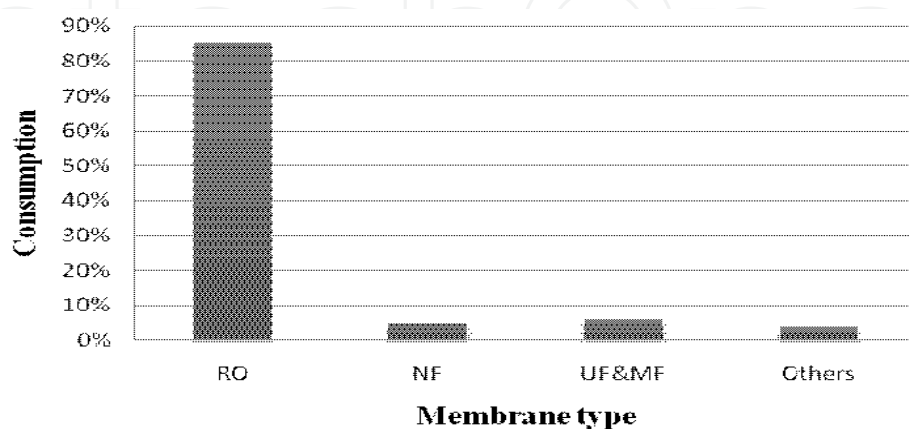

Figure 5. Membrane use in the world based on surface area [16, 10].

3.2. Membrane material

Membrane processes are becoming economically competitive after the development of highly permeable polymer membranes. These membranes are less expensive than inorganic membranes and their implementation is much easier. Several types of polymers can be used such as cellulose acetate, polysulfones, polyamides, polyvinylchloride, and polyimide. The suitable polymer material for membrane and its membrane-forming technique should be first found out to study water desalting with membrane process. Really, selection of the polymer membrane materials for separation process is based mainly on some of the important features such as good chemical resistance and high mechanical strength of the polymer film in the mixture solution. Therefore, it should have good interaction preferably with one of the components of the mixture for separation. The main polymeric materials used for membrane processes have been depicted in Table 3.

Membrane material	Membrane process							
	MF	UF	NF	RO	PV	MD	GS	FO
Cellulose acetate	•	•	•	•	•		•	•
Cellulose nitrate	•							
Cellulose esters	•							
Polyacrylonitrile		•			•			
Aromatic polyamide	•	•	•	•				•
Aliphatic polyamide	•	•	•	•	•			•
Polyimide		•	•	•	•		•	•
Polybenzimidazole			•	•	•			•
Polybenzimidazolone			•	•	•			
Polycarbonate	•							
Polysulfone	•	•			•			
Polyethersulfone	•	•				•	•	
Polyetheretherketone	•	•						
Polyydimethylsiloxane(PDMS)	•				•			
Poly(vinyl alcohol)	•							
Poly(vinyl chloride)	•							
Polyacrylonitrile	•	•						
PVC copolymer	•	•			•			
Polysulfone	•	•						
Sulfonated-PSF		•		•	•			
Polytetrafluoroethylene(PTFE)	•				•			
Polyvinylidenefluoride(PVDF)	•	•			•	•		
Polycarbonate	•							
polyester	•							
Polypropylene	•				•	•		
Polyester	•							
Polyethylene	•				•	•		
Chitosan		•	•	•	•			

Note: PV, pervaporation; MD, membrane distillation; FO, forward osmosis; GS, gas separation

Table 3. Typical applications of various polymeric materials in selected membrane processes [1–67].

- As concluded in Table 3, the more useable membrane materials for RO are as follows:

  ○ Cellulose acetate; Aromatic and aliphatic polyamide; Polyimide

  ○ Polybenzimidazole; Polybenzimidazolone; Sulfonated-PSF; Chitosan

Thus, one or more of these polymers will be selected for membrane desalination using RO.

- Also, as concluded in Table 3, the more useable membrane materials for MD are as follows:

  ○ Polyvinylidenefluoride (PVDF); Polytetrafluoroethylene (PTFE); Polypropylene

  ○ Polyethylene; Polyethersulfone

Thus, one or more of these polymers will be selected for membrane desalination using MD.

4. Preparing desalination membranes

This section aims at preparing desalination membranes in order to get water selective membranes suitable for the retention of salts from water mixtures. Hence, two objectives must be reached: first, the selection of water-selective materials well resistant in almost pure water, and second, the preparation of high flux membranes needed for the recovery of water. The preparation of symmetric (such as dense membrane), asymmetric, and composite membranes made from polymeric materials, to be used in the different membrane processes and applications, are reported also in this part [1, 2].

Typically, the preparation of polymeric membranes, with different physical structures, takes place by two methods [2]:

1. Physical treatment of a certain polymer membrane (such as annealing, elongation, etc.)

2. Preparation of the membranes from a certain polymer by several membrane formation processes (casting process such as wet- and dry-phase inversion)

There are differences between two methods. On the one hand, the physical structure is created by the treatment after preparation of the membranes. On the other hand, in the second case, the structure is created at the same time as membrane formation.

Fortunately, all kinds of different synthetic materials can be used for membrane formation process. In addition, there are a number of different techniques to prepare the required membrane; some of these methods can be used to prepare polymeric as well as inorganic membranes. The equilibrium thermodynamic properties of the ternary system polymer/solvent/nonsolvent play an important role in the description of membrane preparation process. Thus, depending on the choice of the ternary system, three possible results can occur during membrane formation process, which are as follows [17, 18]:

i.   Nonporous film (symmetrical dense membrane)

ii.   Porous film (symmetrical porous membrane)

iii.   Asymmetric membrane which has a thin dense top layer on a porous supporting layer

The asymmetric membrane is the desired structure in the study of desalination. An explanation of these results could be dependent on two sets of factors:

i.   The ternary system (polymer/solvent/nonsolvent) and its equilibrium thermodynamic properties (such as liquid–liquid phase separation and solidification)

ii.   The effect on the kinetics of the above-mentioned demixing phenomena and the exchange of solvent and nonsolvent during membrane preparation process

The preparation process of asymmetric membranes could include two sets of factors. The preparations of symmetric, asymmetric, and composite membranes are reported in this section.

4.1. Symmetrical membrane [19]

- Dense symmetrical membranes (nonporous membrane)

These types of membranes are capable of separating molecules of approximately the same size from each other (such as toluene/heptane). On the one hand, dense symmetrical membranes are widely applied in research, development, and other laboratory studies for characterizing membrane properties (such as swelling, mechanical properties). On the other hand, these types of membranes are, however, rarely used commercially, because the membranes permeate flux is very low for practical separation processes. Moreover, such membranes are used in some applications such as pervaporation, vapor permeation, gas separation, and dialysis. The dense membranes are prepared by two-step mechanism, solution casting and thermal melt-pressing process as described below.

- Two-step mechanism

The dense membranes, such as polyimide membranes, were obtained by addition mixing reaction of a dianhydride and diamine in the presence of suitable solvent. This reaction involves two consecutive steps, which are as follows:

1.   The dianhydride and diamine react at room temperature to give polyamic acid (PAA).

2.   The PAA is casted on a glass plate or Teflon to give PAA membrane, after the casting has been drawn; the casted film is dried at high temperature, thus the solvent will evaporate to leave a thin film. The PAA membrane is converted into polyimide (PI) membrane by thermal treatment under vacuum.

3.   Solution casting (dry-phase inversion)

Solution casting uses a casting knife to cast polymer solution across a casting plate. After the casting has taken place, the solvent evaporates to leave a thin film. The best casting solution concentrations are in the range 15–20 wt% polymer in order to prevent the spreading of polymer over the casting plate. Solvents having high boiling points are unsuitable for this method, because their low volatility needs too long evaporation times.

• Melt pressing (melt forming)

Some polymers do not dissolve in suitable casting solvents. For example, polyethylene, polypropylene, and nylons, which have to be formed into membranes by melt pressing. This process occurs by sandwiching the polymer at high pressure between two heated plates. A pressure of 136–340 bar is used for 0.5–5 minutes, while holding the plates almost above the melting point of the polymer.

4.2. Preparation of porous membrane

In fact, this class of membrane induces separation mechanism by discriminating between solute sizes. Typically, porous polymeric films can be prepared by several ways, such as sintering, stretching, track etching, and phase inversion processes. Really, the final morphology of the prepared membranes is dependent on the properties of the polymer solution and the process conditions. Furthermore, the majority of membranes are formed by controlled phase separation of polymer solutions into two phases: in the former one with a high polymer concentration (rich polymer phase), and in the latter one with a low polymer concentration (poor polymer phase). The rich polymer phase solidifies immediately after phase separation and forms the membrane. The membrane performance is dependent on the morphology of the prepared membrane.

4.2.1. Porous membranes preparation by phase inversion process

Phase inversion can be defined as a process whereby a polymer is changed in a controlled manner from a liquid state to a solid state [1, 2]. Phase inversion of polymer solutions can be induced in several ways [20]. The four main techniques for the preparation of polymeric membranes by phase inversion are as follows [21, 22, 23]:

i.   Immersion precipitation

Most commercially available membranes are formed by immersion precipitation. The phase inversion process induced by immersion precipitation is a well-known technique to get asymmetric polymeric membranes. A polymer solution is casted as a thin film on a plate support (as glass) and is immediately immersed in a coagulant bath. Precipitation can take place because the good solubility between solvent and nonsolvent in the polymer solution.

ii.   Thermally induced phase inversion (TIPS)

The TIPS is dependent on the theory that solubility of the polymer in a solvent usually decreases when the temperature is decreased. After the demixing process is occurred, the solvent is removed by extraction, evaporation, or freeze drying.

iii.   Precipitation from the vapor phase

This process was used as early as 1918 by Zsigmondy. Phase separation of the polymer solution is induced, during this method, by a nonsolvent vapor which penetrates in the polymer solution.

iv. Air-casting of a polymer solution (precipitation by solvent evaporation) [24, 25]

The simplest technique to form phase inversion membranes is precipitation by solvent evaporation. This process was already used in the early years of this century. In this technique, the polymer is dissolved in a mixture of solvent (volatile) and nonsolvent (less volatile). During the evaporation of the solvent, the solubility of the polymer decreases, and then the composition of mixture will shift to a higher nonsolvent and polymer content. This leads eventually to the polymer precipitation, and then phase inversion can takes place leading to the formation of skinned membrane.

It was clear that the differences between the four techniques originate from the differences in desolvation mechanisms.

4.3. Phase inversion membranes

Most of the membranes used today are phase inversion membranes (asymmetric structure membranes as RO) obtained by immersion precipitation [1, 26]. These membranes are asymmetric since their cross section reveals an asymmetric structure: dense skin layer (dense permselective layer <0.1 µm) supported by a porous sublayer (more open porous substrate ≥15 µm). In industrial applications, symmetrical microporous membranes, which induced by precipitation from the vapor phase, have been almost completely displaced by asymmetric membranes, which have much higher liquid fluxes with a good quality.

The asymmetric membrane structure was not recognized until Loeb and Sourirajan [27] prepared the first asymmetric membranes according to the wet-phase inversion process (Loeb–Sourirajan technique) in 1962. The Loeb–Sourirajan technique made a critical breakthrough in membrane process technology. Since the asymmetric membranes were prepared by Loeb and Sourirajan, the research and developments in asymmetric membrane preparation methods and properties were accelerated by using scanning electron microscopes, which enabled the effects of structural modifications to be easily assessed. More importantly, the demonstration of the advantages of the asymmetric membrane structure opens the way to improve the membrane separation processes. In addition, the development of the phase inversion process has preceded many systematic studies on the effects of membrane formation parameters and mechanism.

Figure 6 shows a schematic of the phase inversion process induced by immersion precipitation. This process consists of four main steps:

i. Casting step: the polymer solution is casted by using a film applicator to form a thin film of a polymer solution on a suitable substrate (i.e., glass support).

ii. Preconcentration step: the casted film is left for a certain evaporation time at room temperature (preconcentration time).

iii. Immersion step (phase inversion step): the casted film is immersed into an appropriate coagulation bath (i.e., water). During this step, the solvent will pass into the coagulation bath while nonsolvent will penetrate the polymer solution. The exchange of diffusion of a solvent and a nonsolvent through the interface in a polymer casting

solution and a nonsolvent will yield the phase inversion process for polymer casting solution with different exchange rates which induce membranes with symmetric or asymmetric structures (the interchange of solvent and nonsolvent coagulant due to the diffusion form membrane). The exchange rate is induced by the difference between solubility parameters, the diffusion force of nonsolvent and physical factors of the phase inversion process [28]. Furthermore, the properties of the polymer casting solution are presumed to affect the structure of the resulting membrane [29, 30].

iv.   Drying step: this step *removes traces of water and solvent* from the prepared membranes.
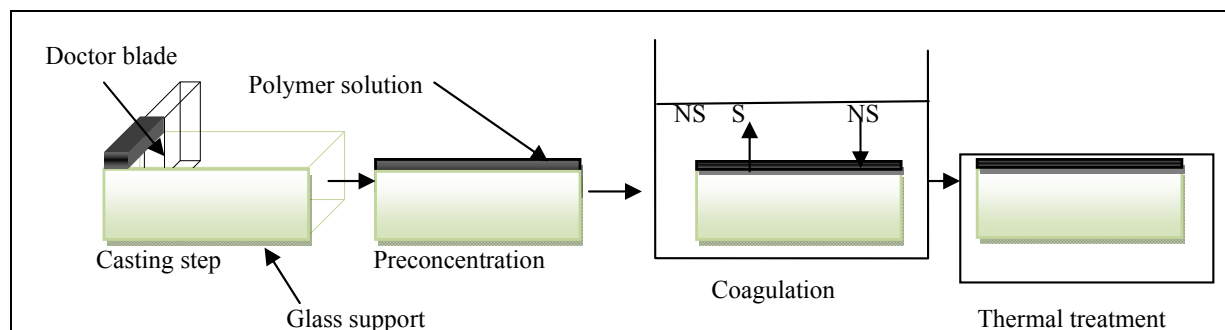
Figure 6. Membrane preparation steps via immersion precipitation. S, solvent; NS, nonsolvent [31].

4.4. Mathematical description of phase inversion process

It known that the state of any system, open, closed, or isolated can be described by state functions: entropy, enthalpy, and free energy. The thermodynamic state of a system of binary, ternary, or more components with limited miscibility can be described in terms of the free energy of mixing. At constant pressure and temperature, three different states can be distinguished [2]:

1.   A stable state (homogeneous solution): in this state, the free energy of mixing is positive

$$\Delta G > 0 \ (P,T=const) \tag{1}$$

2.   An unstable state: the homogeneous solution separates spontaneously into two phases, which is located within the miscibility gap, the free energy of mixing is negative

$$\Delta G < 0 \tag{2}$$

3.   An equilibrium state: given by the phase boundary composition, the free energy of mixing is zero

$$\Delta G = 0 \qquad\qquad (3)$$

4.5. Microporous formation mechanism [2, 32]

The phase inversion process induced by several techniques in a homogeneous solution to form microporous membranes can be related to three basic procedures [2, 32]:

1. Thermogelation of a homogeneous solution of a binary system, ternary system, or more components

2. Evaporation of a volatile solvent from a homogeneous solution

3. Addition of a nonsolvent or nonsolvent mixture to a homogeneous solution

All three procedures may result in symmetric microporous structures or in asymmetric structures with a more or less dense skin at one or both surfaces suitable for nanofiltration, reverse osmosis, ultrafiltration, or microfiltration. The free energy of polymer homogeneous mixing under certain conditions of temperature and composition is negative (an unstable state) that is the only thermodynamic presumption for all three basic preparation procedures; thus the system must have a miscibility gap over a defined concentration and temperature range.

Typically, a binary mixture of a polymer and a solvent should be assumed for understanding the mechanism of liquid–liquid demixing. Phase separation induced by thermal gelation, evaporation of solvent, and addition of nonsolvent can be illustrated with the aid of the phase diagram of a polymer mixture solution. On the one hand, the starting point for preparing phase inversion porous membranes is in a thermodynamically stable state for homogeneous solution, for example the point A at temperature T_1 (Fig. 7). On the other hand, the simplest procedure to yield a microporous system is by thermogelation of a binary (two component) mixture. At high temperature, thermogelation of a binary system forms a homogeneous solution for all compositions, but a miscibility gap over a wide range of compositions is shown at a lower temperature. This behavior is illustrated schematically in Fig. 7, which shows a phase diagram of a binary mixture of a polymer and a solvent as a function of temperature.

From Fig. 7, the points P and S indicate the pure components of polymer and solvent respectively, while points on the line P–S indicate mixtures of these two components. When the temperature of the system decreases, demixing of the homogeneous solution will take place when the binodal is reached. Furthermore, the homogeneous solution will demix into two phases, and this is referred to as liquid–liquid demixing. Thus, if a homogeneous solution mixture of the composition Xp, at a temperature T_1, as represented by the point A (Fig. 7), is cooled to the temperature T_2, as represented by point B, and lies inside demixing (miscibility) gap, it is not stable thermodynamically, and will separate into two different phases, the composition of which are represented by the points B′ and B′′. The point B′ shows the (polymer-rich, solvent-poor) solid phase and the point B′′ shows the (solvent-rich, polymer-poor) liquid phase. The lines B′–B and B′′–B represent the ratio of the amounts of the two phases in the mixture, that is, the overall porosity of the obtained microporous system.
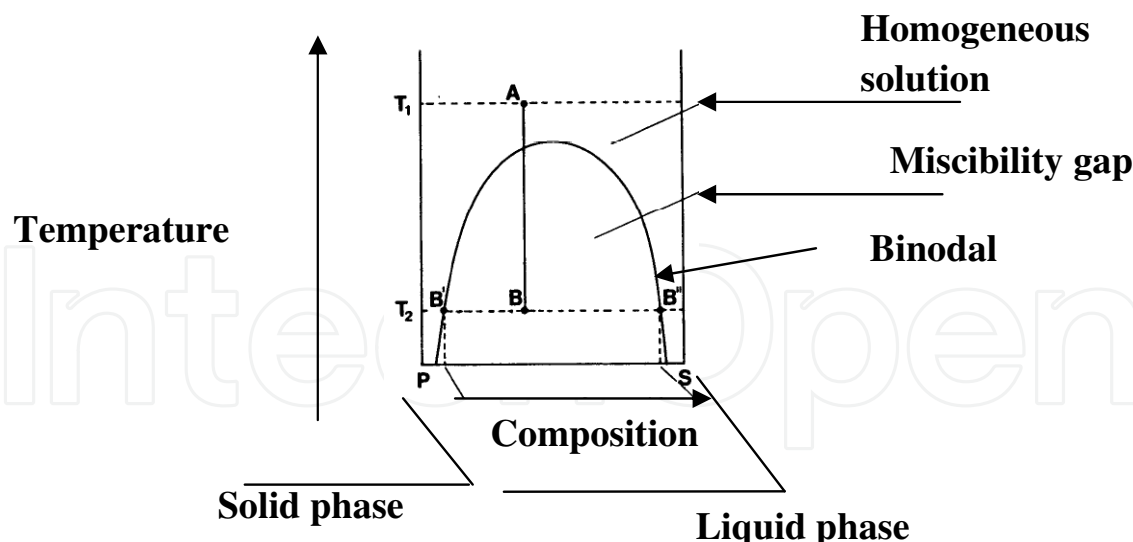
Figure 7. Formation of a microporous system by thermal gelation of a binary (two-component) mixture exhibiting a miscibility gap at certain conditions of temperature and composition, adapted from [2, 32].

4.6. Phase inversion process and ternary phase diagram

In fact, the polymeric membrane preparation usually involves the phase inversion process, in which a homogeneous casting polymer solution induces phase separation into a polymer-rich phase and a polymer-poor phase by the exchange of solvent with nonsolvent in a coagulation bath (i.e, as water bath). Phase separation would continue to form the membrane structure until the polymer-rich phase is solidified. Solidification during phase inversion could be induced by gelation and/or crystallization of the casted polymer solution. The equilibrium ternary phase diagram system is still a good tool for controlling the morphology and inter-preting the membrane structure. Significantly, knowledge of phase equilibria (cloud points, binodals, spinodals, and critical compositions) enables one to change the conditions for the preparation of membranes, such as the compositions of the casting solution, temperature, and coagulation bath type to obtain an optimum membrane structure. The phase diagram has an important role to report the agreement between experimental work in order to get the required membranes, and the ternary phase diagram miscibility gaps for the evaluations of membrane-forming system. In the ternary phase diagram (polymer (p)/solvent (s)/nonsolvent (ns)), a miscibility gap with metastable regions exists. According to the theory of phase separation, three modes of phase separation can take place in such ternary system: nucleation and growth of the polymer-lean phase, spinodal phase separation, and nucleation and growth of the polymer-rich phase. Since polymer is one of the components of the ternary system, solidifica-tion of a part of the system can take place. Phase inversion process (phase separation process) is the most important technique used to prepare both asymmetric and symmetric polymeric membranes. In addition, the morphology and performance of membranes depend on their effects [33], which also depend on the membrane preparation process parameters. From a thermodynamic point of view, study on polymer–solvent–nonsolvent system can be well depicted in a ternary phase diagram, as illustrated in Fig. 8. The Flory-Huggins theory [34]

was found to be a convenient and useful framework for the thermodynamic analysis of component mixing in a membrane preparation system.

The systems include a mixture of ternary components: a polymer, a solvent, and a third component, which may be a nonsolvent. This ternary system is completely miscible over a certain composition range but shows a miscibility gap over another composition range, as shown in Fig. 8, which shows an isothermal phase diagram of the ternary components. The pure components are represented at the corners of the triangle, while the boundary lines between any two corners of triangle represent mixtures of two components, and any point inside the triangle diagram represents a mixture of all three components. The main elements of ternary phase diagram are binodal and spinodal curves, a critical point, tie lines, and a glassy region shown in Fig. 8. For the studied ternary system, the interaction parameters evaluated for the binary mixture allowed a remarkably accurate prediction of the ternary phase diagram.
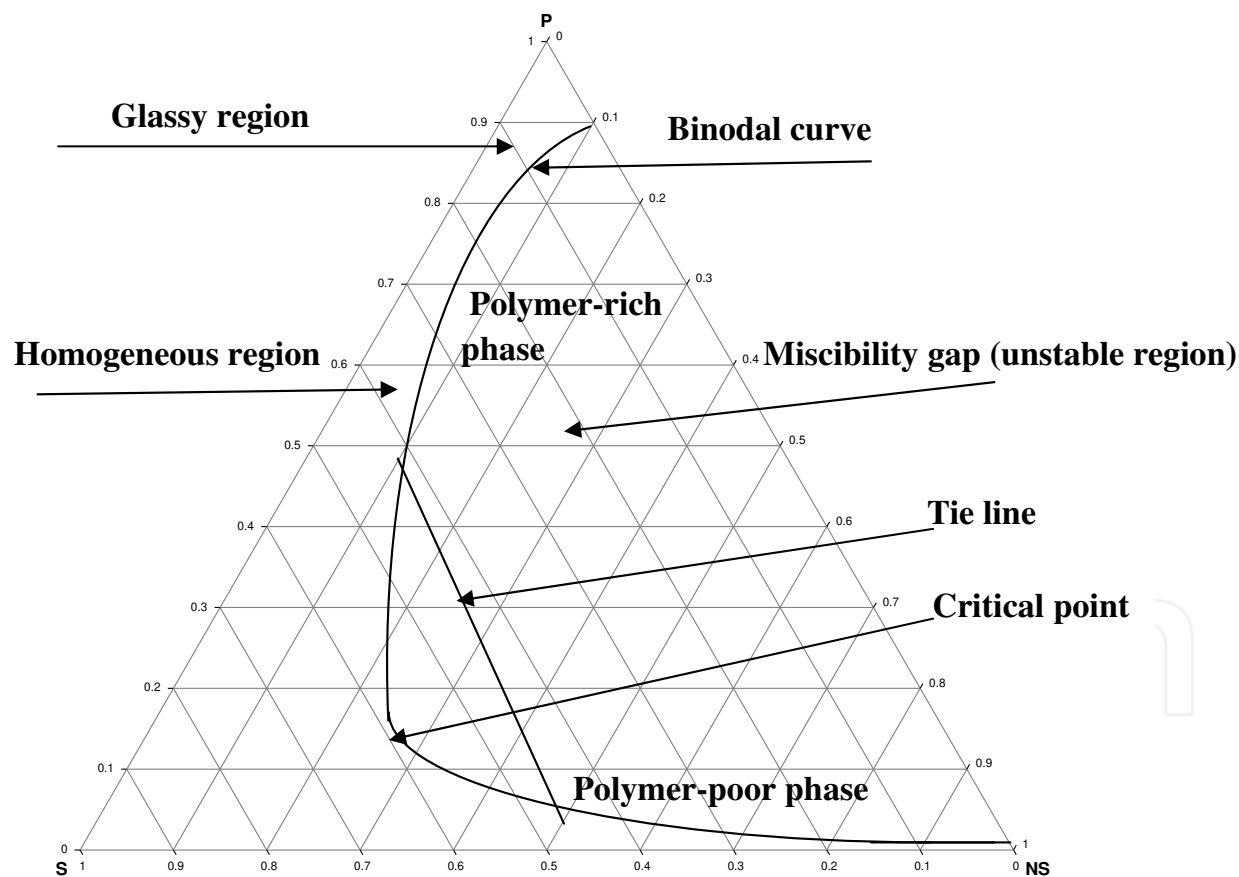
Figure 8. Ternary-phase diagram of polymer (P)–solvent(S)–nonsolvent (NS) system.

If a nonsolvent (such as water) is added to a homogeneous solution consisting of binary mixture of polymer and solvent [2, 32], the membrane casting solution composition is repre-

sented by the point A as shown in Fig. 9. Thus, if the solvent is removed from the polymer solution (this takes place by immersion precipitation), the composition of the casting solution mixture will change to follow the line A–B. At point C, the composition of the yield system will reach the demixing gap, and therefore two produced phases will start to form a polymer-rich phase at the upper boundary of the demixing gap and a polymer-poor phase at the lower boundary of the demixing gap. The polymer concentration in the polymer-rich phase will be high enough to be considered as solid; this occurs at a certain composition of the ternary mixtures, which is represented by point D in Fig. 9. At this point, the membrane structure is more or less formed. Further exchange of solvent and nonsolvent will lead to the final composition of the membrane, the porosity of which is determined by point B (pore fraction = (56/90) = 59.8%). Point B represents a mixture of the solid polymer-rich phase and the liquid solvent-rich phase as represented by points B1 and B2, respectively.

The main important step for membrane formation from such ternary systems is always to prepare a homogeneous polymer solution (thermodynamically stable). This will often represent a point on the polymer/solvent axis as point A in Fig. 9. However, it is also possible to add nonsolvent to such a binary mixture that all the polymer solution components are still miscible (homogeneous region) before the binodal curve is reached.

4.7. Demixing types in a ternary system [35]

In a ternary system consisting of a polymer/solvent/nonsolvent, changes in composition can cause demixing (Fig. 9). The demixing types that can be occurring are as follows:

a. Liquid–liquid phase separation

The addition of such an amount of nonsolvent can induce demixing process when the polymer solution becomes thermodynamically unstable (Fig. 9). When the binodal is reached, liquid–liquid demixing will take place. Free enthalpy of the polymer solution decreases by separating into two liquid equilibrium phases. Demixing can take place by two ways: (1) nucleation and growth of droplets of the second phase and (2) instantaneous spinodal demixing. The composition area surrounds the spinodal demixing gap where phase separation (inversion) by nucleation and growth occurs.

b. Crystallization or gelation

As a matter of fact, many polymers are partially crystalline. Crystallization can take place if the temperature of the solution is lower than the melting point of the polymer. Gelation is a considerable important phenomenon during membrane preparation to form the skin layer (top layer) [1, 2, 32]. When gelation takes place, a dilute or more viscous polymer solution is transformed into a system of infinite viscosity, i.e. a gel. As demixing starts, the free enthalpy of the solution is decreased by polymer molecules to form ordered structures. On the one hand, single crystals can be formed at low polymer concentrations. On the other hand, at higher concentrations of polymer, very small crystalline regions could work as physical crosslink between the polymer molecules and the result is a thermoreversible gel.
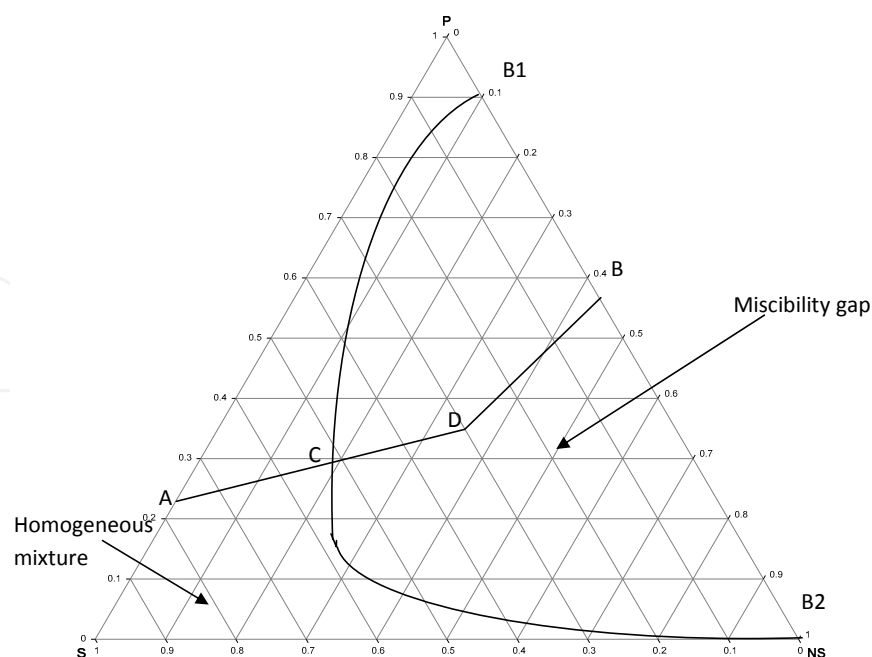
Figure 9. Formation of a microporous system by the addition of a nonsolvent to a homogeneous polymer solution in a ternary mixture exhibiting a miscibility gap at certain conditions of temperature and composition (P, polymer; S, solvent; NS, nonsolvent) [2, 32].

4.8. Mechanism of formation skin top layer and porous sublayer

4.8.1. Mechanism of formation asymmetric membrane [36, 37]

In the phase inversion process induced by immersion precipitation, a polymer casting solution, cast on a support (i.e, glass, Teflon), is immersed in a coagulation bath containing a nonsolvent (as water). The solvent moves from polymer solution to nonsolvent while the nonsolvent penetrates the casted polymer solution.

The mechanism of membrane formation has been reported by some researchers. On the one hand, C. Smolders et al. [38] suggested that the porosity of the sublayer (bottom layer) proves to be liquid–liquid phase separation while the formation of pores may be ascribed to nucleation and growth of the dilute polymer phase. On the other hand, Koenhen et al. [39] suggested that the mechanism for the formation of the sponge-like structure can be ascribed to liquid–liquid phase separation with nucleation and growth of the diluted polymer phase. Furthermore, Bokhorst et al. [40] studied the formation of asymmetric cellulose acetate membranes and reported that the top layer is formed by gelation while liquid–liquid phase separation forms the sublayer of the membrane.

Hence, the skin layer (top layer) is formed by gelation and the porous sublayer (bottom layer) is the result of liquid–liquid phase separation by nucleation and growth. On the one hand, the factor which is determining the type of phase inversion at any point in the cast sheet is the local polymer concentration at the moment of precipitation. On the other hand, in the first split second after immersion in the coagulation bath, there is a fast depletion of solvent from the

casted film and a relatively small penetration of nonsolvent. Thus, this means that the concentration of polymer in the film/bath interface increases, which crosses the gel boundary (transition H to G in Fig. 10). The thin and dense gel-layer which is induced by this way will work as a resistance to solvent out-diffusion and at positions beneath the skin layer (top layer). At lower polymer and higher nonsolvent concentrations, demixing process will take place. Thus, the type of demixing process in that case will be liquid–liquid phase separation (transition H to L in Fig. 10). At the end of the process, the demixing gap is entered at the polymer-rich side of the critical point (CP), so the nuclei consist of the polymer-poor phase, and a porous sublayer structure is formed, the pores of which are filled with the dilute solvent/nonsolvent phase.
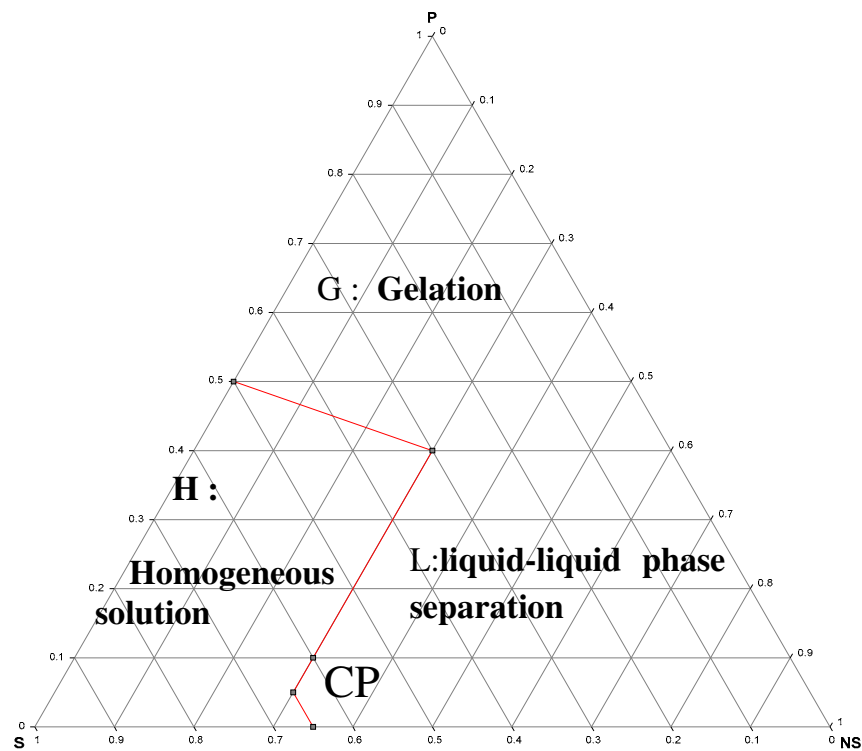
Figure 10. Mechanism of formation of asymmetric membrane, ternary phase diagram containing P, polymer; S, solvent; NS, nonsolvent; CP, critical point; G, gelation (gel region); L, liquid–liquid phase separation(two phase region); H, homogeneous solution (one phase region) [41, 42].

4.8.2. Mechanism of formation symmetric microporous membrane

Conversely to the case of precipitation from the vapor phase, the casted polymer solution, in this case, is in contact directly with a nonsolvent vapor phase. In addition, the nonsolvent vapor phase is saturated with the solvent used. On the one hand, in this process, there is no solvent outflow from polymer casted solution but only a nonsolvent inflow to polymer casted solution. On the other hand, the only possible demixing mechanism is liquid–liquid phase separation to form symmetric microporous membrane without a dense top layer. The change of composition in the casted film is illustrated in Fig. 11 (transition D to E).
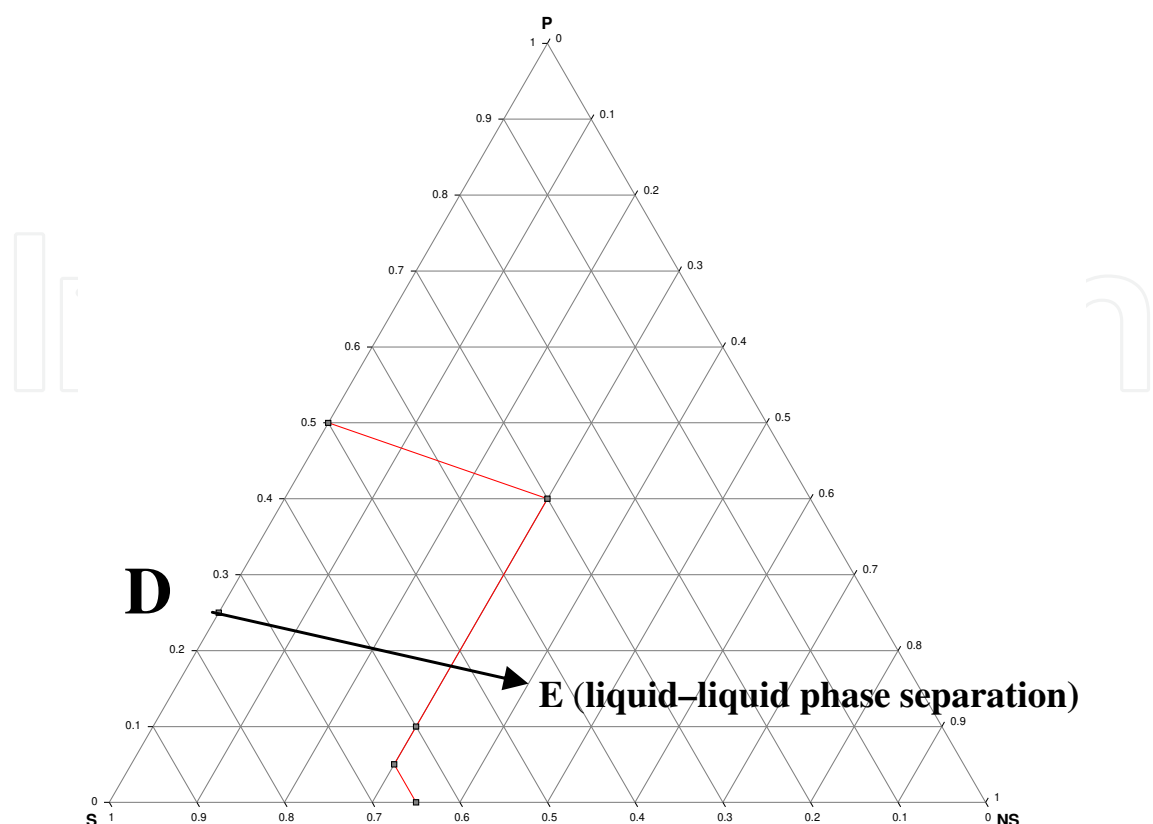
Figure 11. Formation symmetric microporous membrane of a polymer film with initial composition D when brought in contact with a nonsolvent vapor phase saturated with solvent [39–41].

4.9. Effect of some parameters on membrane morphology [43]

In this section, the influence of some parameters on membrane morphology will be described. It is known that there are two different types of membranes can be obtained, asymmetric membranes (i.e., reverse osmosis, nanofiltration, and ultrafiltration) and symmetrical membranes (i.e., dense membrane), depending on the type of formation mechanism, i.e. instantaneous demixing or delayed onset of demixing.

It is obvious that the kinetics of phase separation during the immersion of a polymer/solvent mixture in a nonsolvent bath plays a major role in the control of membrane morphology [44]. The accelerated rate of phase separation due to the addition of nonsolvent additive may be restricted in the rearrangement of polymer aggregates, resulting in the formation of membrane with small macrovoids. Surface properties of membranes can be controlled depending on the casting conditions, polymer solution, and coagulation bath temperature and compositions [2, 32].

The following factors will be described in this section:

- Choice of solvent/nonsolvent (coagulant)systems
- Polymer concentration

- Effect of bath temperature

There are a number of other parameters, in addition to those listed, which will not be considered here.

4.9.1. Solvent/nonsolvent effect

In order to obtain an optimal membrane structure, an additive or cosolvent is frequently used. The addition of a fourth component to a casting solution or a nonsolvent coagulant bath is an important method used in membrane modification. Many researchers studied the effects of additive materials in a coagulation bath with other factors, which can influence membrane formation.

The choice of solvent/nonsolvent is one of the main variables in the wet-phase inversion process which is influenced by the membrane formation. Generally, the membrane morphology can be characterized by scanning electron microscopy (SEM). In the case of delayed liquid–liquid demixing, a sponge-like structure can be formed, and in the case of instantaneous demixing, finger-like structure can be formed [1, 2, 32]. Generally, in the case of higher affinity between the solvent and coagulant, however, instantaneous demixing process takes place, but for a lower affinity between the solvent and coagulant, the delayed demixing process takes place [2, 32].

By addition of cosolvent to polymer/solvent solution with low-affinity coagulant, the polymer solution system will be shifted from instantaneous demixing to delayed demixing process. This is due to the lower affinity of cosolvent with coagulant than solvent. In the case of delayed demixing, a dense skin layer is formed; this inhibits the inflow of nonsolvent (water) into the polymer solution. Further, in the case of delayed demixing, the number and the size of nuclei of polymer-poor phase become smaller. Therefore, macrovoids significantly disappear. By increasing the amount of cosolvent, the numbers of macrovoids become smaller, and the top layer shows a very packed and dense shape. When the ratio of cosolvent to solvent is increased, almost all the macrovoids disappear and the spongy structure starts formation. Without the addition of cosolvent, large fingers are formed because of instantaneous demixing and the upper part of the membrane is porous.

Water-miscible solvent (wms) and water-immiscible solvents (wis) can be used in the casting solution in order to prepare asymmetric membranes. Because (wis) is immiscible with water, it is left in the membrane after coagulation and can further modify the membrane structure through its solvency power.

Kim et al. [45] developed the formation of integrally skinned asymmetric polyetherimide nanofiltration membranes by phase inversion process and showed that the polymer solution system is shifted from instantaneous demixing to delayed-demixing process. This is due to the lower affinity of 1, 4-dioxane (cosolvent) with water (nonsolvent) than DMF (solvent). By increasing the amount of 1, 4-dioxane, the number of macrovoids became smaller and the top layer shows a very packed and dense shape. Without the addition of 1, 4-dioxane, large fingers

were formed because of instantaneous demixing and the upper part of the membrane was porous.

Shieh et al. [46] studied the preparation of polyetherimide membranes from water-miscible/immiscible mixture solvents and reported that the PEI/NMP/H$_2$O system exhibits an instantaneous liquid−liquid phase separation property, but the phase separation rate reduces with the addition of methlyene chloride (MC) into the casting solution. The decrease in the phase separation rate may be mainly due to the difference in solubility parameters; water is 47.9 (MPa)$^{1/2}$, while MC is 19.8 (MPa)$^{1/2}$. The elongated macrovoids diminish gradually as the MC content increases, and no macrovoids are formed when the MC content is 30 wt% in the casting solution.

4.9.2. Effect of Immersion Bath Temperature (IBT)

Immersion bath temperature is an important parameter in membrane morphology and performance. It was found that with asymmetric membranes, the porosity increases with the increase of the immersion bath temperature [47]. Raising the temperature increases mutual diffusivities between the nonsolvent (as water) and the solvent (as DMF) in the casting solution during demixing process. In addition, in the former case, the increase of coagulation bath temperature [48] rises the speed of nucleus growth of polymer-poor phase, that is, increases the formation of porous structure in the membrane. Conversely, in the latter case, at the reduction of the temperature, the speed of nucleus growth is limited and the formation of a large number of small nucleuses is increased, so a great number of pores/voids are formed in the bottom layer of the asymmetric membranes. Therefore, the formation of macrovoids is prevented and denser membrane structures are obtained.

Kim et al. [42] prepared skinned asymmetric polyetherimide nanofiltration membranes by phase inversion process and reported that light transmittance of experiment showed an increase with coagulation bath temperature; demixing of the casting solution was gradually shifted from delayed demixing to instantaneous demixing. When the casting solution [PEI/DMF/1, 4-dioxane (16/28/56)] was coagulated at the temperature of 25°C, porous spongy-like structure was formed. However, lower coagulation temperature (<10 °C) makes the membrane structure dense spongy.

4.9.3. Effect of polymer concentration

Generally, increasing polymer concentrations in the casting solution slows down the demixing process, leads to a much higher polymer concentration at the interface [49], and increases the thickness of the top layer and decreases the porosity of the membrane. The macrovoids formation will be diminished, and the pore size will decrease. Conversely, the reduction of the polymer concentration in the casting solution indeed leads to a more open and porous structure with large pores. Such a phenomenon has been reported in cellulose acetate/dimethyl sulfoxide/water [50] and Nomex/N, N-dimethylacetamide/water systems [51]. Furthermore, mechanical properties of the membranes prepared with a low polymer concentration are lower than for a membrane prepared with a high polymer concentration.

5. Process block flow diagram for membrane desalination

Fortunately, there are different types of membranes which can be used for membrane desalination by using different technologies such as (RO), (MD), and (FO). In this section, major emphasis is placed on the preparation of membrane distillation (MD) and reverse osmosis (RO) via phase inversion process.

5.1. Membrane Distillation (MD)

Membrane distillation is a thermal, vapor-driven transportation process through microporous and hydrophobic membranes. It is a low-cost membrane separation technology and energy-saving process. Membrane distillation (MD) is generally used to remove water from aqueous solutions of inorganic solutes. In this field, desalination is the best-known MD application. The main membrane materials for membrane distillation are typically prepared from polytetra-fluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene, polypropylene (PP), and polyether sulphone (PES). The process block flow diagrams for the preparation of MD from these materials are presented in Figs. 12–18.
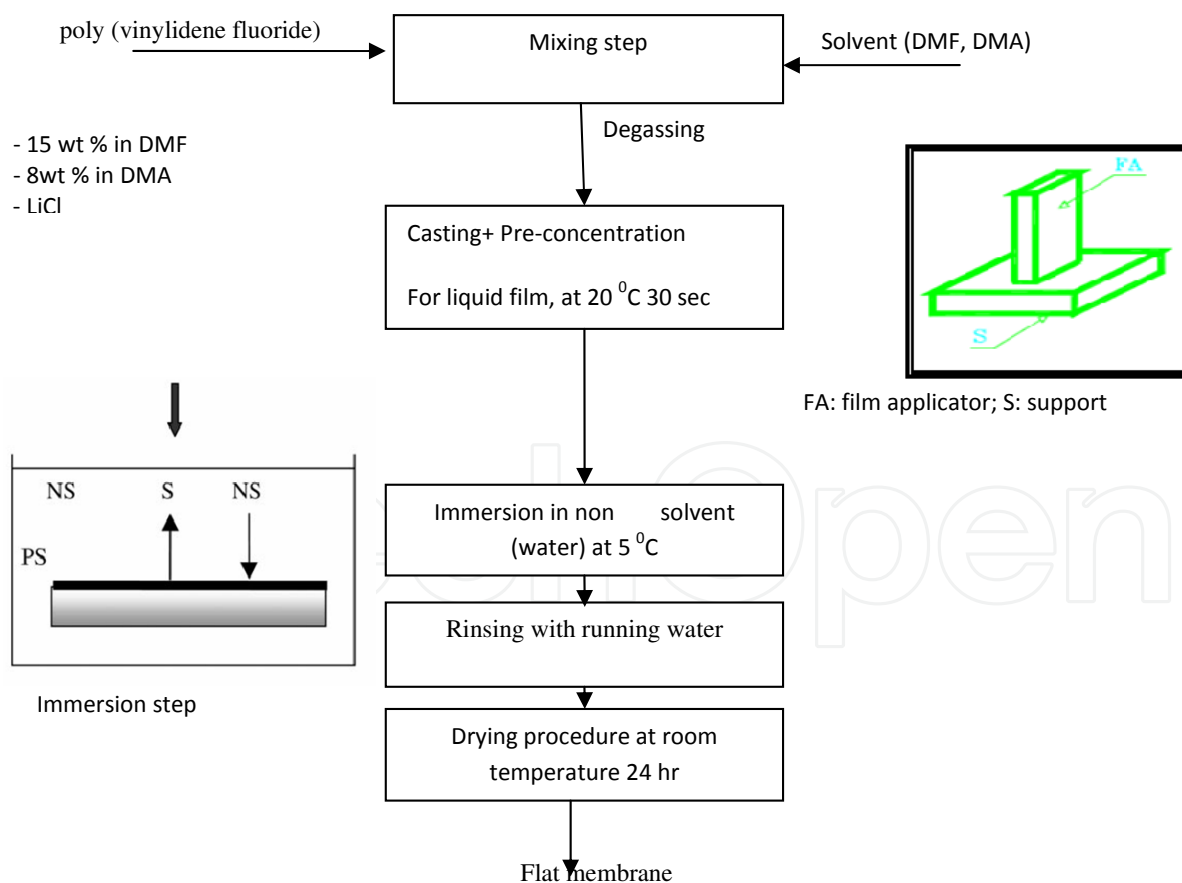
Figure 12. Process flow sheet for the preparation of PVDF membranes for desalination by direct contact membrane distillation [52].
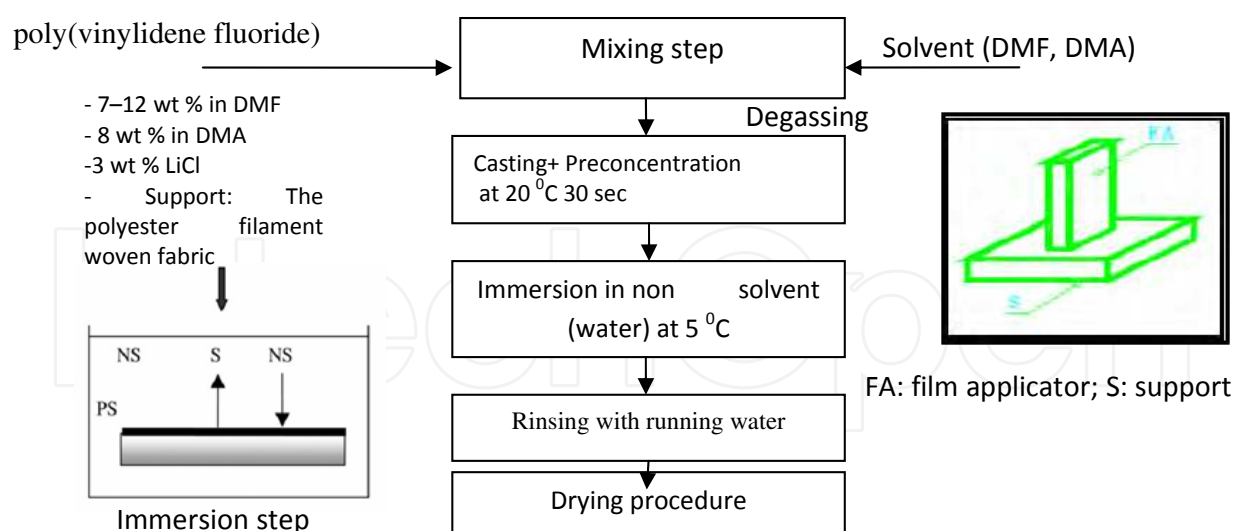
Figure 13. Process flow sheet for the preparation of PVDF membranes for desalination by direct contact membrane distillation [53].
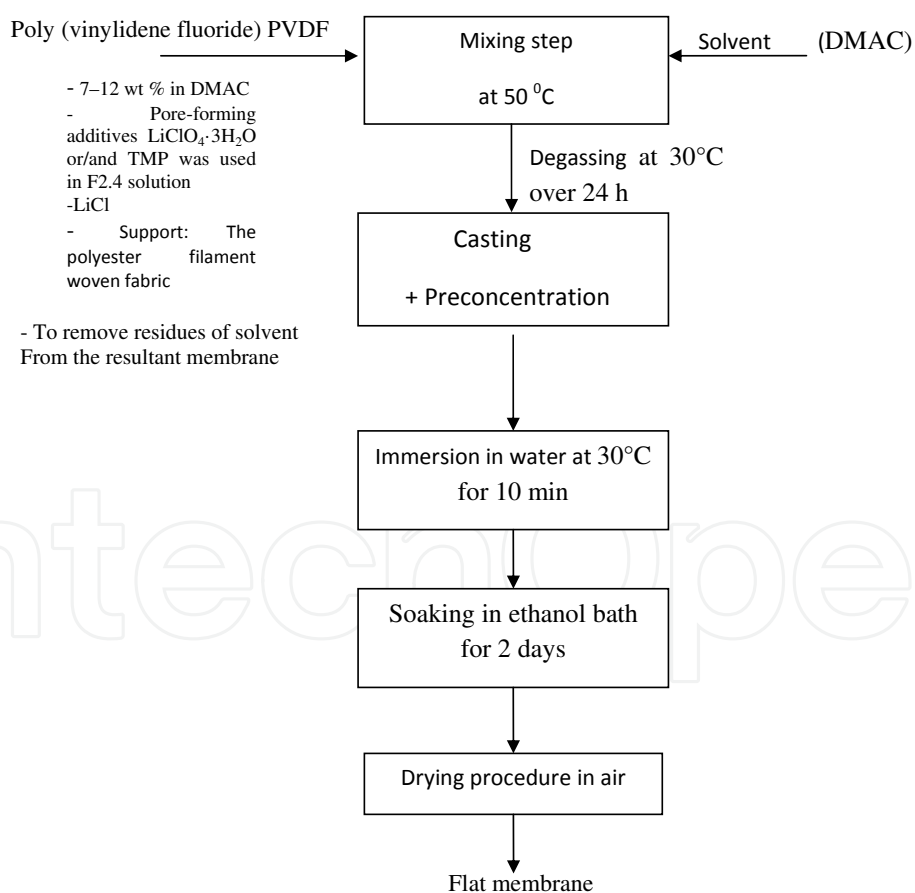
Figure 14. Process flow sheet for the preparation of PVDF membranes for desalination by direct contact membrane distillation [54].
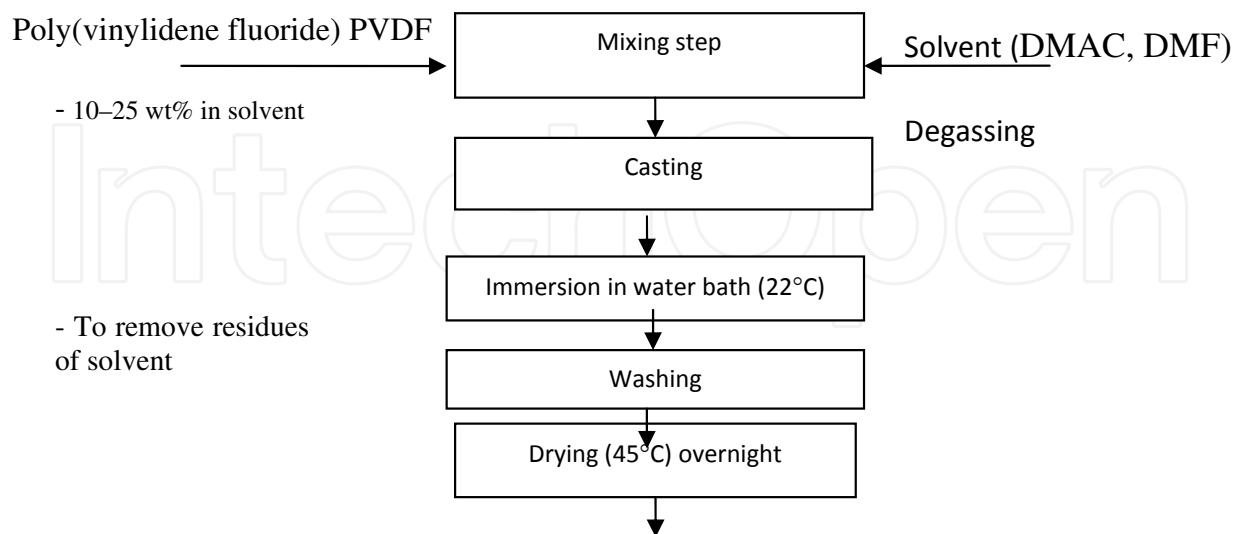
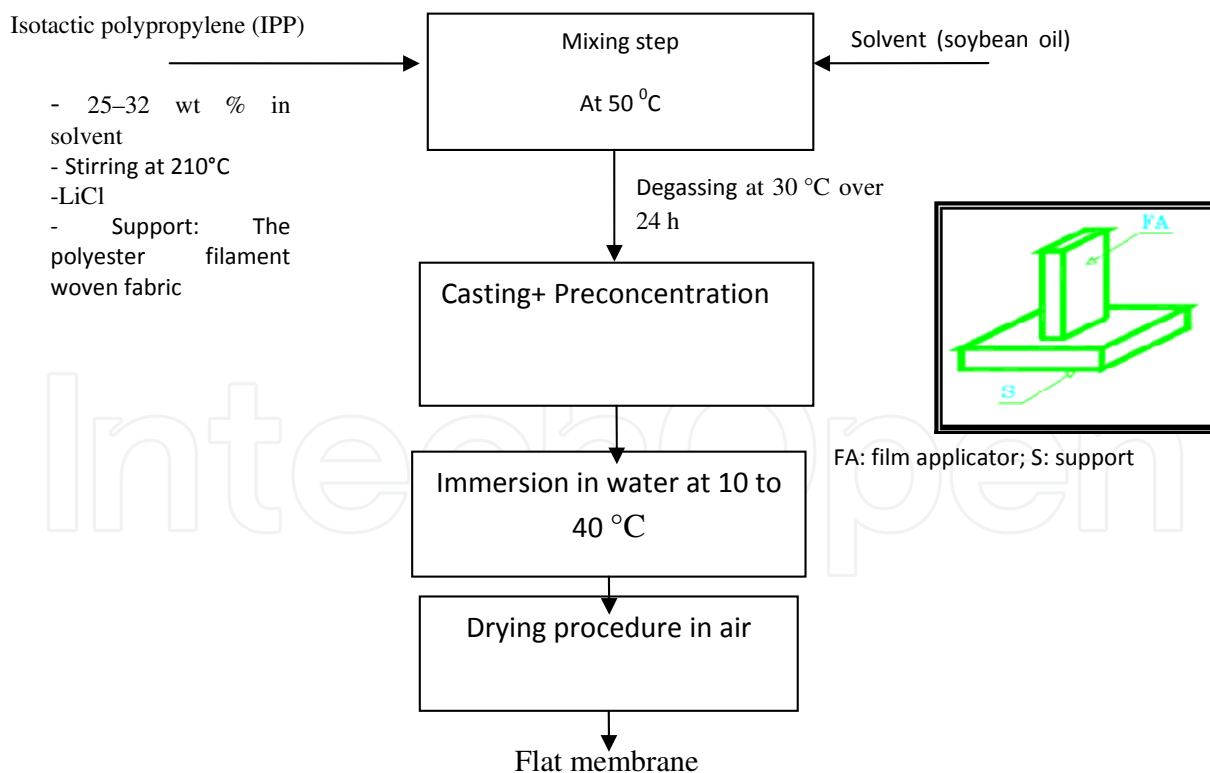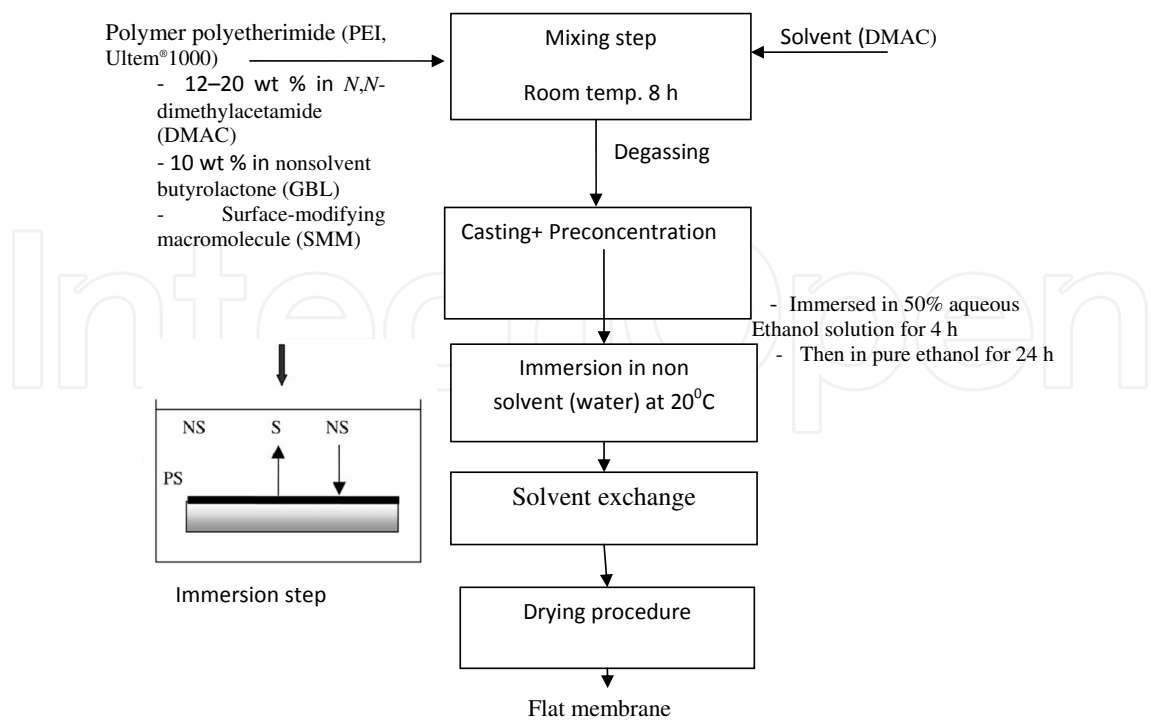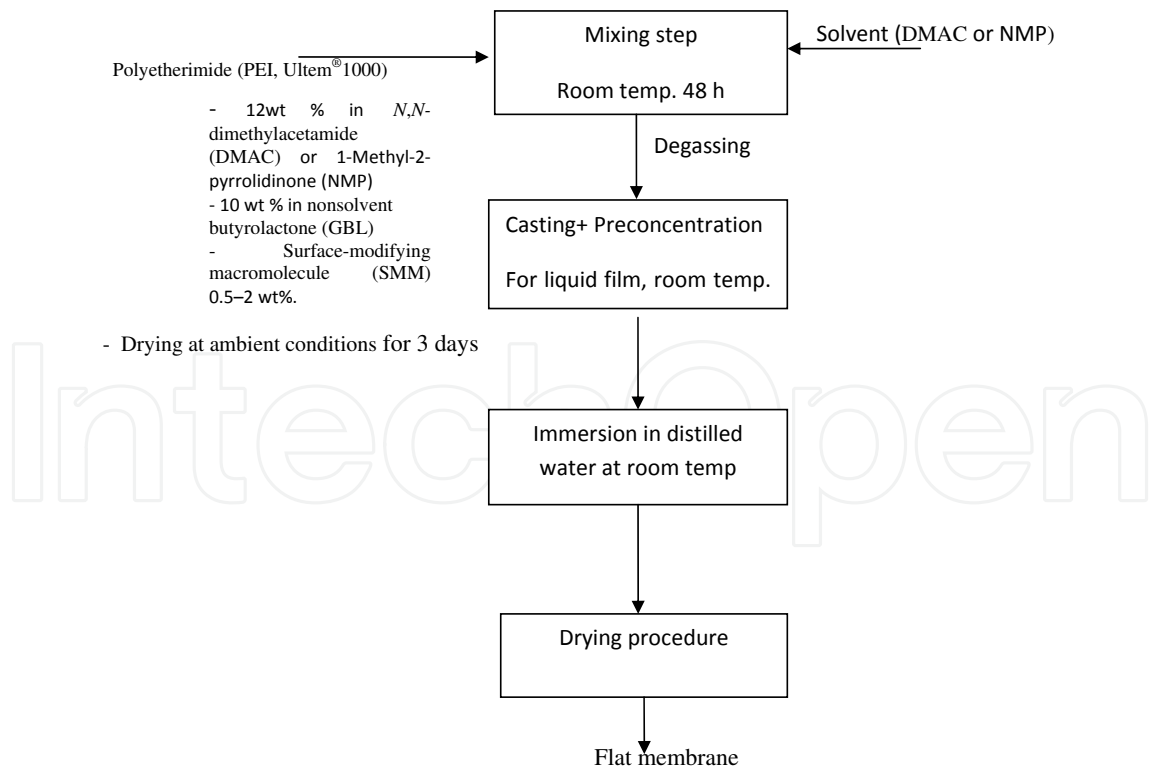**Figure 15.** Process block flow diagram for preparing PVDF membrane [55].

Figure 16. Process flow sheet for the preparation of isotactic polypropylene (IPP) membranes for desalination by direct contact membrane distillation [56].

Figure 17. Process flow sheet for the preparation of polyetherimide membranes by direct contact membrane distillation [57].

Figure 18. Process flow sheet for the preparation of PEI membranes for desalination by direct contact membrane distillation [58].

5.2. Process flow diagram for RO membrane preparation

The more useable membrane materials for RO are cellulose acetate, polyamide, polyimide, polybenzimidazole, polybenzimidazolone, sulfonated-PSF, and chitosan. The process block flow diagrams for the preparation RO membrane from some of these materials are presented in Figs. (19)–(30).
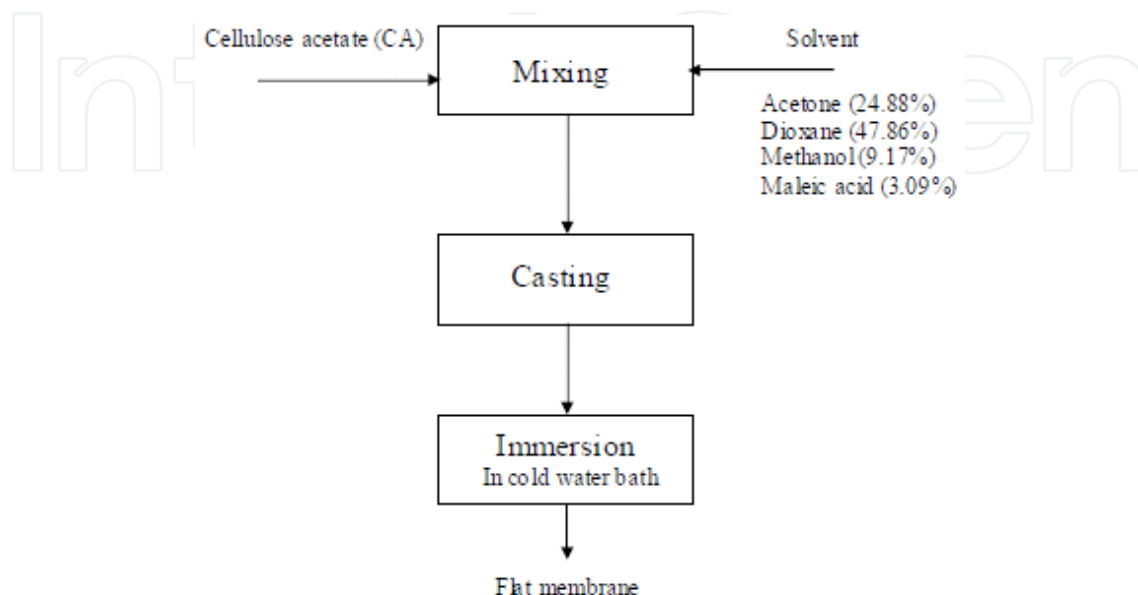
Figure 19. Process block flow diagram for preparing CA membrane [59].
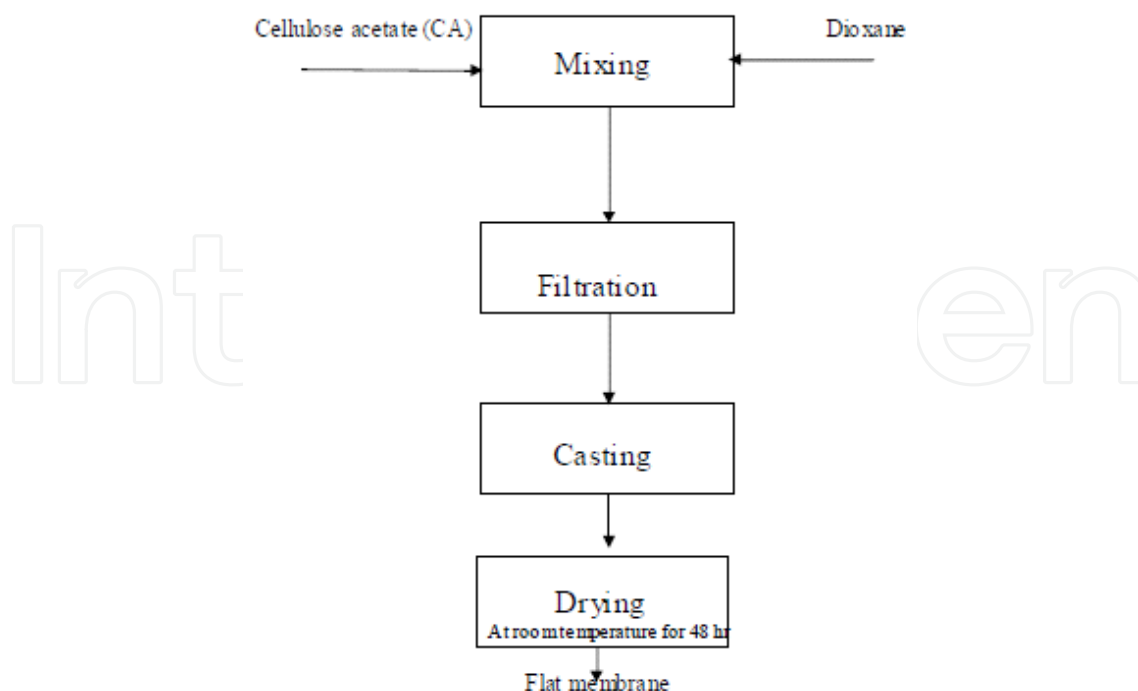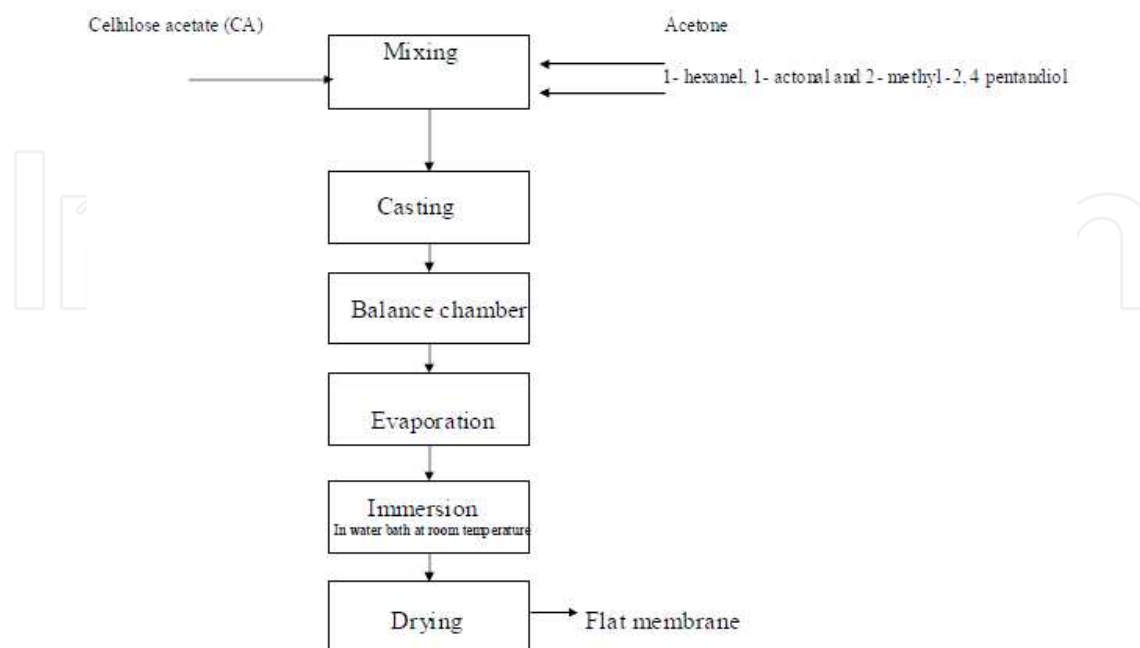
Figure 20. Process block flow diagram for preparing CA membrane [60].

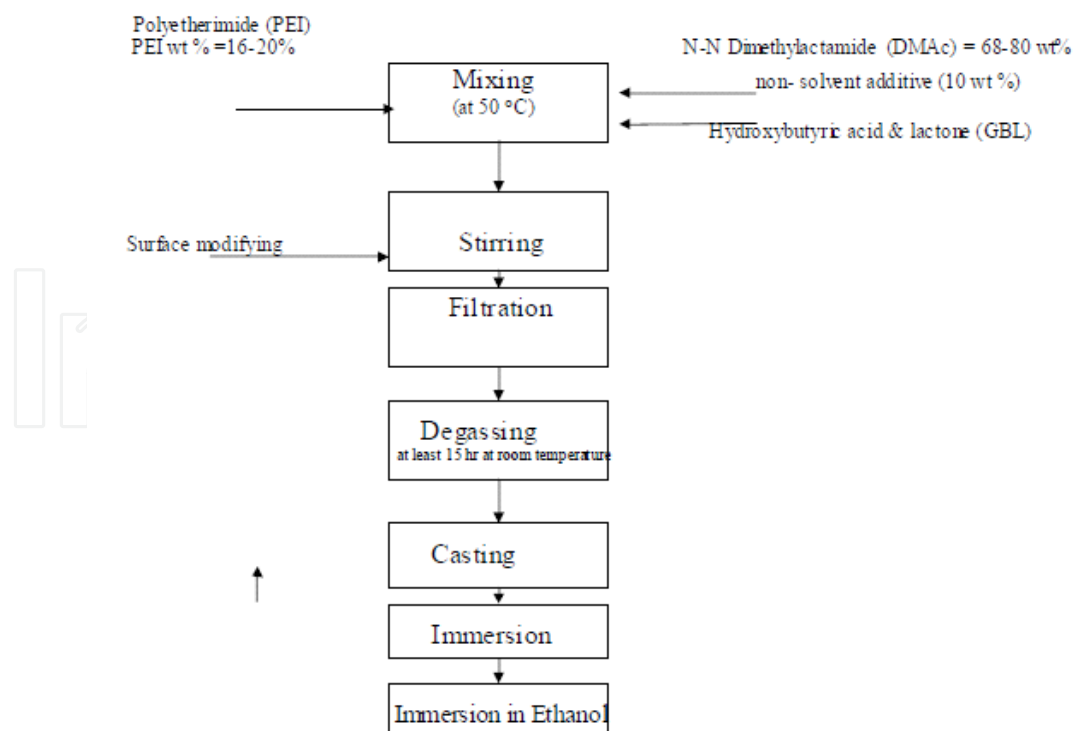**Figure 21.** Process block flow diagram for preparing CA membrane [61].

Figure 22. Process block flow diagram for preparing PEI membrane [62].
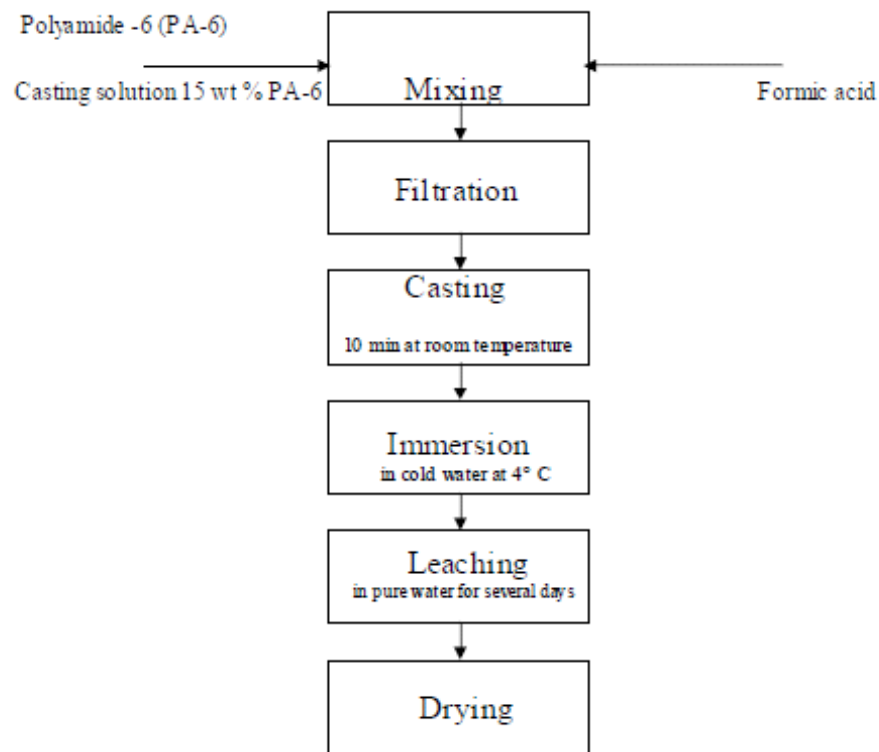
Figure 23. Process block flow diagram for preparing PA-6 membrane [63].
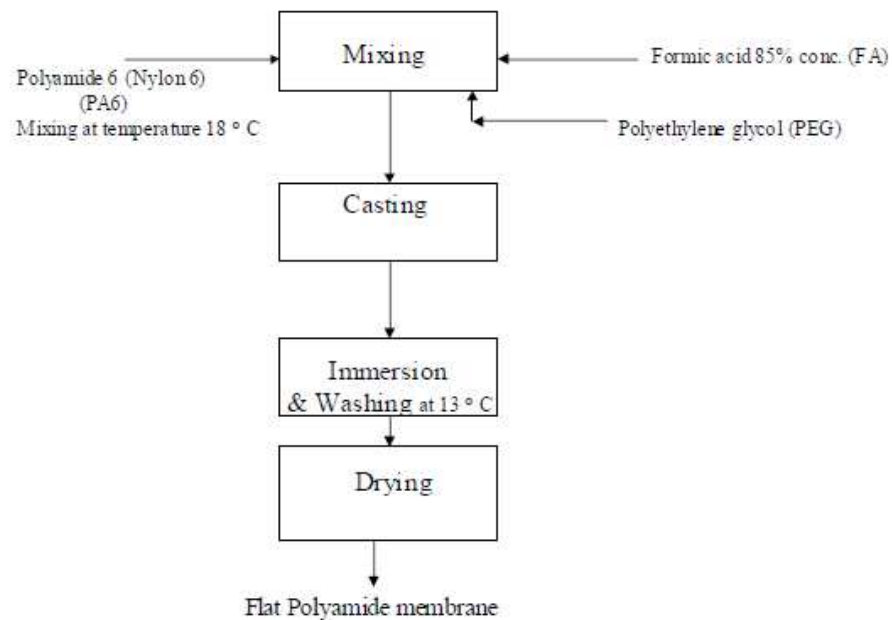

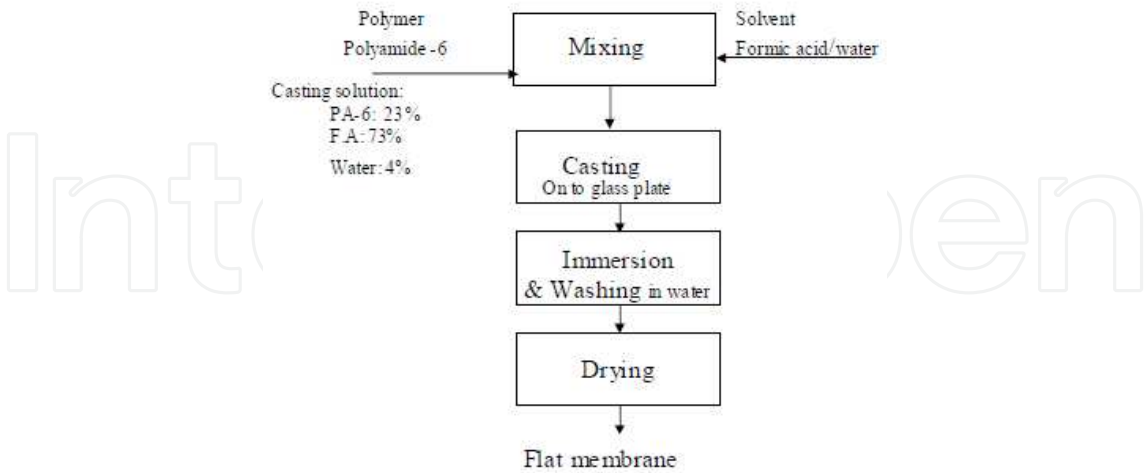**Figure 24.** Process block flow diagram for preparing polyamide membrane [64].

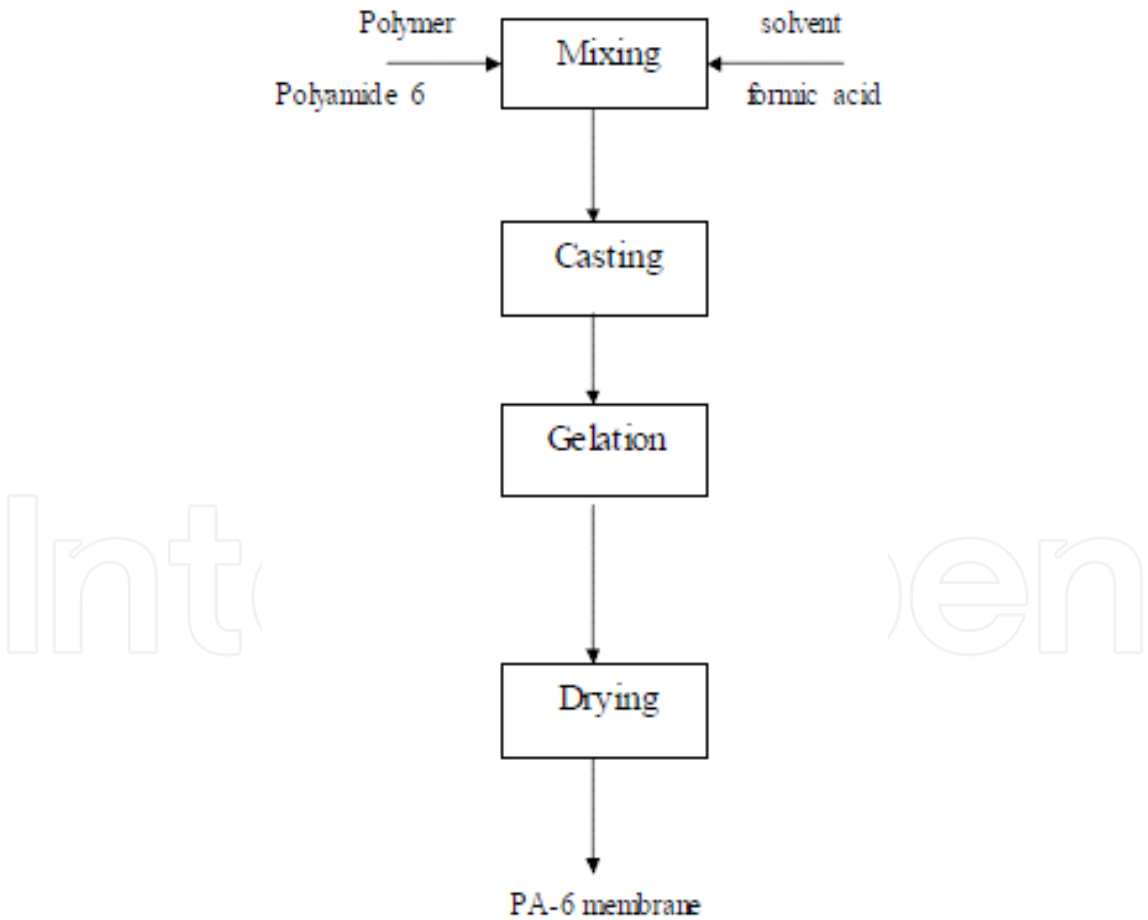**Figure 25.** Process block flow diagram for preparing PA-6 membrane [65].

Figure 26. Process block flow diagram for preparing PA-6 membrane [66].
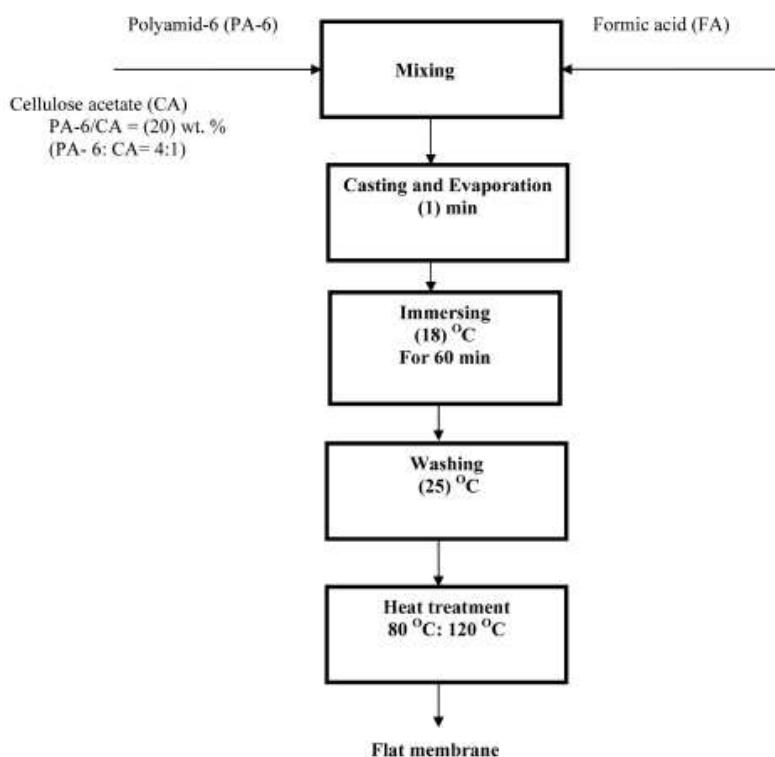
Figure 27. Process block flow diagram for preparing PA- 6/CA membrane [67].
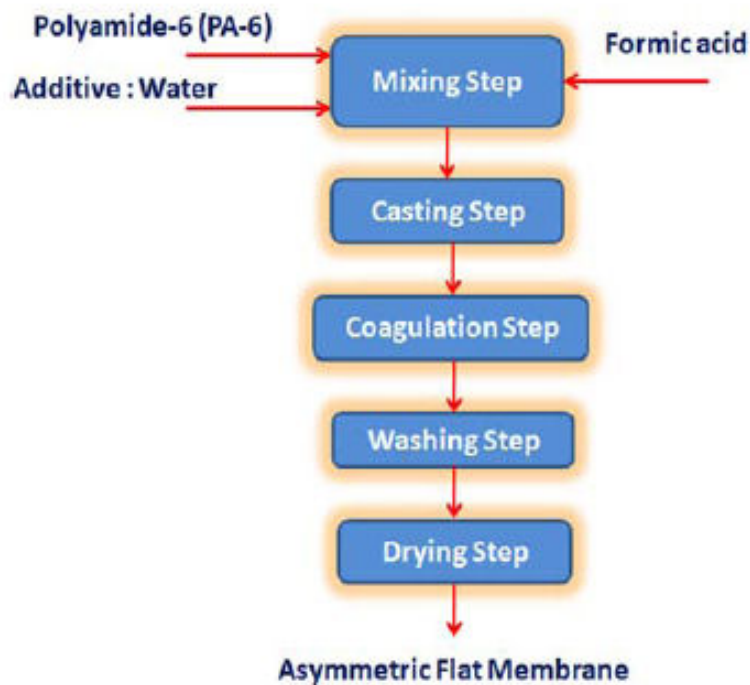

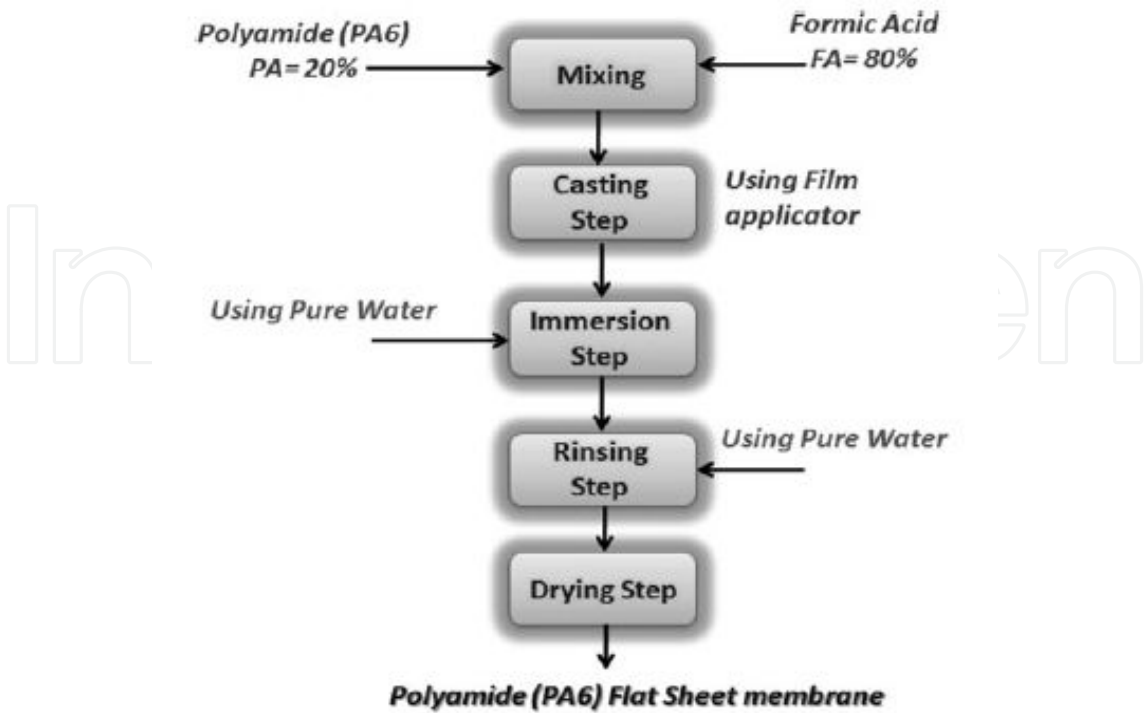**Figure 28.** Process block flow diagram for preparing PA-6 membrane [68].

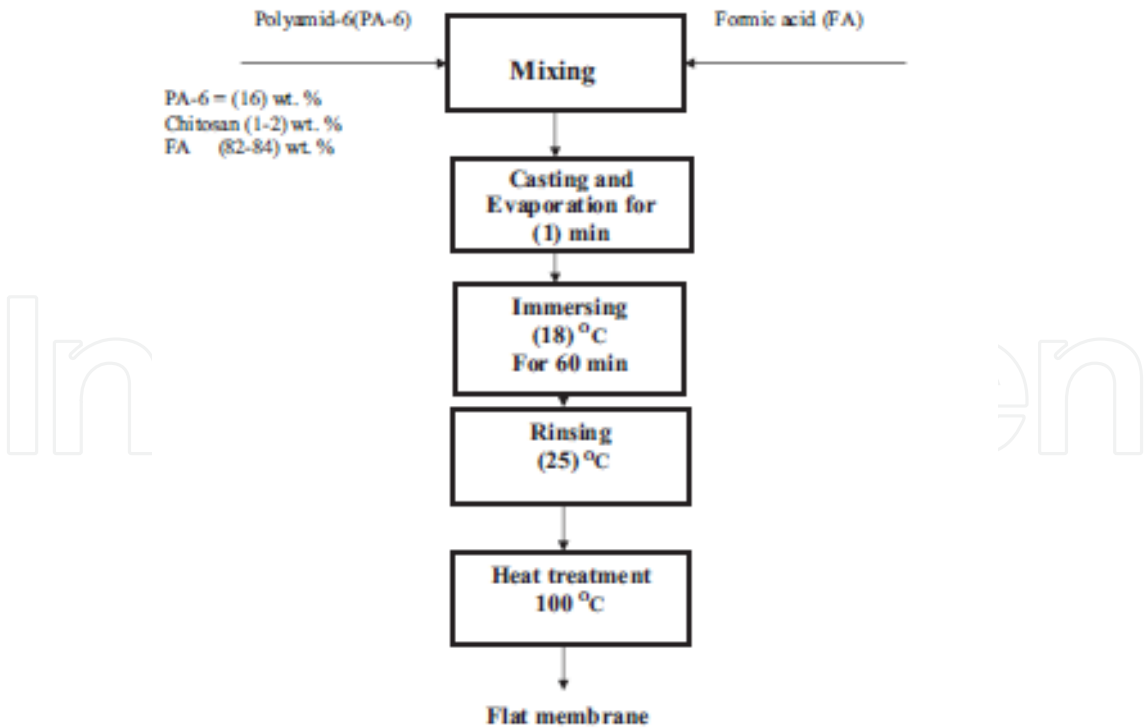**Figure 29.** Process block flow diagram for preparing PA-6 membrane [69].

Figure 30. Process block flow diagram for preparing PA-6/Chitosan membrane [70].

6. Conclusion

The preparations of desalination membranes usually involve the phase inversion process, in which a homogeneous casting solution induces phase separation into a polymer-rich phase and a polymer-poor phase by the exchange of solvent with nonsolvent in a coagulation bath. Phase inversion process is the most important technique used to prepare both asymmetric and symmetric polymeric membranes. From a thermodynamic point of view, study on polymer–solvent–nonsolvent system can be well depicted in a ternary phase diagram. The Flory-Huggins theory was found to be a convenient and useful framework for the thermodynamic analysis of component mixing in a membrane preparation system.

In fact, the equilibrium ternary phase diagram system is still a good tool for controlling the membrane morphology and interpreting the membrane structure to be suitable for the required application such as membrane desalination. Significantly, knowledge of phase equilibria (cloud points, binodals, spinodals, and critical compositions) enables one to change the conditions for the preparation of membranes such as the compositions of the casting solution, temperature, and coagulation bath type to obtain an optimum membrane structure. The phase diagram has an important role to report the agreement between experimental work in order to get the required membranes, and the ternary phase diagram miscibility gaps for the evaluations of membrane-forming system.

Nomenclature

DSI	Desalination Systems, Inc.
MD	Membrane distillation
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse osmosis
FO	Forward osmosis
PV	Pervaporation
GS	Gas separation
NMP	N-methyl-2-pyrrolidone
SEM	Scanning electron microscopy
DMF	N, N-Dimethylformamide
TFC	Thin-film composite membranes
TGA	Thermogravimetric analysis

SEIP	Solvent exchange immersion precipitation
CA	Cellulose acetate
PMDA	Pyromellic dianhydride
PASA	Poly (amidesulfonamide)
PEAH	Polyetheramide hydrazide
PEG	Polyethylene glycol
PI	Aromatic polyimides such as Kapton™
PEI	Polyetherimide
PPSS	Poly (phenylene sulfide sulfone)
PES	Polyether sulfone
PS	Polysulfone
PTMSP	Poly (1-trimethylsilyl-1-propyne)
PVA	Polyvinyl alcohol
PVDF	Polyvinylidenedifluoride
PA	Propionic acid
PA-6	Polyamide-6
PABH	p-Amino benzhydrazide
PAH	Polyamide hydrazides
PAN	Polyacrylonitrile
PP	Polypropylene
PPO	Polyphenyleneoxide
PTFE	Teflon (polytetrafluoro ethylene)
PVAC	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
ZrO_2	Zirconium oxide

Author details

Ayman Taha Abd El-aziem El-gendi

Address all correspondence to: aymantaha2010@yahoo.com

Chemical Engineering & Pilot Plant Department Engineering Research Division, National Research Centre El-Bohouth St., Dokki, Cairo, Egypt

References

[1] Zydney A L., Zeman L J. Microfiltration and ultrafiltration: principles and applications. New York: CRC. ISBN 0-8247-9735-3; 1996.

[2] Mark C P. Handbook of Industrial Membrane Technology. Noyes Publications, Park Ridge, New Jersey, U.S.A; 1990, pp. 61–70.

[3] http://en.wikipedia.org/wiki/Membrane_(selective_barrier).

[4] Baker R W. Membrane Technology and Application. John Wiley & Sons, Ltd; 2004. ISBN: 0-470-85445-6.

[5] Scott K., Hughes R. Industrial Membrane Separation Technology. London: Blackie Academic & Professional, Springer; 1996. ISBN-13: 978-0751403381.

[6] Roudman R., DiGiano F. Surface energy of experimental and commercial nanofiltration membranes: Effects of wetting and natural organic matter fouling. J. Membr. Sci. 2000; 175 61–73.

[7] Inger L A., May B H. Pressure retarded osmosis and forward osmosis membranes: materials and methods, Polymers 2013; 5 303–327.

[8] Mohammad A., Ali N. Understanding the steric and charge contributions in NF membranes using increasing MWCO polyamide membranes. Desalination 2002; 147 205–212.

[9] Drewes J., Reinhard M., and Fox P. Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse. Water Res 2003;37 3612–3621.

[10] Wagner J. Membrane Filtration Handbook Practical Tips and Hints. Second Edition, Revision 2, Printed by Osmonics, November; 2001.

[11] Semiat R. Water International 2000; 25 54.

[12] Bednarski J., Minamide M., Morin O J. Proc., IDA World Congress on Desalination and Water Science, Madrid 1997; 1 227.

[13] Kronenberg G. Proc., IDA World Congress on Desalination and Water Science, Abu Dhabi 1995; 3 459.

[14] Spiegler K S., El-Sayed Y M. A Desalination Primer, Balaban Desalination 1994; 13.

[15] Matsuura T, Sourirajan S Physicochemical criteria for reverse osmosis separation of monohydric and polyhydric alcohols in aqueous solutions using porous cellulose acetate membranes, J. Appl. Polym. Sci 1973; 17 1043.

[16] Jordi R.-M., Joan B., Veronica G., Maria E M., Fernando V., Ricard D., Jose L. C. Integrating membrane technologies and blending options in water production and distri-

bution systems to improve organoleptic properties. The case of the Barcelona Metropolitan Area, Journal of Cleaner Production 2014; 69 250–259.

[17] Frank W, Smolders C, Calculation of liquid-liquid phase separation in a ternary system of a polymer in a mixture of a solvent and a nonsolvent, Macromolecules 1982; 15 1493–1497.

[18] Frommer M., Lancet M A. Reverse Osmosis Membrane Research, In: Lonsdale H K., Podall H E. (Eds.)., Plenum Press: New York; 1972, p. 85.

[19] Baker RW., Cussler EL., Eykamp W., Koros WJ., Riley RL., Strathman RH. Membrane separation systems: recent developments and future directions, ndc, Membrane Technology and Research, Noyes Publications, Mill Road at Grand Ave., Park Ridge, NJ 07656 (USA) ;1991.

[20] Witte P., Dijkstra P., Berg J., Feijen J. Review phase separation processes in polymer solutions in relation to membrane formation, J. Membr. Sci. 1996; 117 1–31.

[21] Strathmann H. Production of microporous media by phase inversion processes, ACS Symp. Ser 1985; 269 165.

[22] Strathmann H. and Koch K. The formation mechanism of phase inversion membranes, Desalination 1977; 21 241.

[23] Wijmans J. and Smolders C. Preparation of asymmetric membranes by the phase inversion process, In: Londsdale H K. and Pinho M H. (Eds.), Synthetic Membranes: Science, Engineering and Applications, Reidel, Dordrecht, The Netherlands; 1986, pp. 39–56.

[24] Zeman L. and Fraser T. Formation of air-cast cellulose acetate membranes. Part I. Study of macrovoid formation, J. Membr. Sci 1993; 84 93.

[25] Zeman L. and Fraser T. Formation of air-cast cellulose acetate membranes. Part II. Kinetics of demixing and microvoid growth, J. Membr. Sci 1994; 87 267.

[26] Scott K., Hughes R. Industrial membrane separation technology, Chapman & Hall: London; 1996.

[27] Loeb M., Sourirajan S. Sea water demineralization by means of an osmotic membrane, Adv. Chem. Ser 1962; 38 117.

[28] Chun K., Jang S., Kim H., Kim Y., Han H., Joe Y, Effects of solvent on the pore formation in asymmetric 6FDA–4, 40ODA polyimide membrane: terms of thermodynamics, precipitation kinetics, and physical factors, J. Membr. Sci 2000; 169 197–214.

[29] Dyukevick A., Yatskova T. Compaction on ultrafiltration membrane under the effect of working pressure, Khim-Tekhnol-Vody, 1991; 13 544–547.

[30] Bulte A., Naafs E., Eeten F., Mulder M., Smolders C., Strathmann H. Equilibrium thermodynamics of the ternary membrane- forming system nylon, formic acid and water, Polymer 1996; 37 1647–1655.

[31] El-Gendi A., Ahmed S., Talaat H., Preparation and evaluation of flat membranes for phenols separation, Desalination 2007; 206 226–237.

[32] Mulder M. Basic principles of membrane technology (2 ed.). Kluwer Academic: Springer. ISBN 0-7923-4248-8; 1996.

[33] Ismail A., Yean l. Review on the development of defect-free and ultrathin-skinned asymmetric membranes for gas separation through manipulation of phase inversion and rheological factors, J. Appl. Polym. Sci 2003; 88 442–451.

[34] Flory P J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY; 1969.

[35] Wijmans J., Baaij J., Smolders C., The mechanism of formation of microporous or skinned membranes produced by immersion precipitation, J. Membrane Sci 1983;14 263–274.

[36] Stern S, Polymers for gas separation; the next decade, J. Membr. Sci 1994; 94 1–65.

[37] Frommer M, Feiner I, Kedem O, Bloch R. The mechanism for formation of skinned membranes, 11, Equilibrium properties and osmotic flows determining membrane Structure, Desalination 1970; 7 393.

[38] Smolders C., Broens L., Altena F., Koenhen D., Asymmetric membrane structures as a result of phase separation phenomena, Desalination 1980; 33–45.

[39] Koenhen D., Mulder M H V., Smolders C A. Phase separation phenomena during the formation of asymmetric membranes, J. Appl. Polym. Sci 1977; 21 199.

[40] Bokhorst H., Altena F., Smolders C. Formation of asymmetric cellulose acetate membranes, Desalination 1981; 38 349.

[41] Chaoyi B., Langer J., Economy J. Chemical modification of P84 copolyimide membranes by polyethylenimine for nanofiltration, J. Membr. Sci 2009; 327 49–58.

[42] Kim C., Kim J., Lee K., Tak T. Preparation of soluble polyimides and ultrafiltration membrane performances. J. Appl. Polym. Sci 1999; 75 1–9.

[43] EL-Gendi A., Ternary Phase Diagram Constraction and Membrane Morphology Evaluation, LAB LAMBERT academic publishing, Germany; 2014. ISBN : 978-3-659-57611-9.

[44] Bottino A., Roda G., Capannelli G., Munari S. The formation of microporous polyvinylidene difluoride membranes by phase separation, J. Membr. Sci 1991;57 1–20.

[45] Kim I., Yoon H., Lee K. Formation of integrally skinned asymmetric polyetherimide nanofiltration membranes by phase inversion process, J. Appl. Polym. Sci 2002; 84 1300–1307.

[46] Shieh J., Chung T S. Phase-inversion poly(ether imide) membranes prepared from water-miscible/immiscible mixture solvents, Ind. Eng. Chem. Res 1999;38 2650–2658.

[47] Smolders C., Reuvers A., Boom R., Wienk I. Microstructures in phase inversion membranes. Part 1. Formation of macrovoids, J. Membr. Sci 1992; 73 259–275.

[48] Amirilargani M., Sadrzadeh M., Mohammadi T. Synthesis and characterization of polyethersulfone membranes, J Polym Res 2010; 17 363–377.

[49] Saljoughi E., Sadrzadeh M., Mohammadi T. Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes, J. Membr.Sci 2009; 326 627–634.

[50] Frommer M., Messalam R., Mechanism of membrane formation. VI. Convective flows and large void formation during membrane precipitation, Ind. Eng. Chem., Prod. Res. Dev 1973; 12 328–333.

[51] Strathmann H., Kock K., Amar P., Baker R. The formation mechanism of asymmetric membranes, Desalination 1975; 16 179–203.

[52] Tomaszewska M. Preparation and properties of flat-sheet membranes from poly (vinylidene fluoride) for membrane distillation, Desalination 1996; 104(1-2) 1–11.

[53] Ruiting H., Zhenya G., Kaijie Z. and Guangming Z., Preparation and properties of PVDF-fabric composite membrane for membrane distillation, Desalination 2009; 249(3) 910–913.

[54] Chunsheng F., Baoli S., Guomin L. and Yonglie W., Preparation and properties of microporous membrane from poly (vinylidene fluoride-co-tetrafluoroethylene) (F2.4) for membrane distillation, J. Membr. Sci 2004; 237(1-2) 15–24.

[55] Ortiz J M., Peria L., Mengual L J. Characterization of membrane distillation prepared by phase inversion, Desalination 1995; 100 139–148.

[56] Na T., Qian J., Huanju Z., Jinjin L., Sha C. Preparation and morphological characterization of narrow pore size distributed polypropylene hydrophobic membranes for vacuum membrane distillation via thermally induced phase separation, Desalination 2010 ; 256(1-3) 27–36.

[57] Khayeta M., Menguala J I., Matsuura T. Porous hydrophobic/hydrophilic composite membranes Application in desalination using direct contact membrane distillation, J. Membr. Sci 2005; 252 101–113.

[58] Qtaishat M., Rana D., Khayet M., Matsuura T. Preparation and characterization of novel hydrophobic/hydrophilic polyetherimide composite membranes for desalination by direct contact membrane distillation, J. Membr. Sci 2009; 327(1-2) 264–273.

[59] Combe C., Molis E., Lucas P., Riley R., Clark M M. The effect of CA membrane prop‐ erties on absorptive fouling by humic acid, J. Membr. Sci 1999; 154 73–87.

[60] Shuguang C., Yanqiao S., Guanwen C. Influence of acetylation degree of cellulose acetate on pervaporation properties for MeOH/ MTBE mixture, J. Membr. Sci 2000; 165 89–97.

[61] Hideto M., Masaaki T., Tsutomu U. Membrane formation and structure development by dry-cast process, J. Membr. Sci 1997; 135 271–288.

[62] Khayet M., Feng C Y., Matsuura T. Morphological study of fluorinated asymmetric polyetherimide ultrafiltration membranes by surface modifying macromolecules, J. membr. Sci 2002; 5502 1–22.

[63] Meier – Haack J., Lenk W., Berwald S., Rieser T., Lunkwitz K. Influence of thermal treatment on the pervaporation separation properties of polyamide -6 membranes, Separation and purification technology 2000; 19 199–207.

[64] Schindler E., (DE): Maier F. (DE). Process for the production of an ultrafiltration membrane from polyamide, U.S. patent 4482514, 1984.

[65] James L T., Martina O., Christin D., Chien-Hsieh S., Carl C G. Polyamide membrane precipitation studied by confocal backscattering microscopy, Polymer V 2002, 43 4153–4157.

[66] Ceynowa – J., Adamczak-P. Enzyme membrane based upon polyamide -6 for oil hy‐ drolysis, J- Appl- Polym –Sci Oct 1992; 46(5) 749–756.

[67] EL-Gendi A., Ali S S., Ahmed S A., Talaat H A. Development of membrane blend us‐ ing casting technique for water desalination, Membrane Water Treatment 2012; 3 201–209.

[68] EL-Gendi A., Abdallah H. Selectivity performance for polyamide-6 membranes using pervaporation of water/methanol mixtures, Desalination and Water Treatment 2013; 51 3263–3272.

[69] EL-Gendi A., Abdallah H., El-Zanati E., Matsuura T. Pervaporation of methanol from methylacetate mixture using Polyamide-6 membrane, Desalination and Water Treat‐ ment 2013; 51 7807–7814.

[70] EL-Gendi A., Deratani A., Ahmed S A., Ali S S. Development of polyamide-6/chito‐ san membranes for desalination, Egyptian Journal of Petroleum 2014; 23 169–173.