

Synthesis of Polysulfone Membrane and Its Application to Separation of Oil from Oil-in-Water Emulsion

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by

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Dedication

To My beloved mother

“Late Purnima Goswami”

for whom I have become what I am today.

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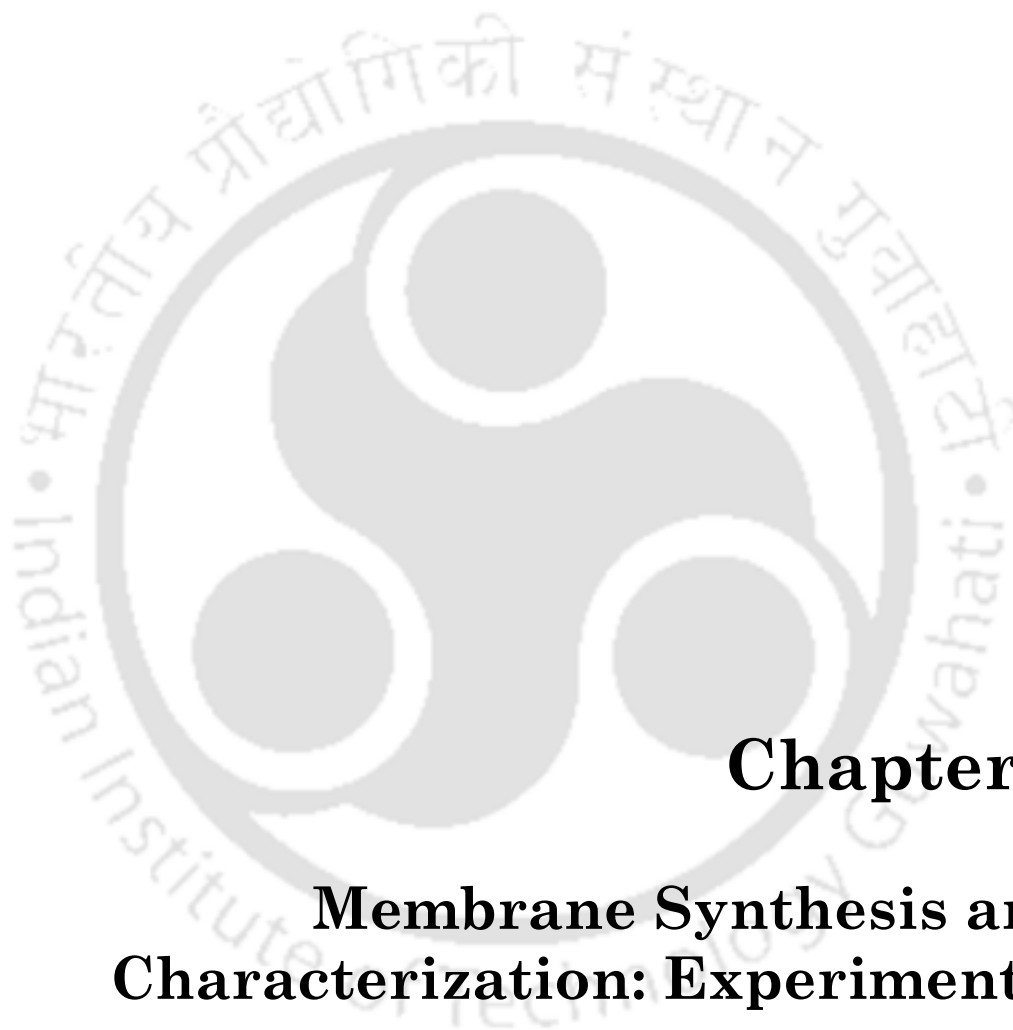
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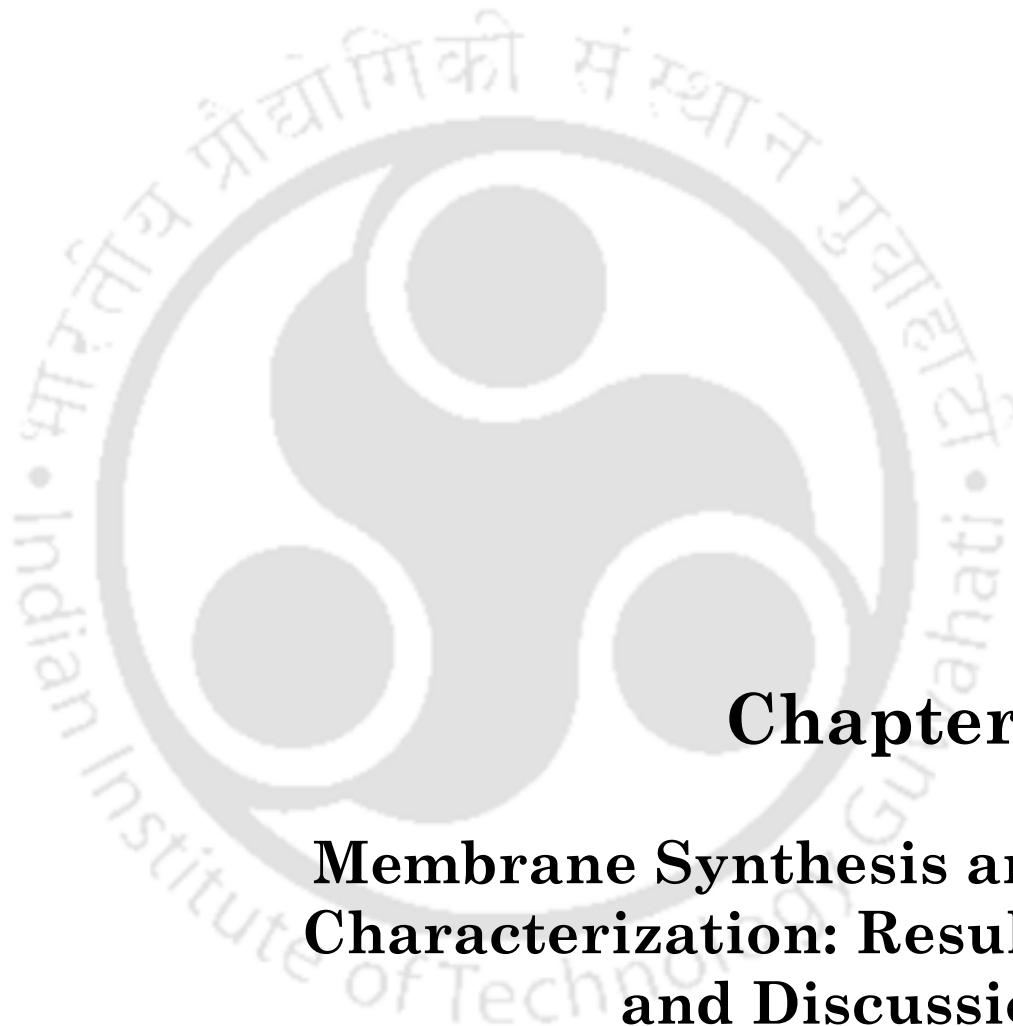
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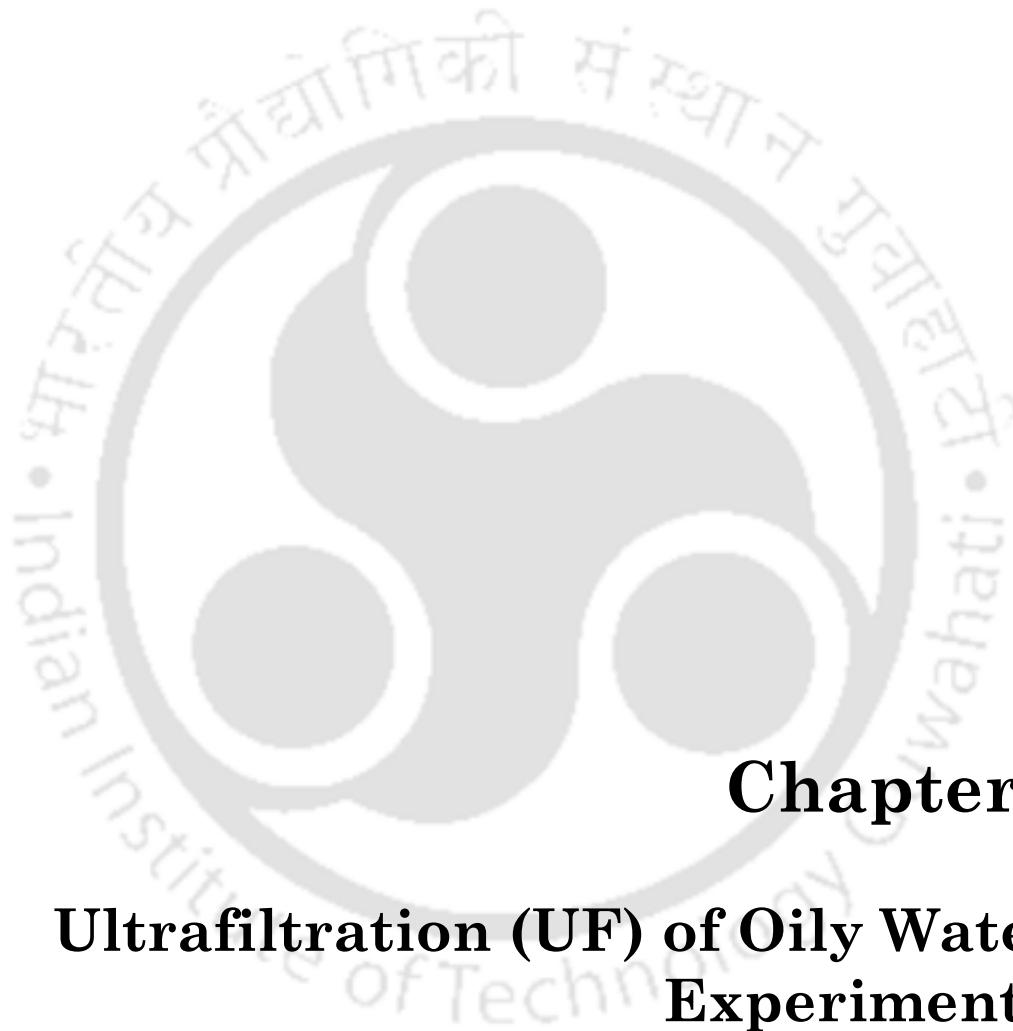
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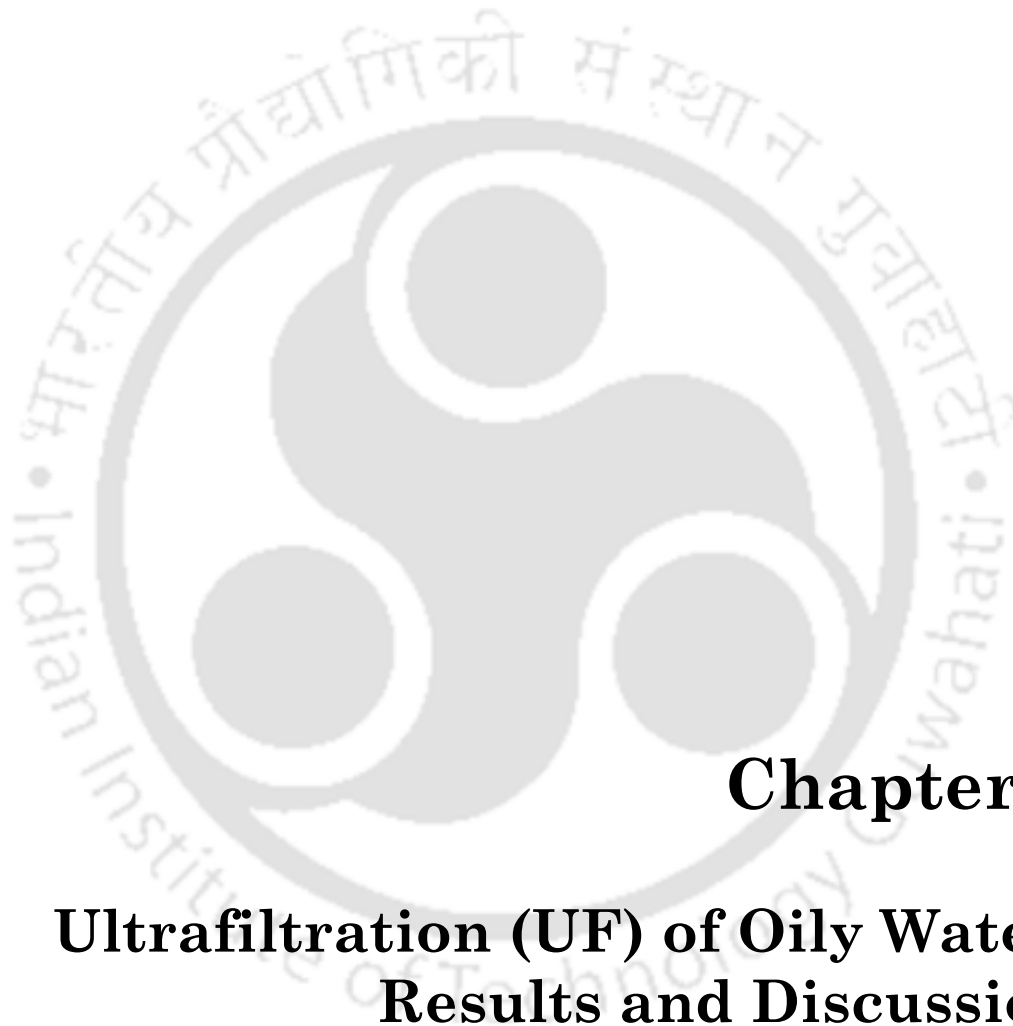
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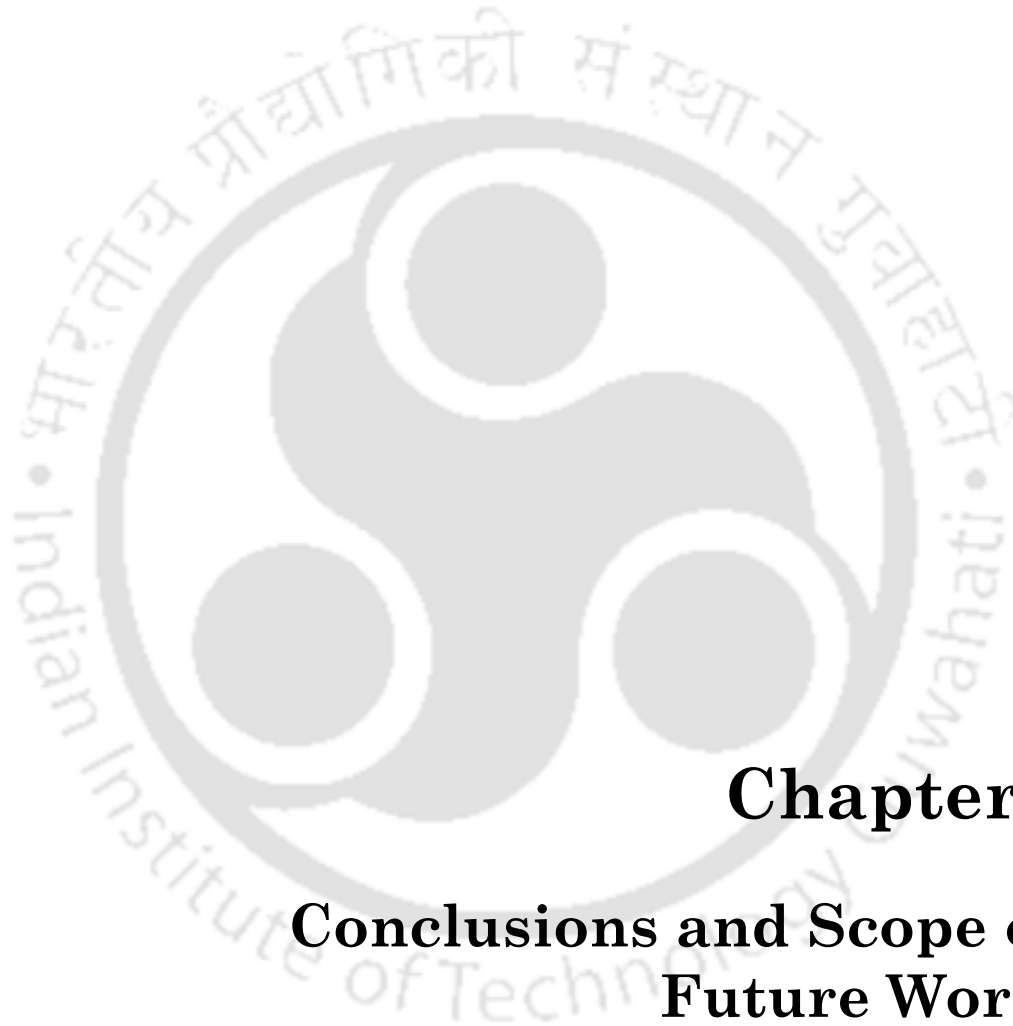
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Chapter 6

Conclusions and Scope of Future Works



Appendix

Abstract

The main objective of this work is to synthesize asymmetric polysulfone membranes with required morphological as well as performance properties so that they can be successfully employed for the removal of micron and submicron sized oil droplets from oily wastewater, generated mainly from the post treatment unit of petroleum refinery sites.

The entire effort carried out in this research work can be divided into two main parts:

- Synthesis and characterization of polysulfone membranes.
- Study of applicability of the prepared membranes for the treatment of oily wastewater.

Flat sheet asymmetric membranes were prepared from homogeneous solution of polysulfone (PSf) by phase inversion method. *N* methyl-2-pyrrolidone (NMP) and dimethyl acetamide (DMAc) were used as solvents separately. Introduction of a suitable additive to the casting solution is a convenient and efficient method in order to get a membrane with suitable structure and permeation property. So, polyvinyl pyrrolidone (PVP) of three different molecular weights (24000 Da, 40000 Da, 360000 Da) and polyethylene glycol (PEG) of three different molecular weights (400 Da, 6000 Da and 20000 Da) were used as the polymeric additives in the casting solution. Altogether twelve membranes of four different compositions (PSf/NMP/PVP, PSf/NMP/PEG, PSf/DMAc/PVP and PSf/DMAc/PEG) were synthesized and characterized by different standard methods for morphological information. The permeation performances of the membranes were evaluated in terms of pure water flux (PWF), compaction factor (CF), equilibrium water content (EWC) and hydraulic resistance (). It was found that with

increase in molecular weight of PEG and PVP, the pore number and porosity of the PSf membrane also increase; however, the average pore size was found to decrease marginally with increase in molecular weight of the two additives. The increase of EWC with increase in molecular weight of both the additives irrespective of the solvents used can be interpreted as an indication of increase in hydrophilicity as well as porosity of the membranes.

A series of experiments carried out with bovine serum albumin (BSA) solution is reported to show the applicability of the prepared membranes for ultrafiltration (UF) applications. From the analysis of the results of these experiments, it is understood that membrane composition and pH of BSA solution play important roles in flux and BSA rejection.

The performances of different PSf membranes were evaluated by treating laboratory made oil-in-water (o/w) emulsion. Experiments were first carried out with the twelve membranes in a batch mode and the influence of operating conditions such as transmembrane pressure (TMP) and feed properties such as initial oil concentration and pH of feed solution on membrane performance were investigated. Results show that all these parameters play a key role in permeate flux as well as percent oil separation. It was found that with increase in TMP, the flux increases while the oil rejection decreases. Again, with increase in oil concentration in feed, flux decreases and rejection increases. The pH of the feed is seen to influence the flux and rejection to different extent depending on the membrane composition. Also, morphological properties of membranes have a significant role on the permeate flow rate and hence subsequent oil removal. Based

on this, four membranes out of the four membrane compositions were selected to carry out the further study. The experimental results showed that oil retentions of almost all the membranes were over 90% and oil concentration in the permeate was below 10 mgL^{-1} , which met the requirement for discharge; hence the developed PSf membranes was found feasible in treating oily wastewater.

The study further highlighted the performance of the selected membranes in cross-flow UF experiments. The study showed that with increase in cross-flow rate, the flux increases significantly; but the oil rejection (%) shows a decreasing trend. Comparing the results of batch mode and cross-flow mode UF, it is inferred that cross-flow mode performance is better in terms of obtaining higher permeate flux at a given TMP; the differences in the performances of the two modes is attributed to the difference in flux decline mechanism.

Finally, the selected membranes were tested to separate oil from the 'produced water' obtained from Oil India Ltd (OIL), Assam, India using both the modes of UF under the optimum TMP condition i.e. 103.4 kPa. In the dead-end mode operation, the percent oil removal was found to be about 85 % for the selected membranes; however, the rejection was found to be below 80 % for all the membranes in cross-flow mode of operation although the flux was reasonably high. This suggests further study needs to be performed incorporating another operational unit e.g. nanofiltration or reverse osmosis to the existing unit in order to meet the discharge standard of 10 mgL^{-1} .



Summary

The research work described in this thesis consists of the experimental studies on the following major topics:

- Synthesis and characterization of Polysulfone membranes using two solvents (NMP and DMAc) and two additives (PVP and PEG) separately.
- Verification of the synthesized membranes for ultrafiltration applicability with bovine serum albumin (BSA) solution. Further experiments with synthetic oily water were conducted using batch and cross-flow (continuous) ultrafiltration mode. Selection of the most suitable membrane/membranes for separating oil from water under the optimum operating conditions based on their performance (i.e. flux and rejection).
- Conduction of batch and cross-flow ultrafiltration experiments with real oily water collected from actual site to study the usability of the selected membranes.

The thesis is organized in the following six chapters:

Chapter 1: Introduction

Chapter 2: Membrane Synthesis and Characterization: Experimental

Chapter 3: Membrane Synthesis and Characterization: Results and Discussion

Chapter 4: Ultrafiltration of Oily Water: Experimental

Chapter 5: Ultrafiltration of Oily Water: Results and Discussion

Chapter 6: Conclusions and Scope of Future Work

Brief descriptions on each of the chapters are presented below.

Chapter 1: Introduction

This chapter discusses the background of the problem undertaken in this work i.e. the problem associated with the discharge of oily wastewater from refineries and petrochemical industries into the surrounding environment. A brief overview of membrane and membrane based separation processes is given in this chapter. It also discusses the features of different techniques of membrane preparation. The objectives of the present work are highlighted in this chapter. The chapter subsequently presents detailed literature review that includes synthesis and characterization of membrane, separation of oil from oily wastewater and the flux declination due to membrane fouling.

Chapter 2: Membrane Synthesis and Characterization: Experimental

This chapter gives the complete description of the experimentations involved in the preparation (e.g. selection of materials, selection of appropriate compositions, etc.) and characterization of polysulfone (PSf) membranes. The preparation method of the PSf membranes is elaborated in this chapter. Altogether twelve membranes of four different compositions were selected and prepared accordingly. The different characterization methods carried out in this work e.g. scanning electron microscopy (SEM), gas permeation test and liquid displacement test to find out the membrane morphology are also discussed here. It also elaborates the ultrafiltration characterizations of the prepared membranes such as measurement of pure water

flux (PWF), compaction factor (CF), equilibrium water content (EWC) and hydraulic resistance (). The effects of increasing molecular weight of PEG and PVP on membrane morphology and permeation behavior are highlighted.

Chapter 3: Membrane Synthesis and Characterization: Results and Discussion

This chapter presents the results and discussion of the experimental works on membrane synthesis and characterization. It discusses individually the effect of addition of different molecular weights of PEG and PVP additives into the membrane casting solution consisting of PSf as membrane forming polymer and NMP or DMAc as solvents.

The entire chapter is divided into two major parts:

- Effect on morphological parameters
- Effect on performance parameters

Brief description of the above is presented below:

Effect on morphological parameters :

The effects of addition of PVP and PEG of different molecular weights on membrane morphological parameters such as average pore size, pore size distribution, porosity, pore density, etc were examined with the help of different methods and the results are reported and analyzed.

Effect on performance parameters :

The synthesized PSf membranes were examined for their performance in terms of CF, PWF, EWC and . The results are summarized and analyzed in this section highlighting the effects of addition of PVP and PEG of different molecular weights.

Chapter 4: Ultrafiltration of Oily Water: Experimental

This chapter, at first, gives an account of the batch ultrafiltration (UF) experiments that were carried out with BSA solution. It further gives a detailed description of the UF experiments with synthetic oily water using the membranes of four different compositions synthesized and characterized accordingly as given in Chapter 2 and Chapter 3. It discusses in details the preparation and characterization of the oil-in-water (o/w) emulsion which is to be used as the synthetic oily water in the UF application. The chapter also gives an insight to the details of the two modes of the UF experiments that is, dead-end (batch) filtration mode and cross-flow mode that were carried out in this study. Finally, the experimental details of both batch and cross-flow ultrafiltration carried out with real oily wastewater also known as ‘produced water’ obtained from Oil India Ltd (OIL), Duliajan, Assam, India, using the selected membranes at optimum value of TMP are explained.

Chapter 5: Ultrafiltration of Oily Water: Results and Discussion

This chapter presents the results and discussions of the batch UF of BSA solution. Mainly effects of pH of BSA solution and the composition of membranes on flux and rejection of BSA are discussed in this section. It further elaborates the batch and cross-flow UF results of both the synthetic and industrial oily water. The effect of increasing porosity and hydrophilicity of membranes due to addition of different molecular weight additives on permeate flux, oil rejection and flux declination have been investigated in detail. At first, the batch UF experiments were considered and the role of transmembrane pressure (TMP) and feed properties (viz. concentration and pH) on membrane performance is

analyzed. A detailed theoretical study is included in this chapter based on the batch UF results to explain the membrane fouling mechanism. The resistance-in-series (RIS) model and constant filtration models are applied to interpret the data and the individual resistances are evaluated. The significances of these resistances are revealed in relation to parameters, namely, TMP and initial oil concentration. The results of cross-flow UF experiments obtained with synthetic oily water are discussed which mainly highlight the effect of cross-flow rate on membrane performance. Finally, the results of both batch and cross-flow UF with ‘produced water’ using the selected membranes at optimum value of TMP are reported to understand the industrial application of the synthesized membranes.

Chapter 6: Conclusions and scope of future work

This chapter reports the inferences drawn from the research work. It also provides suggestions towards the future direction.

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Chapter 1

Introduction

This chapter discusses the background of the problem undertaken in this work i.e. the problem associated with the discharge of oily wastewater from refineries and petrochemical industries into the surrounding environment. A brief overview of membrane and membrane based separation processes is given in this chapter. It also discusses the features of different techniques of membrane preparation. The chapter subsequently presents detailed literature review that includes synthesis and characterization of membrane, separation of oil from oily wastewater and the flux declination due to membrane fouling. The objectives of the present work are also highlighted in this chapter.

1.1. Background

There is a worldwide thrust on application of membrane technology for separation and purification applications in various industrial sectors including the environmental sectors. This is apparently due to advantages such as low energy requirement for separation operation and compact membrane units.

A large amount of wastewater in the form of oil-in-water (o/w) emulsions is generated from various process industries such as metallurgical, transportation, food processing and petrochemical industries as well as petroleum refineries. In o/w emulsions, oil droplets greater than 0.1 μm is dispersed throughout the water medium. Emulsions are frequently quite persistent in the environment and resist their decomposition into their

original constituents of oil and water. O/w emulsions are divided into four categories

based on the size of oil droplets which are shown in Table 1.1 [1].

Table 1.1 Typical features of oil in water according to their forms of existence [1]

Forms of oil in water	Free oil	Mechanically emulsified oil	Chemically emulsified oil	Dissolved oil
Description	Non-miscible with water; rapidly rises to water surfaces forming a film or large droplets.	Present in water due to high shear (passing through pump) stabilized by electrical charges.	Miscible with water; stabilized by surfactants.	Oil that is soluble in water; water is translucent and transparent. Removal by filtration, gravity settling is impossible.
Oil droplet size	>150	20 – 150	<20	<5
Emulsion types	Macro-emulsion	Micro-emulsion	Micro-emulsion	Mini-emulsion

Crude oils are complex mixtures of a large number of hydrocarbons which vary in their toxicity to aquatic and terrestrial life. Presence of oil in water, even in small quantity, is harmful to the environment. It also affects on industries and water treatment processes. Table 1.2 gives an account of effects caused by oil discharged effluents [1]. Due to these hazards, oil field effluents must be treated before disposing to the environment.

Waste streams from onshore and offshore oil and gas production sites are usually the largest sources of oily wastewater. ‘Produced water’, which is the water co-produced during oil and gas manufacturing, contains dispersed oils and suspended particles. These ‘produced waters’ constitute the single largest waste stream from oil and gas exploration and production activities. The volume of oily waste or ‘produced water’

generated annually in the US onshore oil and gas operations is estimated to be 33 billion barrels [2] which contains high concentrations of oil, grease, and suspended particles. Typical composition ranges include 50-1000 mgL⁻¹ of total oil and grease, and 50 - 350 mgL⁻¹ of total suspended solids. Environmental regulations require that

Table 1.2 Effect of oil-discharged effluents [1]

Effect on environment	Effect on human health	Effect on industries and water treatment processes
(1) Free oil hinders the penetration of sunlight in river water distracting aquatic life and restricts natural cleansing of water in rivers or lakes.	(1) Consumption of un-treated chemically emulsified oil disposed in river causes several health problems including cancer.	(1) In steam generation and cooling process, oil contaminated water causes foaming, priming, over heating of tubes, which leads to poor heat transfer from metal to water.
(2) Untreated oily waste forms a layer on the banks of river causing spoiling of vegetation present on bank.	(2) Bathing in contaminated oily water causes skin cancer.	(2) Free and emulsified oil can clog and coat the filters and ion-exchange beds, decreases effectiveness of filtration and interface with backwashing.
(3) Oily waste may coat the gills of fish and stop the oxygen transfer causing death.	(3) Fish affected by toxic oils, if consumed can cause nausea and vomiting.	(3) In biological treatment of wastewater, a layer of oil adheres to the micro-organism creating additional resistance to oxygen and nutrient transfer to biomass and reduces the treatment efficiency.
(4) Undesirable odour from oily waste is a nuisance.		

maximum total oil and grease concentrations in discharge waters be 10-15 mgL⁻¹ [3].

Current technologies for treatment of refinery wastes are very expensive and are mostly inadequate for present and future regulations. Some of these technologies are

centrifugation, thermal desorption, solvent extraction, and hydrothermal processing. None of these technologies are quite successful in meeting the environmental regulations. Industrial oily wastewater can be divided into three broad categories [4]:

- Free-floating oil,
- Unstable o/w emulsion and
- Stable o/w emulsion

Free oil which usually consists of large oil droplets (size 150 μ m) can be readily removed by normal mechanical separation processes (gravity separation, flotation or skimming). Such processes may be regarded as the primary treatment steps which take advantage of the differences in the specific gravities of the oil and the water. This treatment step normally involves retaining the oily wastewater in a holding tank while allowing gravity separation of the oily material, which is subsequently skimmed from the wastewater surface. The most common and standard instrument in refinery waste treatment is the API Separator, although effluents from this unit may still contain 400–500 mgL⁻¹ of oil [5]. The effectiveness of a gravity separator depends upon a proper hydraulic design and wastewater retention time. Short retention times of less than 20 min result in a less than 50% oil/water separation. In addition to the API separator, two other gravity separators viz. the corrugated plate interceptor (CPI) and the parallel plate interceptor (PPI), both referred to as plate separators, are used in this treatment phase.

Primary treatment steps are often followed by secondary treatment steps. Unlike primary treatment, which consists only of gravity separation and skimming, any of the secondary treatment processes are directed toward breaking of the o/w emulsion

followed by separating the demulsified oil from the water phase. Emulsions may be broken chemically or physically. Chemical methods are the most widely used methods in destabilizing the o/w emulsions which require various coagulant chemicals such as sulphuric acid, iron and aluminium sulphates, etc. The process usually consists of rapid mixing of the coagulant chemicals with the wastewater followed by flocculation and flotation, filtration or settling. The flotation method which includes several techniques such as dissolved air [6], induced air [7] and electroflotation [8] is also widely practised for relatively smaller oil droplets. Physical methods for breaking emulsions include heating, centrifugation, precoat-filtration, fiber beds and electrochemical methods. Centrifugation is normally applied to oily sludges. Precoat-filtration and coalescers have also been successfully employed for breaking oil emulsions [9] which are in the 20-100 μm size range. Electrocoagulation [5, 10] and electroflotation technologies utilize both chemical and physical emulsion separation mechanisms in the presence of an electric field.

All these conventional methods are found to be quite effective for removing unstable o/w emulsion (size 20-150 μm); however, these methods are found to be suffering from many disadvantages [4] such as:

- large volumes of sludge are produced due to coagulation which becomes an additional problem for disposal;
- the operating costs can be high, depending on the application;
- there could be corrosion problems due to addition of acid into the feed;
- the process is highly susceptible to changes in influent quality;

- it is more suitable for large volumes, e.g., >300 000 gal (1135 m³) per day; it is difficult to operate and maintain in smaller facilities with fewer resources;
- due to gradual adsorption of material on the coalescing media, problems can be encountered in coalescers that leads to loss of effectiveness.

Also, those traditional methods are not efficient enough for treating stable o/w emulsions (size) especially when the oil droplets are finely dispersed and the concentration is very low. Because the emulsion droplets, which are of micron and submicron size, require a very long residence time to rise onto the top for enabling gravity separation and even addition of chemicals cannot break the emulsions effectively. Reports say that these techniques can reduce oil concentration to hardly 1 % by volume of the total wastewater and cannot efficiently remove oil droplets below 10 size [10, 11]. The water phase obtained from such treatment is generally required to be further purified to meet the accepted effluent standard for discharge into the river. To solve problems with such emulsions, new sophisticated methods have been developed. The emulsion breaking may be achieved by heating the wastewater, which results in a significant increase of the size of oil droplets; but such thermal process of oily wastewater treatment is not cost effective as it requires a large amount of energy. One of the recently utilised solutions to the problems of the oily wastewater treatment is the biological method which is practised based on biodegradation and biotransformation of fats and oily wastes [12]. However, this method possesses several disadvantages in terms of low efficiency, operational difficulties, and high operation costs [13].

Under such circumstances, membrane separation process is regarded as a useful process for concentration and purification of oily wastewater. The use of membrane offers a potential solution to the problem of micron sized oily wastewater. The porous membrane matrix can promote coalescence of micron and submicron oil droplets into larger ones that can be easily separated by gravity [14]. The problem of good emulsion stability in oily wastewater becomes a positive factor when such water is treated by membrane processes.

Some of the most promising methods based on membrane separation processes are dehydration of oil emulsion by pervaporation [15], reverse osmosis [16], flocculation followed by microfiltration [17], cross-flow microfiltration [2, 18], membrane distillation [13] and ultrafiltration [19]. It has been demonstrated that pressure driven membrane separation processes can be successfully employed for the removal of oil from oily wastewater, with some distinct advantages over the more conventional processes. In most cases the membrane processes are used as one or more of the treatment steps in complex oily wastewater treatment schemes combining conventional and membrane treatment technologies. These combined systems have proved to offer superior treatment capabilities, particularly in cases where conventional methods alone could not perform the task to desired efficiency or effectiveness.

1.2. Overview of membranes and membrane separation processes

In recent years, membranes and membrane separation processes have grown from a simple laboratory tool to an industrial process with considerable technical and

commercial impact. A precise and complete definition of a “membrane”, which covers all its aspects is rather difficult. Usually, membranes are defined as semi-permeable barriers that prevent intimate contact between two homogeneous phases, but allow preferential passage of certain species across their structures. There are a number of definitions of the word “membrane”, which are seen to vary considerably. The most popular definitions of “membrane” found in technical literature are provided below:

A membrane is defined as

- “an intervening phase separating two phases and/or acting as an active or passive barrier to the transport of matter between phases” - the European Society of Membrane Science and Technology (now the European Membrane Society) [20].
- “an interphase separating two homogenous phases and affecting the transport of different chemical components in a very specific way” - Prof. Heiner Strathmann, former Head of the Department of Membrane Technology, University of Twente [20].
- “a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process” - Prof. George Solt, former Director of the School of Water Sciences, Cranfield [20].
- “a region of discontinuity interposed between two phases” – Hwang and Kammermeyer, 1975 [21].

The roles of membranes are to change the composition of a solution on the basis of relative permeation rates (membrane separation processes), to physically or chemically modify the permeating species (ion-exchange membranes and

bio-functional membranes), to conduct electric current, to prevent permeation (packaging or coating) or to regulate the rate of permeation (controlled release).

Membrane processes are currently gaining a lot of interest in separation technology. Separation operation, in fact, occupies a key position in process industries that include foods, pharmaceuticals and other industries. The rapid growth in membrane technology has made it a serious competitor for other conventional separation technologies like crystallization, distillation, etc. particularly for small scale operations. The membrane separation processes offer following advantages over other means of separation:

- Separation can be carried out continuously;
- Low energy utilization as no phase change or temperature change is involved;
- Low maintenance as the systems are easy to operate and maintain;
- Constituents in the concentrated stream remain chemically unaltered due to non-requirement of any chemical addition which facilitated their subsequent utilization;
- Capability of generating permeates of acceptable quality which can be reused as make-up water for emulsification and discharged directly into a receiving water body.

However, membrane separation processes suffer from the following drawbacks due to membrane fouling and concentration polarization:

- Low membrane life time;
- Low selectivity or flux.

Measures are explored to reduce membrane fouling and concentration polarization so as to overcome these limitations. Nowadays, membrane technology is seen to be applied in various industrial areas such as food and beverages, metallurgy, pulp and paper, textile, pharmaceutical, automotive, dairy, biotechnology, chemical industries, etc. [22].

1.2.1. Classification of membrane

In the most general sense, a synthetic membrane is a barrier which separates two phases and restricts the transport of various chemical species in a rather specific manner. Membranes can be solid or liquid. They may be either neutral or may carry negative or positive charges or both. They can be homogeneous (i.e. completely uniform in composition and structure) or heterogeneous (i.e. containing pores of finite dimensions or consisting of some form of layered structure). Membranes can be further classified by (i) nature, (ii) structure and (iii) mechanism of action [21 - 23].

By nature, membranes can be classified as biological and synthetic membranes. These two types of membranes differ completely in structure and functionality. Biological membranes can be subdivided into living and non-living membranes. Synthetic membranes can be subdivided into organic (polymeric, liquid) and inorganic (ceramic, metal) membranes. This study emphasizes only on the polymeric membranes.

According to morphology or structure, solid membranes can be divided into two main classes – symmetric (or isotropic) and asymmetric (or anisotropic). The symmetric membranes can be subdivided further into porous, nonporous or dense and electrically charged membranes. Symmetric porous membranes have a rigid, highly voided structure with randomly distributed, interconnected pores. In general, only molecules

that differ considerably in size can be separated effectively by such membranes, e.g. ultrafiltration and microfiltration. On the other hand, nonporous, dense membranes consist of a dense film through which permeates are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material e.g. pervaporation and reverse osmosis. Electrically charged membranes (or ion-exchanged membranes) can be dense or porous, but are most commonly very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. The separation is affected by the charge and concentration of the ions in solution e.g. electrodialysis.

Asymmetric membranes consist of a very dense top layer or skin of thickness 0.1 – 0.5 μm supported by a porous sub-layer with a thickness of about 50 -150 μm . The top layer and its substructure may be formed in a single operation or separately. In composite membranes, the layers are usually made from different polymers; each layer of which can be optimized independently. The separation properties and permeation rates of the membrane are determined exclusively by the top layer; the sub-layer functions as a mechanical support. The advantages of the higher fluxes provided by such membranes are so great that almost all commercial processes use such membranes.

There are two types of liquid membranes – supported liquid membranes and unsupported liquid membranes. Supported liquid membranes have a microporous structure which is filled with the liquid membrane phase; the microporous structure provides the mechanical strength and the liquid-filled pores the selective separation

barrier. The microporous substructure should have a high porosity and a pore size small enough to support the liquid membrane phase sufficiently under hydrostatic pressure. Unsupported liquid membranes are composed of thin films of liquid stabilized by a surfactant in an emulsion type mixture. Fig. 1.1 shows membrane classes according to their morphology.

On the basis of mechanism of action, membranes are classified as adsorptive or diffusive, ion-exchange, osmotic or nonselective (inert) membranes [22].

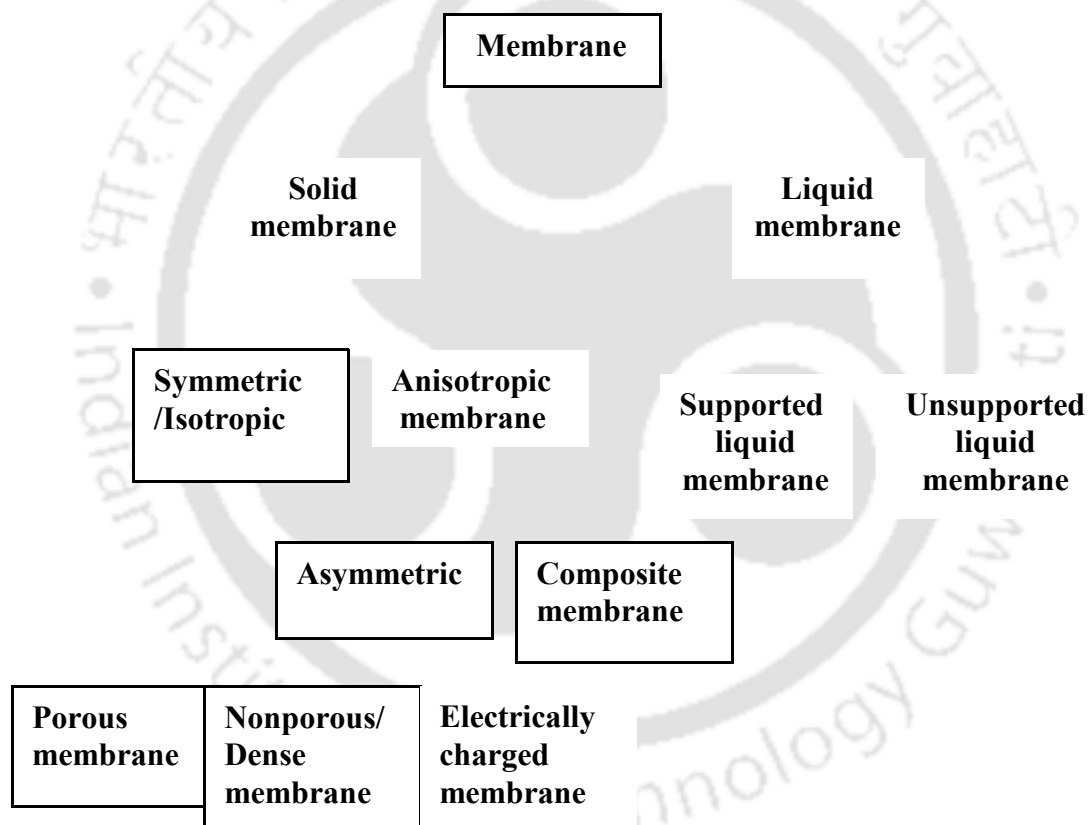


Fig. 1.1 Membrane classifications according to the morphology

1.2.2. Classification of membrane separation processes

The wide variety of membrane separation processes differ from one another in the type and configuration of the membrane, the mechanism of trans-membrane transport

for various feed components, the nature of the process driving force and other features. Some processes which are well proven in full scale industrial applications, have been widely used for separation, purification and concentration of water-soluble solutes or water dispersible materials in industries such as pharmaceutical, chemical processing, food processing, oil industries, wastewater treatment plant, etc. Other processes, which are still in experimental stage, are yet to get into industrial use.

Membrane separation processes may be classified and categorized by a number of criteria. It is a filtration technique in which a membrane acts as a selective barrier between two phases [22]. As a result of a driving force across the membrane, components are transported towards the membrane surface, where some components pass the membrane and others are retained at the membrane surface. Membrane processes are available for numerous applications, each with its own driving force and separation characteristics:

- Pressure driven processes, e.g. microfiltration, ultrafiltration, nanofiltration and reverse osmosis;
- Concentration driven processes, e.g. gas separation, pervaporation, dialysis, membrane extraction, supported liquid membrane (SLM), emulsion liquid membrane (ELM), non-dispersive solvent extraction with hollow fibre contactors;
- Temperature driven processes, e.g. membrane distillation, thermo-osmosis;
- Electrically driven processes, e.g. electrodialysis, electrodialysis with application of liquid organic membranes, membrane electrolysis, electrosorption, electrofiltration, electrochemical ion exchange.

A simplified overview of the common membrane separation methods arranged by the main process driving force and the respective application range is shown in Fig. 1.2.

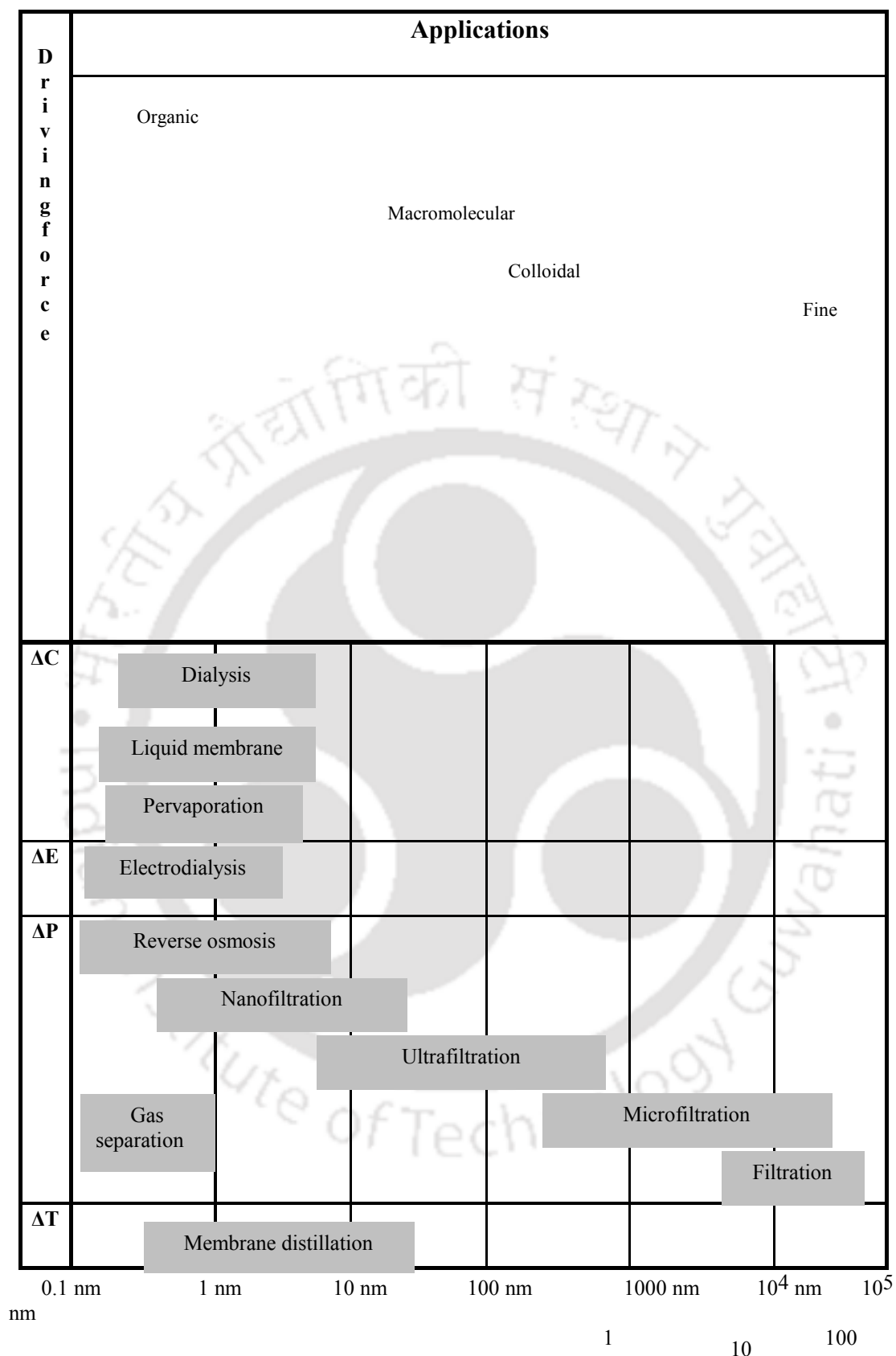


Fig 1.2. Typical membrane separation methods (ΔC , ΔE , ΔP and ΔT are concentration, electric potential, pressure and temperature differences respectively) [23]

Pressure driven membrane separation processes differ mainly in the pore size of their membranes, which makes a particular membrane effective for the removal of a specific range of impurities. Table 1.3 provides further information on these processes, such as membrane type, method of separation and range of applications [23, 24]. Reverse osmosis has the smallest membrane pore size and therefore is

Table 1.3 Typical membrane separation processes: Operating principles and applications [23, 24]

Separation process	Membrane type	Separation mechanism	Range of application
1. Microfiltration	Symmetric and asymmetric microporous membrane	Sieving mechanism as a function of pore size and adsorption	Sterile filtration clarification
2. Ultrafiltration	Asymmetric microporous membrane	Sieving mechanism	Separation of macromolecular solutions
3. Nanofiltration	Asymmetric 'skin type' membrane	Solution diffusion mechanism	Separation of divalent ions from solutions
4. Reverse osmosis	Asymmetric 'skin type' membrane	Solution diffusion mechanism	Separation of salts and microsolute from solutions
5. Dialysis	Symmetric microporous	Diffusion	Separation of salts and microsolute from macro-molecular solutions
6. Electrodialysis	Cation and anion exchange membrane	Selective transport of ions or molecules according to electric charge	Desalting of ionic solutions
7. Supported liquid membrane	Microporous membranes supporting adsorbed organic liquid	Solution diffusion via carrier	Separation and concentration of metal ions and biological species

8. Membrane distillation	Microporous membrane	Vapour transport into hydrophobic membrane	Ultrapure water concentration of solutions
9. Pervaporation	Asymmetric membrane	Solution diffusion mechanism	Separation of organics

used to remove all ionic species. Nanofiltration is sometimes referred to as ‘loose reverse osmosis’ as it can remove divalent ions and low molecular weight contaminants while allowing monovalent ions to pass through. Ultrafiltration is used for removal of macromolecules such as proteins and small colloids, but not ionic species. Microfiltration is used to remove particulates, bacteria, and other larger colloids only.

In pressure driven membrane systems the pressure of the feed solution permits passage of the major portion of the solution through a semi-permeable membrane. The portion of the feed solution that passes through the membrane is called permeate, or filtrate. The portion of the feed solution that does not pass through the membrane is called concentrate or retentate. A simple schematic representation of a membrane process is shown in Fig. 1.3.

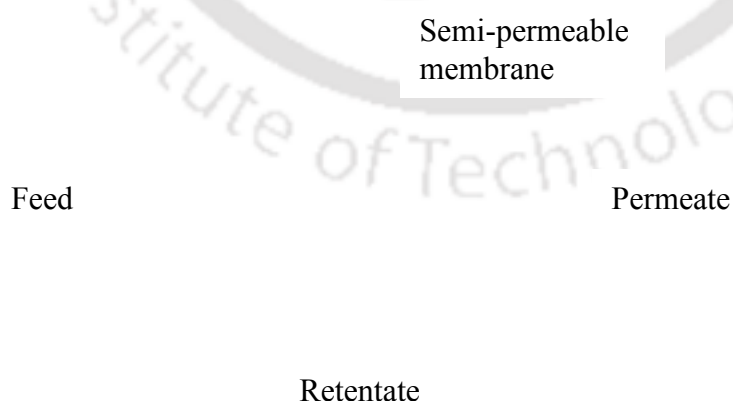


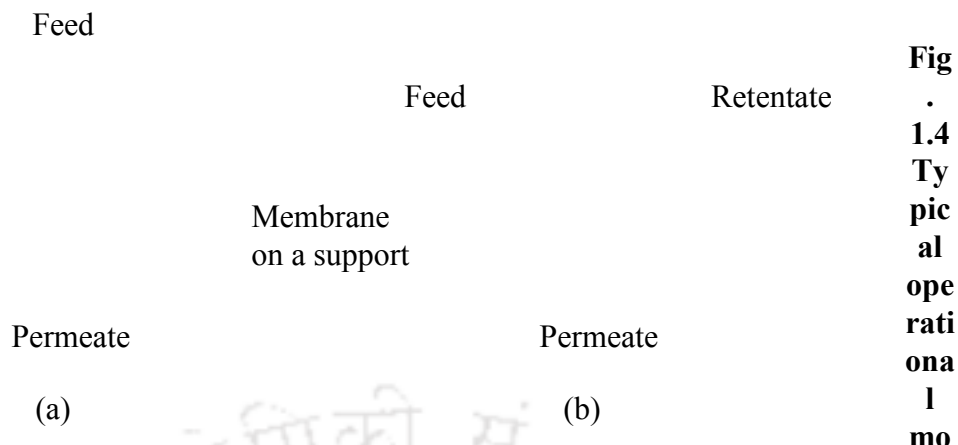
Fig. 1.3
Schematic
representati
on of a
membrane
process

Table 1.4 reports a summary of the main characteristics of the pressure driven processes in terms of pressure, pore size and removable components. Pressure driven membrane processes can be operated either in cross-flow mode or in dead-end (batch) mode. A schematic comparison of dead-end and cross-flow filtration is shown

Table 1.4 Characteristics of the pressure driven membrane processes [22]

Membrane process	Transmembrane Pressure, (bar)	Pores, (nm)	Removable components
Microfiltration	1 - 2	100 - 1000	Suspended solids, bacteria
Ultrafiltration	2 - 10	1 - 100	Macromolecules, viruses, proteins
Nanofiltration	10 - 30	0.5 - 5	Micropollutants, bivalent ions
Reverse osmosis	35 - 100	< 1	Monovalent ions, hardness

in Fig. 1.4. The simplest design is the dead-end operation where the feed is forced to pass through the membrane; this implies that the concentration of rejected components increases in the feed resulting in cake formation over the membrane, which grows with time and consequently the flux decreases with time. In the cross-flow operation, the feed enters the membrane module at a certain composition and flows parallel to the membrane surface; the feed stream is separated into two streams viz. a permeate stream and a retentate stream. Flux decline is relatively



des for ultrafiltration membrane processes:

(a) dead-end configuration and (b) cross-flow configuration [22]

smaller in cross-flow and can be controlled and adjusted by proper choice of cross-flow velocity.

1.2.3. Ultrafiltration (UF)

Microfiltration (MF) and ultrafiltration (UF) membranes are operated under similar process conditions, but differ in pore size characteristics. An UF membrane, due to its smaller membrane pores, is better capable of removing the micron and submicron sized oil particles from oily wastewater than a MF membrane. O/w emulsion separation has now become a large application for UF in industrial sectors such as metal cleaning, food processing, wool scouring, oil industries, etc. and is still growing with the implementation of new environmental legislation.

The UF membrane is considerably more porous, i.e., its nominal pore size is larger compared to the reverse osmosis (RO) membrane. As a result, most soluble species including inorganic salts pass through the membrane with the water; but colloids, suspended solids and high molecular weight organic molecules (e.g. oil) do not pass through the membrane with the water. They are rejected and remain in the concentrate (retentate) stream. The porous nature of the UF membrane allows the

process to be operated with high fluxes at relatively low pressures (e.g. 2 – 10 bars). This is possible because the osmotic pressure of colloids and high molecular weight organics is extremely low. The degree and quantity of the separation are a result of the pore size of the membrane and the molecular structure, size, shape and flexibility of the colloids and organic molecules. Pore sizes ranging from 0.001–0.01 μm allow separation from solution of molecules with a molecular weight between 500 and 3,00,000. The most common terms that are used in UF processes are briefly described in section 1.2.3.1.

1.2.3.1. Common terminologies

Flux

An important property of a membrane is its permeate flux, which is defined as the permeate volume (or mass) through the membrane per unit of membrane area. The permeate flux or simply the flux, J through the membrane is given by the general relation shown in Eq. (1.1) [22, 24]:

(1.1)

where J = flux, ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) or ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)

V = permeate volume, (m^3) or (L)

t = time, (s) or (h)

A = membrane area, (m^2)

The pressure difference across a membrane surface is called the transmembrane pressure (TMP) and is the difference between the pressures at the feed side and at the

permeate side. The relationship between J and TMP is defined by a modified form of Darcy's law as shown in Eq. (1.2):

$$(1.2)$$

where, ΔP = pressure difference, TMP (Pa)

μ = viscosity, (Pa.s)

R_m = total resistance to permeate flow, (m^{-1})

Rejection

Another important characteristic of a membrane to measure its performance is its selectivity [22]. Selectivity can be expressed in terms of rejection (or retention), R , which expresses the extent to which a solute is retained by the membrane and is defined in Eq. (1.3).

$$(1.3)$$

where, R = retention

C_p = concentration in the permeate ($mg\ L^{-1}$)

C_f = concentration in the feed ($mg\ L^{-1}$)

When solutes are completely retained by the membrane, the membrane has $R = 1$.

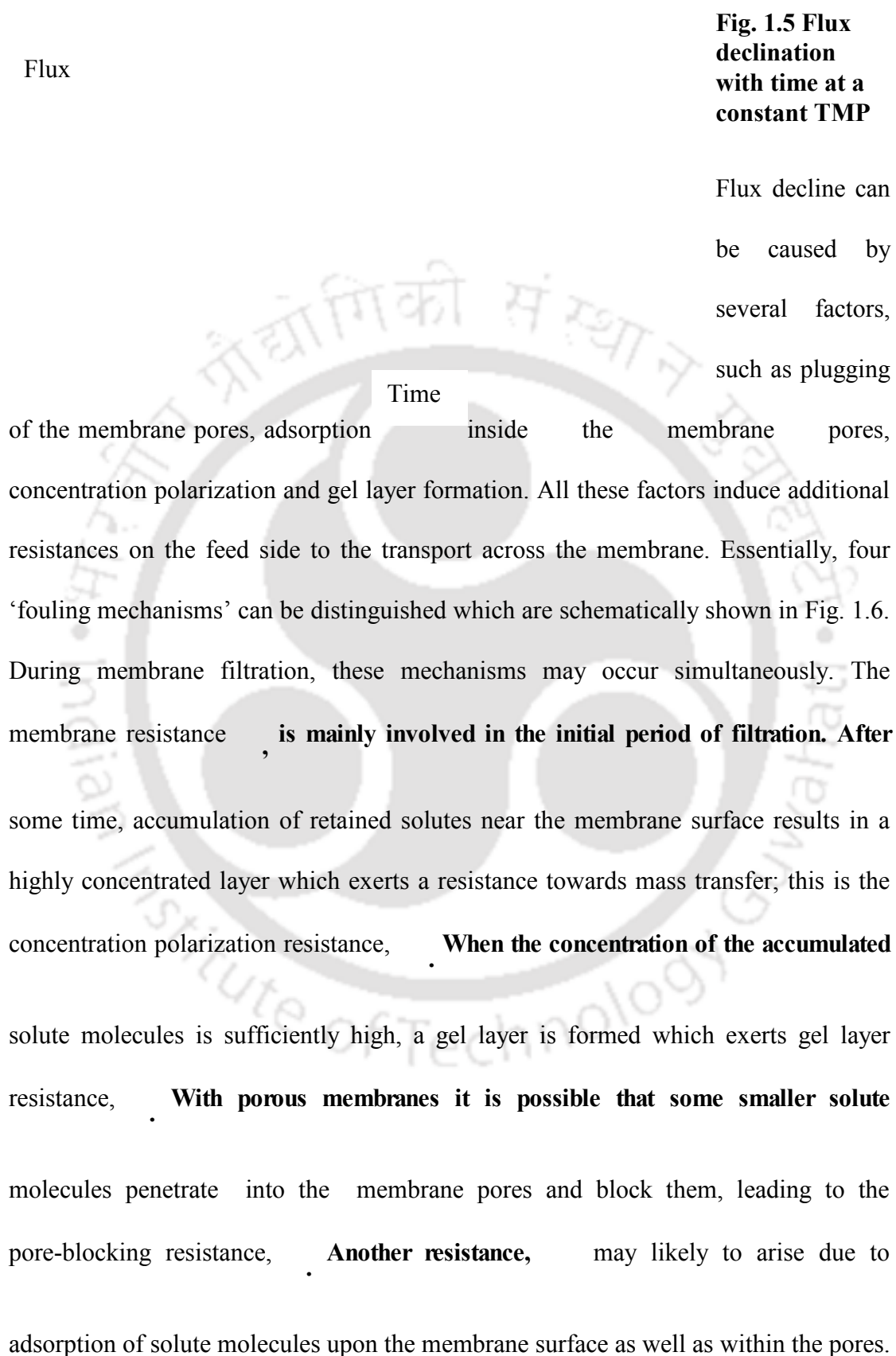
Fouling and its mechanism

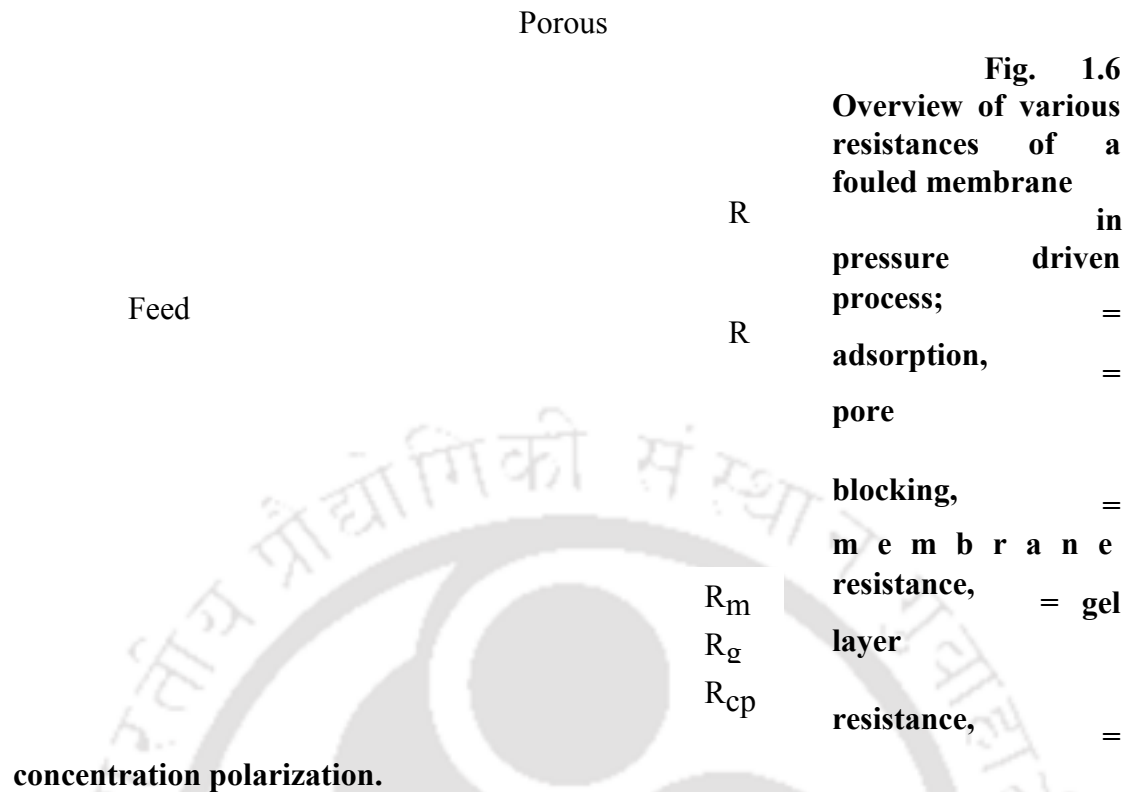
During UF, some constituents of the feed deposit on the membrane surface and/or in the membrane matrix resulting in gradual decrease in permeate flux. This process is often referred to as fouling of the membrane. The common definition of membrane fouling is provided by the International Union for Pure and Applied Chemistry (IUPAC), which defined fouling as: *'Fouling is the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores'* [25].

Mulder (1997) gave a second definition of fouling as: *'The (ir)reversible deposition of retained particles, colloids, emulsions, suspensions, macromolecules, salts etc. on or in the membrane'* [22].

Wiesner and Aptel (1996) defined fouling as an irreversible flux reduction: *'A reduction in permeate flux that cannot be reversed'* [26].

The easily removable part of the retained material is called the reversible part of the fouling layer, the remaining part is called the irreversible fouling layer. The feed constituents that are retained on or in the membrane surface are called foulants. The retention of feed constituents causes an increase of the total resistance over the membrane, resulting in a decreased flux at a constant TMP. The decrease in flux that is found during membrane filtration is schematically shown in Fig. 1.5.





1.2.3.2. Different aspects of ultrafiltration

The successful performance of UF operation depends on mainly four different aspects: Firstly, the feed properties such as concentration, viscosity, pH, etc. influence the membrane filtration process. Feed properties can be changed by pre-treatment either with physical processes or with chemical processes. Physical processes include pre-filtration to remove suspended particles, clay, etc; while chemical processes include pH adjustment, precipitation, coagulation and flocculation in order to remove bigger sized particles.

Secondly, the process configuration influences the membrane filtration process. For industrial applications, a cross-flow operation is usually preferred to dead-end flow because of the lower fouling tendency compared to the dead-end mode. Cross-flow configurations always give better performance than dead-end in terms of high flux;

but these systems consume more energy than dead-end configured systems [27]. Other operating parameters like TMP, temperature, etc. are also important factors that influence the UF performance.

Thirdly, the filtration behaviour is influenced by the membrane characteristics to a great extent. Generally, minimum membrane fouling is found for membranes with a narrow pore size distribution, with a hydrophilic rather than a hydrophobic surface and with a negative surface charge [28, 29]. In the current research work, therefore an attempt has been taken to modify the membranes used for UF experiments.

The fourth aspect of the success of membrane UF is the cleaning of the membrane in order to reduce fouling. Four cleaning methods are generally practised viz. hydraulic cleaning, mechanical cleaning, chemical cleaning and electric cleaning; the choice of the appropriate method depends mainly upon the module configuration, the type of membranes, the chemical resistance of the membrane and the type of foulant encountered [22].

Hydraulic cleaning methods include back-flushing, where the flow is reversed and the permeate is flushed through the membrane pores. As a result, the retained material in the membrane pores and on the membrane is released, lifted up and is flushed out of the membrane module. Typical back flush periods of 30 to 60 seconds are maintained at every 10 to 30 minutes. By regular back flushing during UF under constant TMP, a reasonable flux recovery is possible.

Mechanical cleaning can be applied to only tubular systems using oversized sponge balls [22].

When the components are strongly adsorbed onto the membrane, chemical cleaning

methods are usually very effective. The concentration of the chemicals and the cleaning time are important parameters for efficient use of a chemical cleaning procedure. In order to prevent membrane degradation during a chemical cleaning, the chemical properties of the membrane should be known. Effective cleaning must inhibit the redeposition of the foulants back on the membrane surface. The chemicals that are used for cleaning can be classified in the following way [30]:

- Acids, to dissolve calcium salts and metal oxides;
- Alkalis, to remove silica, inorganic colloids and many biological/organic foulants. The working mechanisms consist of neutralization of acidic material, saponification (hydrolysis) of fat and oil and dispersion/emulsification of colloidal material;
- Surfactants, to displace foulants, to emulsify oils and to dissolve hydrophobic foulants. Surfactants can possess neutral (non - ionic) groups, negatively charged (anionic) groups or positively charged (cationic) groups.
- Oxidants, for oxidation of organic material and bacteria (disinfection);
- Sequestrates (chelating agents), for removal of metal cations from a solution;
- Enzymes, to degrade foulants e.g. proteases to degrade proteins, amylases to degrade polysaccharides and lipases to hydrolyse fatty acids.

Relatively new cleaning methods for UF membranes are developing; they are ultrasound associated cleaning (at 45 kHz) [31] or vibration (50-1000 Hz) of the module [32]. However, these cleaning methods are not yet applied in real practice.

1.2.4. Selection of membrane

Selection of the membrane material and its configuration are the most important aspects of the membrane system design. A wide variety of membranes are commercially available with different operational characteristics. The choice of a membrane must be based not only on the performance data (i.e. rejection and flux), but also on the interaction of the membrane with the feed solution to know whether this will lead to stable operation and minimal fouling.

Membrane separation processes are governed by both the chemical nature of the membrane materials and the physical structure of the membranes. The desired separation attainable with a particular membrane depends on the relative permeability of the membrane for the particular feed solution. The most important characteristics of membranes are pore size distribution, porosity, surface chemistry, chemical and physical compatibility with process feed, and cost. Beside this, there are some other factors which decide the final selection of membrane. For example, the membrane has to be of suitable thickness to be able to withstand the pressure within the operating pressure range i.e. it should have sufficient mechanical strength. This characteristic is disadvantageous in operation as it creates a higher hydraulic resistance to flow. The conflicting requirements to have a membrane with low hydraulic resistance but to contain pores small enough to effectively reject oil particles can be found in asymmetric membranes (Section 1.2.1) which can be successfully prepared by the phase inversion method [22]. The selectivity of the separation process is controlled by the properties of the skin layer while the porous supporting layer only serves to improve the mechanical properties of the membrane. In this work, organic i.e. polymeric materials are chosen as the material for the membrane which is to be applied in UF of oily water treatment. Ceramic material is not considered due to its

high cost and also due to the inability to prepare membrane by phase inversion method. A brief summary of the important polymers used in membrane manufacture is given in the next section.

1.2.5. Materials for organic membranes

The most important class of material for organic membranes includes the polymers. The choice of the polymeric material for a particular membrane is based on its chemical and physical properties originating from structural factors such as molecular weight, chain flexibility and chain interaction. Those factors also determine the membrane permeability [22]. Chemical properties describe how the material chemical structure changes under certain circumstances such as change in pH, temperature, etc. Physical properties include density, melting point, glass transition temperature, compressibility, etc [33].

The process of making the UF and MF membranes has to control both the surface characteristics, and the supporting sub-structure. Polymers should have good mechanical properties to produce membranes, with a reasonable degree of flexibility. Also, they need to have good chemical resistance, tolerance limit of a wide pH range, and high chlorine concentrations, enabling rigorous cleaning to be conducted if necessary. In addition, thermal resistance should be good, so that moderate elevated temperatures can be used without affecting the membrane properties or life [34].

Commercial thermoplastics and cellulose were primarily used as membrane materials for large scale production. Basically all polymers can be used as membrane material but the chemical and physical properties differ so much that only a limited number is

used in practice. Since the initial development of the first asymmetric cellulose acetate membrane, significant progress has been made in the field of non-cellulosic membrane materials that are more durable, less susceptible to biodegradation, and perform well within broad pH and temperature ranges. The materials most commonly used for the production of UF membranes by phase inversion method are:

- Cellulose acetate (CA);
- Aromatic Polyamide (PA);
- Polysulfone (PSf) and Polyethersulfone (PES);
- Polyvinylidene fluoride (PVDF);
- Polyacrylonitrile (PAN)
- Polypropylene (PP)
- Polyethylene (PE)

Commercial UF/MF membranes cover the range from fully hydrophilic polymers such as cellulose acetate (CA), to fully hydrophobic polymers such as polypropylene (PP) and polyethylene (PE). Between the two extremes, there is the polysulfone (PSf) / polyethersulfone (PES) family, polyacrylonitrile (PAN), and polyvinylidene fluoride (PVDF) [34]. Though these polymers are hydrophobic, various methods are adopted to make them hydrophilic and less prone to fouling. The methods include surface coating by adsorption, free radical or radiation grafting of hydrophilic polymers, plasma treatment, chemical conversion of polymer side chains to hydrophilic groups, blending with hydrophilic polymers, etc [21]. It is important that the membrane polymer is a product of low or medium price in large scale applications.

Figure 1.7 compares the common polymers in terms of strength and flexibility [35].

PES has similar mechanical properties to those of PSf. It shows that PSf and PVDF

are the strongest polymers, whilst PVDF is more flexible. Of the polymers discussed above, the PSf/PES family has the widest chemical resistance, and can tolerate a pH range from 1.5 to 13, as well as moderate chlorine levels. PVDF tolerates acids, but is limited to pH 11 with caustic. However, its major advantage is a very high tolerance to chlorine, which makes it ideal for membrane reactors. Chlorine cleaning is preferred for PVDF membranes while PSf/PES may choose for caustic cleaning. PAN

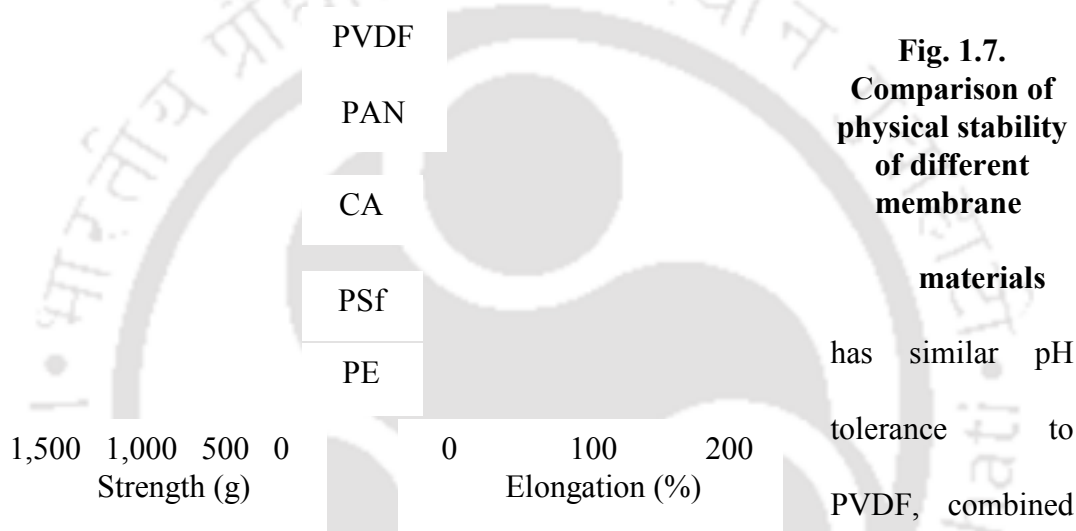


Fig. 1.7.
Comparison of
physical stability
of different
membrane
materials

has similar pH
tolerance to
PVDF, combined

with a moderate chlorine tolerance (almost similar to PSf/PES). CA is much more limited in its chemical resistance, since its natural hydrophilicity makes it susceptible to hydrolysis in the presence of acids below pH 4 and alkalis above pH 8. It tolerates chlorine, but is biodegradable which makes it sensitive to bacterial attack. Despite these limitations, CA can be effectively used in applications where chemical cleaning requirements are limited, such as groundwater and some surface waters. The polyolefin family, PP and PE, has good tolerance to acid and caustic, but low tolerance to chlorine, particularly in the case of PP. The lack of chlorine tolerance is a major limitation in the water industry, and this has limited the prospects for these membranes.

The solubility of PSf/PES makes these polymers ideal candidates for polymer blend membranes since other polymers can be co-dissolved, allowing the hydrophilic properties of the finished membrane to be modified and enhanced. Thus PSf/PES can be made hydrophilic with the appropriate blend polymers [36], thereby gaining the advantage of the hydrophilicity of CA, whilst avoiding the primary disadvantages of CA, namely biodegradability, and poor tolerance to caustic cleaning chemicals. PVDF membranes though can be formed by phase inversion methods, it is more difficult to modify since hydrophilic additives tend to lead to macrovoid formation and a weakening of the structure. Accordingly, most commercial PVDF membranes are relatively hydrophobic with surface characteristics close to the unmodified polymer. For this research work, polysulfone (PSf) has been chosen as the key polymer for the fabrication of UF membranes for oil separation due to the following advantages [21]:

- High chemical resistance.
- Usability in a wide pH range.
- Soluble in solvents like DMAc and NMP, making it easily applicable for the conventional phase inversion processes.
- High thermal stability.
- Good mechanical strength and permeability.
- Ability to modify properties through blending with other polymers.

The first developments of PSf membranes appeared in the 60's as an alternative to cellulosic membranes [23]. A major disadvantage of PSf made membranes is their hydrophobic character, which prevents spontaneous wetting with aqueous media. It is well known that hydrophobic materials often possess a powerful non-specific adsorption capacity, which leads to a rapid deterioration of the membrane

permeability. One effective way to make PSf membranes more hydrophilic is to prepare the membranes from a mixture of sulfonated and non-sulfonated PSf [23]. Insolubilization can also be achieved by cross linking with additives such as polyols or polyphenols. Preparation of membranes from polymer blends with hydrophilic polymers has been well described in the literature [23]. Polyvinylpyrrolidone (PVP) and poly(ethylene glycol) (PEG) are the two commonly applied polymers for this purpose.

The work reported here aims to synthesize polysulfone (PSf) membranes with required morphological and performance properties in order to make them suitable to separate oil from oily wastewater generated from petroleum sites. An attempt has been made to enhance porosity and hydrophilicity of the synthesized membranes through the use of different molecular weight additives such as PVP and PEG. The information regarding structural formulae and physical properties of PSf, PVP and PEG are given in the Appendix I.

1.2.6. Preparation of synthetic membranes: some common techniques

The aim of preparing synthetic membranes is to modify the materials by means of an appropriate technique to obtain a membrane structure with a morphology suitable for a specific separation.

There are several methods of preparation of polymeric membranes. Dense homogeneous polymer membranes are usually prepared (i) from solution by solvent evaporation only or (ii) by extrusion of the molten polymer. Usually the permeate flow across such membrane is quite low. Most of the presently available membranes are either porous or consist of a very thin dense selective top layer on a porous

structure of reasonable mechanical stability (asymmetric or composite membrane). The asymmetric membranes, which can produce high permeate flow resulting from the underlying porous structure, characterize most of the presently available commercial membranes and are produced from a wide variety of polymers as discussed in Section 1.2.5. By far the most common method used in preparation of asymmetric membranes, particularly in the case of UF, is the “phase inversion” process. The other conventional techniques used for preparing polymeric membranes are sintering, stretching, track-etching and solution coating. A brief description of these conventional techniques is given in the subsequent section.

Sintering

This technique involves compressing a powder consisting of particles of a given size and sintering at elevated temperatures. During sintering, the ‘interfaces’ between the contacting particles disappear. It is a very suitable process for preparing membranes from Polytetrafluoroethylene. Only MF membranes can be prepared by this technique [22].

Stretching

This method is suitable only for semi-crystalline polymeric materials (e.g. PTFE, PP, PE). Here the extruded film or foil made from the polymeric materials is stretched perpendicular to the direction of the extrusion. When a mechanical stress is applied, small ruptures occur and a porous structure is resulted [22]. Microporous PP membranes made by this process are commercially available under the trade name “Celgard”. “Gore-Tex” is the trade name for poly(tetrafluoroethylene) (PTFE) membrane made by stretching technique.

Track-etching

The simplest pore geometry in a membrane is an assembly of parallel cylindrical shaped pores of uniform dimension. Such structures can be obtained by track-etching in which a film or foil (often a Polycarbonate) is subjected to high energy particle radiation applied perpendicular to the film. The particles damage the polymer matrix and create 'tracks'. The film is then immersed in an acid or alkaline bath and the polymeric material is etched away along these tracks to form uniform cylindrical pores with a narrow pore size distribution. Pore size can range from 0.02 to 10 μ m, but the surface porosity is low [22]. A feature of the track-etch preparation technique is that the pores are uniform cylinders traversing the membrane at right angles. The membrane tortuosity is, therefore, close to one, and all pores have the same diameter. Nuclepore membranes remain the principal commercially available track etch membranes.

Solution coating

Dense polymeric membranes in which transport takes place by diffusion generally show low fluxes. To increase the flux, composite membranes are prepared. Some composite membranes consist of two different materials, with a very selective membrane material being deposited upon a more or less porous sub-layer as a thin layer. The actual selectivity is determined by the thin top layer, where the porous sub-layer serves as a support. Several coating procedures can be used such as dip coating, plasma polymerization, interfacial polymerization and in-situ polymerization to achieve these membranes [22].

Phase inversion

This versatile technique allows all kinds of morphologies (i.e. both symmetric and

asymmetric) to be obtained. The term phase inversion describes the process most clearly, which is, changing a one-phase casting solution into two separate phases. In all phase inversion processes, a liquid polymer solution is precipitated into two phases: a solid, polymer-rich phase that forms the matrix of the membrane and a liquid, polymer-poor phase that forms the membrane pores. By controlling the initial stage of phase transition, the membrane morphology can be controlled i.e. porous as well as nonporous membranes can be prepared. Phase inversion membranes can be prepared from a wide variety of polymers – the only condition is that the polymer must be soluble in a solvent or a solvent mixture. Here, the polymer solution or the casting solution is often cast directly upon a support by means of a casting knife (doctor's knife). Precipitation of the cast liquid polymer solution to form the membrane can be achieved in several ways, as summarized in Table 1.5 [37]. Two different techniques have been employed for the precipitation of membranes from a polymer casting solution. In the first method, the precipitant is introduced from the vapor phase. The significant feature of the vapor-phase precipitation process is the slow diffusion of precipitant from the vapor phase adjacent to the film surface into the polymer solution which results in a more or less homogeneous structure without a dense skin on the top i.e. a symmetric membrane.

Table 1.5 Procedures for preparation of membrane by phase inversion [37]

Procedure	Process
(1) Water precipitation (the Loeb-Sourirajan process)	The cast polymer solution is immersed in a nonsolvent bath (typically water). Absorption of water and loss of solvent cause the film to rapidly precipitate from the top surface down.

(2) Water vapour absorption	The cast polymer solution is placed in a humid atmosphere. Water vapour absorption causes the film to precipitate.
(3) Thermal gelation	The polymeric solution is cast hot. Cooling causes precipitation.
(4) Solvent evaporation	A mixture of solvents is used to form the polymer casting solution. Evaporation of one of the solvents after casting changes the solution composition and causes precipitation.

In the second membrane precipitation procedure, the precipitant is added to the casting solution by immersing the cast polymer film in a bath of the precipitation fluid. In this case, the precipitation is rapid, and an asymmetric membrane structure is obtained.

Precipitation by immersion in a bath of water was the technique first discovered by Loeb and Sourirajan. Precipitation can also be caused by absorption of water from a

humid atmosphere which is the second method. The third method, known as thermal gelation, is to cast the film as a hot solution. As the cast film cools, a point is reached at which precipitation occurs to form a microporous structure. In the fourth method, evaporation of one of the solvents in the casting solution is carried out to cause precipitation. In this technique, the casting solution consists of a polymer dissolved in a mixture of a high volatile solvent and a less volatile solvent. When the solution is cast as a film and allowed to evaporate, the high volatile solvent evaporates first, as a result of which the film becomes enriched in the less volatile solvent, and finally

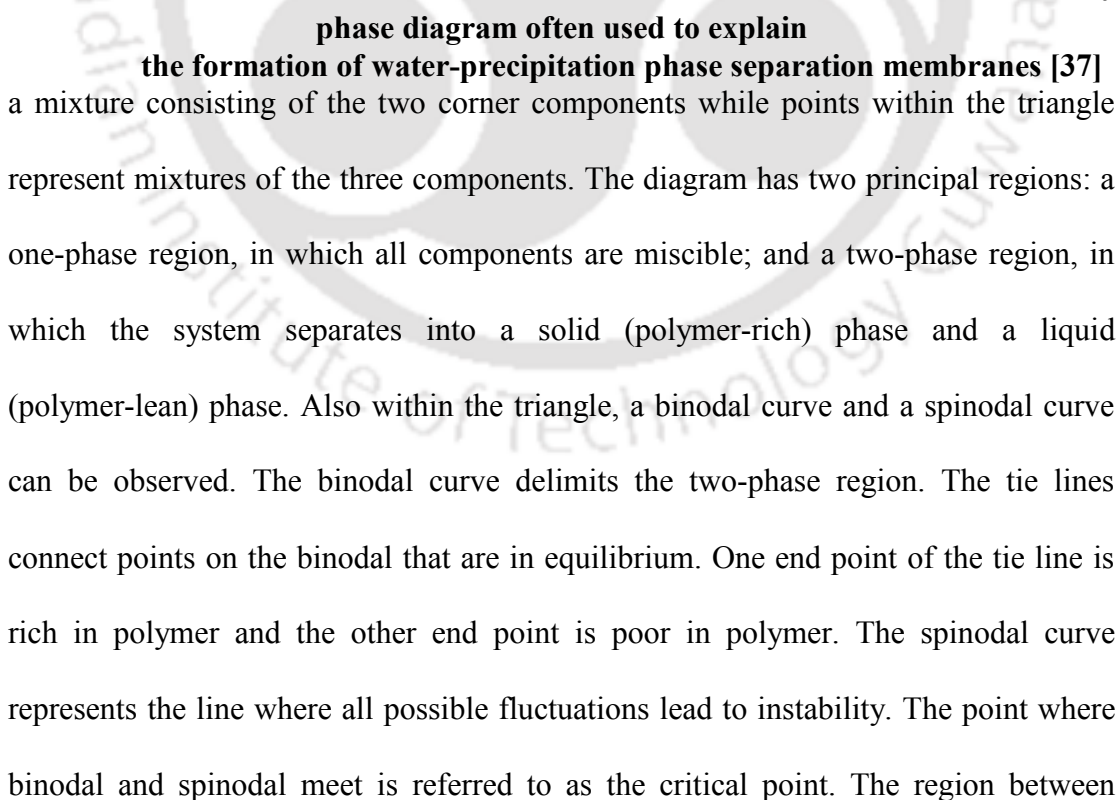
precipitates. In this work, the membranes are prepared by immersion precipitation technique.

1.2.6.1. Immersion precipitation

In this technique, the polymer solution (polymer plus a solvent) is cast on a suitable support (e.g. a glass plate) and precipitation is induced by immersing the cast film of polymer solution in a coagulation bath containing the nonsolvent. The solvent diffuses into the coagulation bath whereas the nonsolvent diffuses into the cast film. The exchange of solvent and nonsolvent continues till the solution becomes thermodynamically unstable and demixing takes place and precipitation occurs [22]. Water is often used as the non-solvent but organic solvent such as methanol can also be used. Selection of nonsolvent is an important parameter in obtaining the desired structure of the membrane. Other important parameters which determine the ultimate membrane morphology and hence its performance (i.e. flux and selectivity) are choice of polymer and its concentration, selection of appropriate solvents, use of any modifiers or additives, evaporation time, humidity, temperature and the composition of the casting solution [22, 37]. The membrane structure finally obtained results from a combination of mass transfer and phase separation. The morphology is usually asymmetric, with a selective skin on the surface.

1.2.6.2. Theory of membrane formation by immersion precipitation

Phase inversion by immersion precipitation involves a phase separation of a polymer solution into polymer rich and polymer lean phases. This can be explained with the aid of the three-component isothermal phase diagram (also known as ternary phase diagram) shown schematically in Fig. 1.8.



binodal and spinodal corresponds to metastable compositions where phase separation by nucleation and growth takes place. Initially, when the polymer is dissolved in the solvent, a homogeneous (i.e. thermodynamically stable) polymer solution is obtained. When the solution comes in contact with the nonsolvent, the solution becomes thermodynamically unstable as a result of which, precipitation of the polymer solution occurs.

During precipitation of the membrane casting solution, the solution loses solvent and gains water. The casting solution moves from a composition in the one-phase region to a composition in the two-phase region. When binodal is reached, liquid-liquid demixing occurs. During the precipitation process, the casting solution enters the metastable two-phase region of the phase diagram by crossing the so-called binodal boundary. Polymer solution compositions in this region are thermodynamically unstable but will not normally precipitate unless well nucleated. The metastable region in the phase diagrams of low molecular weight materials is very small, but can be large for high molecular weight materials. The path **A - D** represents the entire precipitation process along which the solvent is exchanged by the precipitant. If the precipitation path crosses the binodal below the critical point, nucleation of a polymer rich phase initiates the phase separation process. On the other hand, if the precipitation path crosses the binodal above the critical point, nucleation of polymer lean phase may occur [22]. The tiny droplets (i.e. nuclei) formed consist of a mixture of solvent and nonsolvent with little polymer dispersed in the polymer-rich phase. These droplets grow further until the surrounding continuous phase solidifies. Coalescence of these droplets before solidification leads to the formation of a more porous structure. As more solvent leaves the casting solution and water enters the

solution, the composition crosses the spinodal boundary and enters into the unstable region of the phase diagram in which a one-phase solution is always thermodynamically unstable. In this region, polymer solutions spontaneously separate into two phases with compositions linked by tie lines. Thus, the membrane precipitation process occurs in a series of steps. First, solvent exchange with the nonsolvent i.e. liquid-liquid demixing occurs. Then, phase separation or precipitation begins as the composition enters the two-phase region of the phase diagram. Finally, the polymer phase converts to a relatively solid gel phase, and the membrane structure is fixed.

Strathmann et al. [38] presented the process of membrane formation through the line (**ABCD**) as shown in Figure 1.8 which gives the concentration at any point in the film at a particular moment. During membrane formation, the composition changes from the initial casting solution composition **A**, to the final membrane composition **D**. At composition **D**, the two phases are in equilibrium: a solid (polymer-rich) phase, which forms the matrix of the final membrane, represented by point **S**, and a liquid (polymer-poor) phase, which constitutes the membrane pores filled with precipitant, represented by point **L**. The position of composition **D** on the line **S - L** determines the overall porosity of the membrane. The point **B** along the path is the concentration at which the polymer initially precipitates. As precipitation proceeds, more and more solvent is lost and the viscosity of the solution is raised. At some point, the viscosity becomes high enough for the precipitated polymer to be regarded as a solid. This composition is shown at point **C** in the figure. Once the precipitated polymer solidifies, further bulk movement of the polymer is hampered [37].

The description of the formation of membrane by means of the phase diagram, as illustrated in Figure 1.8 is based on the assumption of thermodynamic equilibrium. Such assumption is not able to offer any explanation about structural variations within the membrane cross section, that is, whether the membrane has a symmetric or asymmetric structure. These parameters are determined by kinetic effects, which depend on system properties, such as the diffusivities of the various components in the mixture, the viscosity of the solution and the chemical potential gradients which act as driving forces for diffusion of the various components in the mixture. As these parameters change continuously during the phase separation, no transient states of equilibrium will be achieved. The chemical potential and diffusivities of the various components in the system, and their dependency on composition, temperature, viscosity, etc., are difficult to determine by independent experiments [39]. Thus a quantitative description of the membrane formation mechanism is not possible with the concept of ternary phase diagram; however, this may be considered as a very useful tool in understanding how the casting solution is altered to form membranes of varying pore size and permeability. The tool is limited because it does not provide direct information about pore sizes nor does it distinguish between the dense skin and the porous sub-layer. However, if we assume that a membrane having a larger overall porosity will have a higher porosity in the skin as well as in the substructure, and that the higher porosity is associated with higher permeability and larger number of pores, the model can be very instructive [38]. The overall porosity of an anisotropic membrane is determined by the polymer content of the casting solution and by the relative rates at which nonsolvent enters and solvent leaves the casting solution (i.e. the precipitation path in the phase diagram). It has been demonstrated that when water

(nonsolvent) enters the film faster than the solvent leaves, an open porous membrane results; while a tight dense membrane results when solvent leaves the film faster than water enters [39]. Figure 1.9 is a ternary phase diagram for a casting solution made of cellulose acetate (CA) and acetone; it shows several different paths of precipitation which lead to the formation of porous UF membranes and dense RO membranes [39].

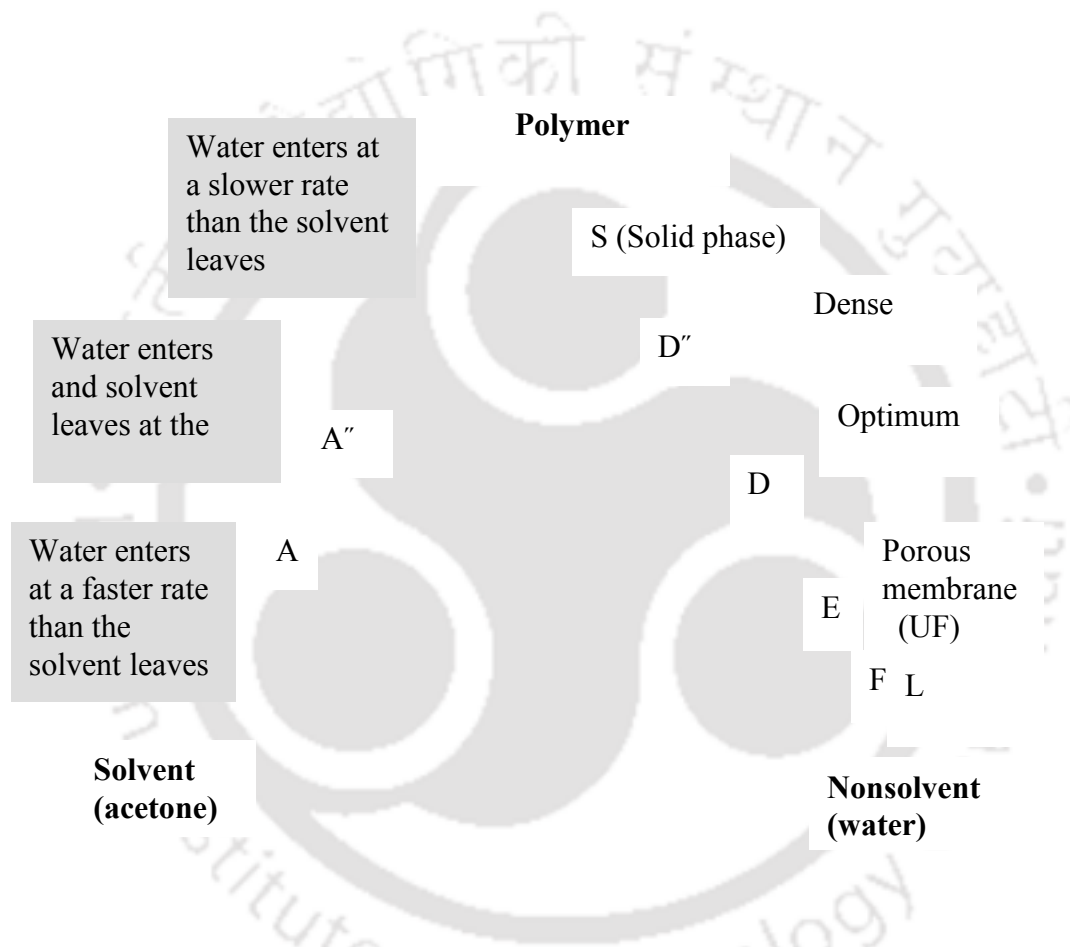


Fig. 1.9. Ternary phase diagram for formation of RO and UF membranes from cellulose acetate and acetone [39]

1.2.6.3. Instantaneous demixing and delayed demixing

According to Mulder [2], during membrane formation, two types of liquid-liquid demixing can occur viz. instantaneous demixing and delayed demixing (Fig. 1.10). When demixing occurs immediately after immersion, it is instantaneous demixing which leads to the formation of membranes with a relatively porous top layer and a

sub-layer with finger-like cavities. When no demixing occurs immediately after immersion, delayed demixing is said to occur which results in membranes with a relatively dense top layer and a sub-layer with less macrovoids (sponge-like structure). The macrovoid formation in the membrane sub-layer is believed to be due to the formation of nuclei of the polymer-poor phase as a result of liquid-liquid demixing process. Most of the macrovoids start to develop just beneath the top layer, due to initiation and growth of the nuclei formed directly beneath the top layer. When liquid-liquid demixing takes place instantaneously, the first droplets of the

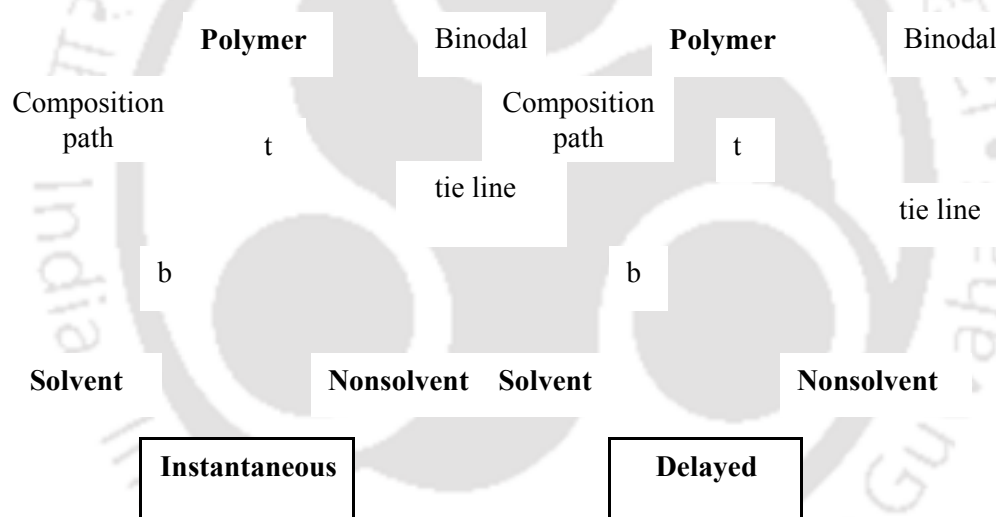


Fig. 1.10 Schematic showing mechanism of instantaneous demixing and delayed demixing; t – composition at the top of the film; b – composition at the bottom of the film.

polymer poor phase form at a very early period and the growth of macrovoids occurs due to diffusion of solvent-nonsolvent into the first nuclei. Thus growth of nuclei continues until the polymer concentration at the macrovoid-solution interface becomes sufficiently high so that solidification starts. This results in finger-like cavities in the sub-layer. On the other hand, in the case of delayed demixing,

nucleation is not possible until a certain period of time has elapsed. So only after a certain time, the nucleation starts which cannot grow for a long time due to high polymer concentration; so the tendency of macrovoid formation is less in this case. The presence of too many macrovoids in the sub-layer is generally not favourable, because they signify weak spots in the membrane especially when high pressure is applied e.g. gas separation. Also such membranes lead to high compaction when applied for MF or UF purposes.

Fig. 1.10 is a schematic representation of the composition path of a polymer film at the very moment of immersion into a nonsolvent bath (time < 1 second). The left figure indicates that all the compositions directly beneath the top layer have crossed the binodal which means the liquid-liquid demixing starts immediately after immersion; in contrast, in the right figure all the compositions beneath the top layer still lie in the one phase region indicating that no demixing has taken place immediately after immersion.

1.2.6.4. Important parameters influencing membrane structure

It is essential to know the key factors which affect the membrane morphology after immersion of the polymer/solvent mixture into the nonsolvent coagulation bath. The overall porosity of the membrane is determined by the polymer content of the casting solution and by the relative rates at which nonsolvent enters and solvent leaves the casting solution.

The choice of polymer is important as it limits the solvents and nonsolvents to be used in the phase inversion process. As discussed in the previous section, effect of polymer-solvent-nonsolvent interaction plays a major role on membrane structure and

properties. Membrane structure can be correlated with the rate of precipitation. Very high precipitation rates always lead to a “finger-like” structure in the sub-layer, while slow precipitation rates lead to asymmetric membranes with a “sponge-like” substructure, and very slow precipitation rates very often lead to symmetric membranes with no defined skin at the surface. The solvent and the nonsolvent (precipitant) used in membrane preparation determine both the activity coefficient of the polymer in the solvent-precipitant mixture and the concentration of the polymer at the point of precipitation and solidification [39]. The polymer-solvent-precipitant interaction can be approximately correlated in terms of the difference of the solubility parameter of polymer and solvent. The smaller the difference in solubility parameter, the better the compatibility of solvent and polymer and the slower is the precipitation of the polymer. In such case, the tendency is to form membranes with sponge-like structure. The higher the difference in solubility parameter, the less compatible are polymer and solvent, and the faster will be the precipitation. The tendency to change from a sponge to a finger structure will thus increase with decreasing compatibility of polymer and solvent.

The polymer concentration is another significant parameter for tailoring a membrane in terms of its structure and separation properties. With increasing polymer concentration, the structure changes from a typical finger structure to a typical sponge structure.

The nature of the solvent is seen to have a marked influence on the transport properties of the resulting membrane. A high affinity between the solvent and the nonsolvent is a strong factor in the formation of a highly porous membrane. Eirich et

al [40] found that regardless the nature of the polymer, the highest porosity membranes could be made from casting solutions using solvents with high solubility parameters. Water (the precipitant) has a solubility parameter (23.4) higher than the solvents commonly used, such as dimethyl formamide (DMF), dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dioxane, acetone, tetra-hydrofuran (THF), etc. The porous membrane structure seems to be related to the greater compatibility of water with solvents having higher solubility parameters. When the polymer begins to precipitate, the residual solvent may tend to exclude water if there is too great a disparity between the solubility parameter. The result is a dense, low porosity membrane. On the other hand, smaller differences in the solubility parameter would tend to favor inclusion of water resulting in a membrane with higher porosity.

Additives if added to the casting solution also has significant role in membrane properties. They adjust the rate of solvent-nonsolvent flow in order to have desired membrane structure. Addition of additives (both low molecular weight and high molecular weight) also prevents macrovoid formation to certain extent. From a thermodynamic point of view, any additive in the casting solution would increase the rate of water entry and decrease the rate of solvent removal resulting in more porous membranes. Addition of salts such as zinc chloride and lithium chloride and polymers such as poly(vinyl pyrrolidone) and poly(ethylene glycol) are commonly used which make the membrane more porous [22]. Although most of these water-soluble polymers and salts are removed during precipitation and washing of the membrane, a portion remains trapped, making the final membrane more hydrophilic.

Temperature of the water used to precipitate the casting solution is another factor affecting membrane morphology. Generally, low-temperature precipitation produces denser membranes.

1.3. Literature review

This section describes the published experimental and theoretical works relevant to the present work. Literature survey was carried out to understand the state-of-the-art information regarding the synthesis and performance of membranes. The section discusses in detail the studies carried out by different researchers in synthesizing organic membranes by phase inversion method. It elaborates the studies that have been carried out to see the effect of addition of additives into the membrane casting solution. It further focuses on the research works that have been performed so far in oily water treatment by membrane technology. Finally it highlights the literature related to membrane fouling and the developed model equations to evaluate the fouling mechanism.

1.3.1. Synthesis of membrane

Phase inversion, as discussed in Section 1.2.6 is one of the most important processes for preparing both symmetric and asymmetric polymeric membranes. The predominant mechanism of phase inversion leading to pore formation and the thermodynamics involved are the subject of a fruitful and sometimes controversial discussion in the literature. Reuvers et al. [41] developed a model which explained the two types of demixing taking place during the phase inversion process i.e. instantaneous demixing and delayed demixing. Membranes formed by instantaneous demixing generally show a highly porous substructure (with macrovoids) and a finely

porous, thin skin layer. Membranes formed by a delayed demixing mechanism show a porous (often closed-cell, macrovoid-free) substructure with a dense, relatively thick skin layer. In order to get membrane with suitable structure and permeation property, introduction of a suitable additive to the casting solution is a convenient and efficient method. It is reported that the additives can affect the final membrane characteristics either by changing solvent capacity or by changing phase separation kinetics and thermodynamic properties [42]. The additive can be a single component or a mixture. Generally the additive being a weak non-solvent for the polymer, reduces the solvent power in the solution. A number of researchers [36, 43, 44] have reported their observation on the role of additives in the membrane structures. Glycerol in a system of polysulfone (PSf)/dimethyl acetamide (DMAc)/water, maleic acid in a system of cellulose acetate (CA)/dioxane/water, polyvinyl pyrrolidone (PVP) in a system of polysulfone (PSf)/N-methyl-2-pyrrolidone (NMP)/water and polyethylene glycol (PEG) in polyvinylidene difluoride (PVDF)/dimethyl formamide (DMF) or dimethyl acetamide (DMAc)/ water system are examples of some well known additives in different systems [36, 43]. Either enlargement or suppression of macrovoid can be obtained using the same additive, but with a variation of additive concentration or additive molecular weight. While some additives have the tendency to form macrovoids, others help in suppressing the macrovoids improving interconnectivity of the pores and resulting in higher porosities in the top layer and the sub-layer. Study of Boom et al. [36] using PVP as an additive in the formation of the membrane with poly (ether sulfone) (PES) in NMP as solvent showed that PVP suppresses the formation of macrovoids by reducing the possibility of delayed demixing. They suggested that the macromolecular nature of the additive is responsible for the suppression of formation

of macrovoids. It was shown that the nodular structure appearing in the top-layer of ultrafiltration membranes was probably a result of spinodal demixing. Study of Yeo et al. [43] using PVP in the casting solution of PSf and DMF indicated the enlargement of the macrovoid structure in the prepared membranes rather than the suppression of that structure. Wienk et al. [44] discussed the effects of addition of a high molecular weight PVP in solutions of PSf and PES in NMP and low molecular weight dicarboxylic acids as additives in polyimide/DMF solutions for the preparation of UF membranes. They proposed a mechanism for the formation of nodular structures in the top layer of membrane. According to their proposed mechanism, the nodular structure is due to the collapse of polymer molecules during formation of the top layer in the direction perpendicular to the surface. This one dimensional collapse into a "flat" conformation of the molecules in the nodules causes large tensions in the other two dimensions, as well as voids inside the nodules. The flat molecular conformations rearrange into spherical conformations and a large surface shrinkage results during drying process. Han and Nam [45] reported the effect of PVP (55,000 Da) introduction on the thermodynamic and rheological properties in PSf casting solution. They concluded that at low PVP concentration (5 wt%), the flux increases with the enhancement in the phase separation, but it drops with further increase of PVP in the casting solution rather than improved. Han [46] showed that the number of the polymer aggregates or of the nucleation sites is increased by the addition of propionic acid (PA) into PSf casting solution. The overall results indicated that in the specific concentration of 15 wt% PSf solution, the PA added in the casting solution works as a significant "demixing enhancer" in the phase inversion process. Lee et al. [47] prepared PSf membranes via diffusion-induced phase inversion process from casting

solutions consisting of PSf and DMF, using PVP as a polymeric additive. The effect of addition of PVP to the casting solutions was analyzed by measuring the prepared membranes' morphology and water permeability. They suggested that the thermodynamic variation due to PVP addition works in favour of the enhancement of demixing in the casting solution, but the rheological variation induces the opposite trend, or the delay of demixing. Zheng et al. [48] in their recent work described the effect of rheological and thermodynamic variation of PSf casting solution due to PEG introduction on the kinetics of membrane formation. PSf membranes were prepared via phase-inversion process from a homogeneous casting solution containing PSf/PEG/DMAc/NMP. Ethanol solution (20 wt%) was added to the coagulation bath. In the casting solutions, PSf concentration was maintained at 18 wt% and PEG concentrations were separately maintained at 4, 8, 10, 12 and 16 wt%. They observed that PEG addition could work in favour of the thermodynamic enhancement and rheological hindrance in PSf casting solution demixing. On the basis of the relationship between wet membrane thickness (d) and coagulation time (t), kinetics parameter (K) was calculated using the equation ($K = \frac{d}{t}$). It was found that K increased first and then decreased at a certain temperature (20 °C) with the increase of PEG concentration; while t increased continuously with the increase of coagulation bath temperature. Hou et al. [49] studied the interaction between PSf and 71 low molecular weight organic compounds with different functional groups by the gas liquid chromatography (GLC) and proposed a model to explain the experimental results. PEG with molecular weight of 600, 2000, 6000 and 12,000 Da was used as additives to control the thermodynamics and kinetics in casting solution of PSf

membranes in Kim and Lee's work [50]. Chen et al. [51] found that in the PSf/NMP/water ternary system, polar additives such as ethanol, propanol, butanol and pentanol cause rapid demixing of casting solution and form porous asymmetric membranes with defective skin layer while non-polar additive such as chloroform delays the demixing rate of casting solution and form asymmetric membranes with defect-free skin layer. Several other researchers have reported effects of addition of PEG and PVP into casting solution of polymer compositions other than PSf. Ochoa et al. [52] carried out a study to observe the effect of small amount of PVP as additive of two molecular weights viz. 40,000 Da and 3,60,000 Da on PES ultrafiltration membranes made by phase inversion method. The solvents were DMF and THF. The PES concentration was 17 wt.% in a casting solution formed by DMF with 1.5 wt.% of THF and 2 wt.% of PVP. It was proved that the addition of small quantities of PVP of different molecular weights resulted in an increase of membrane permeability without significant changes in selectivity. Chaturvedi et al. [53] studied the effect of different additives such as maleic acid (MA), PEG-12000 and piperazine (PP) on performance of PES UF membranes. The additives were selected specifically to study the effects of acidic or basic nature (of the additive) on the membrane performance. PES membranes were prepared by phase inversion method using NMP and DMF as solvents. The weight ratio of the polymer, solvent and additive in the casting solution was maintained at 15:70:15. They found that the acidic/basic nature of the additive affects the viscosity of the casting solution as well as the water permeation rate of the resultant membranes. Jimenez et al. [54] studied the effect of four processing variables on the final properties of PES UF membranes which were the concentration of base polymer in the casting solution, the solvent evaporation time, the addition of

surface modifying macromolecules (SMMs) and the use of the additive PVP and found that the addition of PVP increased the molecular weight cut off (MWCO) and pure water permeation of the membranes. Other researchers studied the effect of different molecular weight PVP such as PVP K10, PVP K30, PVP K90 and PVP K360 on performance of PES membranes [55, 56]. Jung et al. [57] reported that in case of PAN/ DMSO/PVP system, the top layer of the membrane and suppression of macrovoid formation strongly depends upon the molecular weight of PVP. They also found that the addition of different molecular weight of PVPs changes the pure water permeability of the membranes. The effects of PEG concentrations on the porosity of polycarbonate (PC) membranes prepared via dry/wet-phase inversion methods was studied by Deniz [58]. The casting solutions were obtained by dissolving PC and PEG in different compositions (3 – 15 wt%). PEG concentration was ranged from (0 - 20 wt%) to investigate the effect of PEG concentration on membrane porosity. It was observed that the porosity of the membrane increased with an increase in the initial PEG concentration ranging from 5 to 20 wt%. Kim and Lee [59] investigated the effect of various molecular weights of PEG on the formation of Polyetherimide (PEI) asymmetric membrane and they reported that small molecular weights of PEG such as PEG 200 and PEG 400 work as pore reducing agent for PEI membranes. Shieh et al [60] reported that PEG 600 being hydrophilic in nature, is used to improve membrane selectivity and as a pore forming agent. They found that PEG as additive in the PEI spinning dopes suppresses the growth of macrovoids and produces a membrane morphology having a more porous skin surface and more compact substructure, which provides a lower skin resistance and a higher substructure resistance for gas permeation. Idris et al. [61] investigated the performance of asymmetric PES UF flat

sheet membranes with PEG of different molecular weights. The membranes were prepared by phase inversion process from casting solution containing PES as polymer, DMF as solvent and PEG of different molecular weights namely as PEG 200, PEG 400 and PEG 600 as additives. The PES concentration was kept constant at 20%, PEG of different molecular weights were varied from 5 to 25 wt% and the DMF content in the casting solution was progressively reduced from 75 to 55 wt%. The results revealed that membranes with PEG of higher molecular weights have higher pure water permeation and larger pores. Also, the membrane surface was found to become more rough with increased molecular weight of additives. Chou et al. [62] prepared asymmetric CA hollow fiber membranes by dry/wet spinning process from a dope composed of CA, DMF, and PEG. The results showed that the addition of PEG suppressed the formation of macrovoids and the effect on the suppression was more obvious for PEG with higher molecular weight and higher content. The pure water flux (PWF) increased with the additive content but slightly decreased with the increase of molecular weight. Several PES UF membranes have been made by Marchese et al. [63] with small quantities of PVP of different molecular weights to increase the permeability without a significant reduction in selectivity. Mahendran et al. [64] prepared membranes based on CA and epoxy resin with and without PEG 600 and found that concentration of PEG 600 has major influence on the UF characteristics of the membranes prepared. Sivakumar et al. [65] in their study, showed the effect of concentration of the additive, PVP on the performance of CA/polyurethane (PU) blend membranes. They reported that an increase in PVP concentration from 0 to 2.5 wt % though reduced the BSA rejection but the flux was seen to be increased reasonably. Arthanareeswaran et al. [66] in their investigation,

prepared a novel membrane by blending of CA and LCD PSf (low cyclic dimer polysulfone) in DMF as a solvent with different molecular weight of PEG viz. (PEG 200, PEG 400, and PEG 600). The addition of different molecular weight PEG was seen to influence the membrane properties and morphology remarkably. With a 5 wt% of PEG, the hydrophilicity of the blend membrane was increased. Experiments showed that the increase in molecular weight of PEGs (200, 400, and 600) in casting solution resulted in the increase of the PWF, the equilibrium water content (EWC) and the porosity of the membrane. Malaisamy et al. [67] reported preparation of blend membranes based on PU and sulfonated PSf (SPSf) in the presence of PEG 600 as additive using DMF as solvent by the phase inversion technique. They optimized the polymer blend composition, the additive concentration and the casting and gelation conditions. The suitable compositions were found to be 80/20 wt% and 75/25 wt% of PU/SPSf and the maximum compatible concentration of additive was found to be 7.5 wt% in terms of obtaining higher PWF and water content and lower membrane resistance.

From the above review, it is understood that a number of studies has been reported using both PVP and PEG as additives in different polymer/solvent systems to study their effect on membrane morphology and performance. Many researchers studied on the effect of addition of different additives into the membrane casting solutions of identical compositions. Some studies are based on the effect of addition of the same additive of different molecular weight into the membrane casting solution; while others are investigating the effect of varying concentrations of the same additive. PEG and PVP are the most widely used additives in membrane preparation process as both are soluble in water which is

the conventional nonsolvent used in the membrane casting solution. However, most of the works are associated with low molecular weight PEG and PVP till date. Also, a study related to the effect of both the additives on the morphology of PSf membrane under similar circumstances has not been carried out so far. NMP and DMAc are found to be the common solvents in most of the studies because they are miscible with water.

1.3.2. Separation of oil from oily wastewater

Petroleum encompasses liquid hydrocarbons mostly referred to as crude oil. Major groups of compounds found in petroleum are saturated hydrocarbons, including straight chained, branched and cyclic hydrocarbons, simple aromatic hydrocarbons, small sulphur bearing compounds, resins and very large aromatic asphaltene compounds. The largest petroleum fraction is between C_1 and C_9 , the so called light hydrocarbons which usually constitute well over 50% of the carbon in crude oils [68]. These hydrocarbons vary in their toxicity to aquatic and terrestrial life. Thus, discharging of these wastewaters to the surrounding environment has become a serious issue, which needs to be resolved urgently.

A number of researchers have reported their works on membrane UF/MF process for oily water treatment. It has been demonstrated that pressure driven membrane separation processes can be successfully employed for the removal of oil from oily wastewater, with some distinct advantages over the more conventional processes. Most studies have focused on the use of UF and MF membranes in rejecting oil droplets. Ideally, in such a mode of operation, oil droplets are completely retained and the continuous phase is permeated. However, because the oil droplets are deformable,

depending on the applied pressure, they can be squeezed through the pores and contaminate the permeate. Lipp et al. [69] has reported such permeate contamination. In their study, factors affecting both flux and rejection in the UF of o/w emulsions were investigated using CA (YM5, YM30), PSf (PM30), polyacrylic (IRIS 3038) and polamide (CJT 35) membranes. The concentrations of soluble oil in prepared emulsions were varied from 0.5 to 10 vol %, in distilled water. Oil rejections were high (> 99.9%) with less than 20 ppm oil in the permeate. Karakulski et al. [70] carried out investigation for purification of oily wastewater by a combination of UF/RO processes. A tubular UF system using CA, PVC, and PAN membranes was tested. The solution of PVC and PAN in DMF with a concentration of 12 wt% was prepared while the CA casting solution prepared at room temperature was composed of 17 wt% CA, 29 wt% formamide and 54 wt% acetone. The o/w emulsion characterized low contents of oil (124 ppm) and chemical oxygen demand (COD) (346 mg O₂/dm³), with oil droplets varying from 1 – 12 μ m in size. All the membrane types produced a permeate with an oil content less than 10 ppm. Lin and Lan [71] investigated the treatment of waste drawing oil which is a high strength waste o/w emulsion commonly used in the cable and wire industries. Semi-batch UF and ion-exchange processes were employed to treat the emulsion. Three types of Amicon UF membranes e.g. hydrophilic Amicon YM30 and YM100 (both are CA membranes) and hydrophobic PM30 (PSf membrane) were employed. Ion-exchange treatment were carried out with the UF permeate to further lower the COD and improve turbidity. The test results showed very good performances of the combined UF and ion exchange processes. Nazzal and Wiesner [72] also investigated the effects of TMP

and membrane pore size. They found that emulsion rejection could be maximized if TMP were below a critical pressure. Conversely, Hlavacek and Daiminger and his co-workers [14, 73] described the use of porous hydrophobic membranes to induce separation of o/w emulsions due to coalescence on the membrane pores. In those studies, the membranes were used as coalescers rather than as rejecting membranes.

Hlavacek [14] used a standard 0.2 PP hollow fibre module having 1 m² filtration area for separating the two phases of an industrial emulsion from the aluminium industry. Demulsification occurred as a result of permeation of the emulsion through the membranes. After the permeate was allowed to settle for 2 h, the oil concentration in the lower layer was found to be as low as 30 ppm compared to 30,000 ppm in the original emulsion. Daiminger and his co-workers [73] proposed two novel methods of separation of o/w emulsions where wetting plays an essential role. The membrane materials used were polytetrafluoroethylene (PTFE), PVDF and cellulose nitrate and the module used was hollow fiber module. A high degree of separation (80-90%) was observed. Ueyama et al. [74] reported the effects of emulsion drop size, stirring velocity during permeation experiment, volume fraction of the oil phase and surfactant concentration in the feed on oil permeation flux using a microporous PTFE flat sheet membrane. Mueller et al. [2] tested the performance of both ceramic and polymeric PAN MF membranes in treating synthetically produced water, containing 250-1000 mgL⁻¹ of heavy crude oil droplets of 1-10 diameter and found that

though the permeate produced was of very high quality with less than 6 mgL⁻¹ oil, the fouling and flux decline were severe. Kong and Li [75] investigated the separation of dilute o/w mixtures using flat sheet hydrophobic PVDF membranes based on the

preferential wetting principle and found that feed flow rate, operating pressure, membrane pore size and porosity affected the separation efficiency significantly. Field et al. [76] investigated the influence of different types of surfactant on water flux through hydrophobic microfiltration PVDF membranes. Koltuniewicz and Field [77] focused on the process factors affecting the permeation fluxes in the process of separating o/w emulsion e.g. membrane type, module type, operating conditions such as TMP, recirculation velocity, feed concentration and temperature. The performance of the polymeric membranes Millipore 0.45 μm and Gelman 0.1 μm were compared with the ceramic membranes Ceramesh 0.1 μm and Membralox 0.1 μm . The used ceramic membranes were found to be advantageous over the used polymeric membranes for separation of o/w emulsions. Cumming et al. [78] investigated the effect of pore size on the rejection of oil using Nuclepore filters with pore sizes of 2, 5, 8 and 10 μm . The oil emulsion drop size was in the range of 1-40 μm and was stabilised using an aqueous solution of polyvinyl alcohol (PVA). The rejection of oil and the size distribution of the permeate were determined for TMP varying from 400 to 3000 Pa. A simple theory based on interfacial tension, contact angle and pore size was developed. Comparing the measured and predicted results for both the permeate size distribution and the oil rejection, it was found that there was good agreement between them for the 2 μm filter, but the model reliability decreased with increasing pore size. Li et al. [79] developed a hydrophilic hollow fiber UF membrane for oil–water separation fabricated from a new dope containing cellulose/monohydrate N-methylmorpholine-N-oxide (NMMO·H₂O)/PEG 400 using the immersion

precipitation technique. An o/w emulsion containing machine oil of 800 ppm in de-ionized water was used to test the separation performance of the membrane. The oil droplets were in the range of 0.2–5 μm with an average size of 2.1 μm . The experimental results showed that oil retention of the membrane was over 99% and oil concentration in the filtrate was below 10 ppm. Ohya et al. [18] studied the effect of the average pore size in porous glass tube membranes on the performance of the cross-flow MF of o/w emulsion and found that filtration mechanism varied with membrane pore diameter. The o/w emulsion was prepared by emulsifying 1 ml of mineral oil in 1000 ml of distilled water with 0.1 ml of surfactant, polyoxyethylene (20) sorbitan trioleate using a homogenizer at 6000 rpm for 5 min. Droplet size distributions in the feed were in the range from 1 to 40 μm . The oil rejection was found to decrease from 94 to 80 % as the membrane pore size increased from 0.27 to 1.47 μm . Effectiveness of a PVA membrane selected for UF of synthetic oily water was evaluated in a study carried out by Wu et al. [80] using a pilot-scale continuous cross-flow membrane filtration system. The effects of temperature, oil concentration, TMP, and cross-flow velocity (CFV) on the membrane permeation flux and oil retention were investigated. Gasoline at various concentrations (200 – 800 mg L^{-1}) was added to tap water and a blender with a high-speed stirrer was used for producing the o/w emulsion. The average size of the emulsion droplets was 0.36 μm . Within the range of experiments, the PVA UF membrane had a superior permeate flux (more than 200 $\text{L m}^{-2}\text{.h}^{-1}$) and a relatively high oil retention (93%). Hua et al. [81] carried out cross-flow MF processes with oily wastewater (oil concentration 500 ppm)

using a ceramic (Al_2O_3) membrane with 50 nm pore size. The o/w emulsion was prepared by mixing edible oil with distilled water and surfactant for 15 min at a speed of 5000 rpm using a homogenizer. The influence of parameters such as TMP, CFV, oil concentration in feed, pH and salt concentration on the separation behaviours were investigated by the measurements of permeate flux, total organic carbon (TOC) removal efficiency, and size and zeta potential of the emulsion droplets. The TOC removal efficiencies higher than 92.4% were achieved under all experimental conditions. Zhao et al. [82] studied dynamic membranes for oily water separation and showed that magnesium hydroxide suspension on ceramic support could be a suitable material for dynamic membrane which gave more than 98% oil retention from a model oil emulsion in an alkaline environment. Treatment of oily wastewater produced from post-treatment unit of refinery processes using flocculation and MF with zirconia membrane was studied by Zhong et al. [83]. The results of MF tests showed that the tendency of membrane fouling decreased and the permeate flux and permeate quality increased with flocculation as pre-treatment. The permeate obtained was found to meet the standard discharge limit and the recommended operating conditions for pilot and industrial application were TMP of 0.11 MPa, and CFV of 2.56 ms^{-1} . Bhanumurthy et al. [84] studied UF of cutting oil with PSf membranes. They observed that increase in flux at higher CFV was due to washing away of the polarized layer. They also proposed a model for the prediction of the permeate flux which incorporates droplet coalescence and shear rate. Lobo et al. [85] studied the effect of CFV and pH on UF of model metalworking o/w emulsion using Carbosep tubular ceramic membranes with two different cut offs (50 and 300 kDa) in a TMP

range of 0.05–0.4 MPa and concluded that both permeate flux and COD retention decreased drastically at low pH values. A model o/w emulsion was prepared using a vegetable oil as base oil, an anionic surfactant (Dioctyl sulfosuccinate sodium salt) and a non-ionic surfactant (Merpol OJ, an ethoxylated alcohol). The emulsion used for all experiments was 1% w/w oil in deionized water, whereas surfactant concentrations were kept around their critical micelle concentration (CMC) value. Li et al. [86] in their study used a tubular UF module equipped with PVDF membranes modified by inorganic nano-sized alumina particles to purify oily wastewater from an oil field. They found that the addition of nanosized alumina particles improved membrane antifouling performance, and the flux recovery ratio of modified membranes reached 100% after washing with 1 wt% of OP-10 surfactant solution (pH 10). Results indicated that retentions of COD and total organic carbon (TOC) were more than 90% and 98%, respectively. Gorouhi et al. [87] conducted the MF operation to separate oil from oily wastewater using PP membrane with 0.2 μm pore size manufactured by MEMBRANA in cross-flow mode. O/w emulsions were made using gas oil and distilled water as dispersed and continuous phases, respectively. The concentration of emulsion was 5 wt % of gas oil in water. It was found that increasing temperature, TMP and flow rate increases both permeate flux and water content in permeate. Elmaleh and Ghaffor [88] used M9 Carbosep membrane to separate hydrocarbons from synthetic emulsion (containing oil and biological suspended solids) made with an Iranian crude oil. The M9 membrane was an inorganic composite membrane whose zirconia-active layer was deposited on a carbon support. The membrane MWCO as given by the manufacturer was 3,00,000 Da. The UF was found to produce an effluent free of hydrocarbons and suspended solids. Um et al. [89] introduced gas injection

technique to achieve flux improvement in cross-flow UF of oil emulsion. By the Nitrogen gas injection, homogeneous liquid phase o/w emulsion was changed to heterogeneous gas–liquid phase. The membrane used was a PSf ultrafilter (GR40PP, MWCO; 100 kDa, Dow Co.). The oil used was commercial cutting oil (Hocut SSK, Korea Houghton Co.) which was the semi-synthetic type oil including mineral oils, surfactants and various additives. It was diluted to 5 wt% and was used as feed solution. The size of oil droplets in the feed solution was $0.1-4 \mu\text{m}$ and the average size was $0.44 \mu\text{m}$. The oil rejection was found to be more than 99%; however, COD rejection was about 95%. Investigations on the treatment of oily wastewater by a combination of UF and membrane distillation (MD) as a final purification step have been performed in the study conducted by Gryta et al. [13]. A tubular UF module equipped with PVDF membranes and a capillary MD module with PP membranes were tested using a typical bilge water collected from a harbour without pre-treatment. The oil content in the bilge water was in the range of 124–360 ppm. The permeate obtained from the UF process generally contains less than 5 ppm of oil. A further purification of the UF permeate by MD results in a complete removal of oil from wastewater and a very high reduction of the TOC (99.5%) and total dissolved solids (TDS) (99.9%). Scott et al. [90] investigated the behaviour of the cross-flow MF of "stable" dispersions of an immiscible organic solvent (tridecanol) in water with mean droplet size of $1 \mu\text{m}$, using commercial MF membranes composed of either PSf, nylon, PTFE (all having mean pore size of $0.2 \mu\text{m}$) or a mixed cellulose acetate/nitrate (having mean pore size of 0.2, 0.45 and $1.2 \mu\text{m}$). The membrane pore size

which achieved rejections of greater than 90% was 0.2 when the TMP was at 0.8 bar and the CFV was held between 3 and 4 ms⁻¹. The fluxes were between 10 and 60 dm³h⁻¹m⁻² depending upon the membrane material. All the membranes experienced some form of decay in flux with time resulting from a combination of concentration polarization and membrane fouling by pore blocking and/or surface cake formation. Lin and Reed [91] compared the performance of a conventional tubular cross-flow UF system with the performance of a centrifugal membrane system in treating an oil/grease emulsified industrial wastewater. The waste consisted of an oil and grease concentration of about 2500 - 6000 ppm. Oil and grease removal in the tubular system averaged 97% while oil and grease removal in the centrifugal system was greater than 99%. Xu et al. [92] studied the performance of the asymmetric hollow fiber membranes prepared from wet-spun 25 wt% solids of 20:5:75 (wt ratio) PEI/PEG 600/DMAc and 19:1:5:75 PEI/polybenzimidazole (PBI)/PEG 600/DMAc solutions for oil-surfactant-water separation. PEI is hydrophobic while PBI and PEG are hydrophilic and have been employed as additives to the membranes. For the oil-surfactant-water emulsion (1600 ppm surfactant and 2500 ppm oil), experimental results illustrated that the rejection rates for surfactant, TOC and oil obtained were 51.4-79.1%, 83.1-92.7% and more than 99%, respectively. Ju et al. [93] prepared PSf UF membranes employing cross linked poly(ethylene glycol) diacrylate (XLPEGDA) as a coating material on the surface and were employed in oil/water cross-flow filtration experiments. Results showed that the coated PSf membranes had water flux values 400% higher than that of an uncoated PSf membrane after 24 h of operation, and the coated membranes had higher organic rejection () than the uncoated

membranes. The feed contained 1350 ppm canola oil, 150 ppm DC-193 neutral surfactant, and water. The experiments were performed at a feed pressure of 10 bar and at 25 °C and the cross-flow rate was 68 Lh⁻¹ with a Reynolds number of 1300. Li et al. [94] developed a hydrophilic hollow fiber UF membrane fabricated from a new dope containing cellulose/monohydrate N-methylmorpholine-N-oxide (NMMO.H₂O)/ PEG 400 with a mass ratio of 8/88/4 using the immersion precipitation technique for oil–water separation. The o/w emulsion containing machine oil of 800 mg L⁻¹ in deionized water was generated by mixing machine oil with water at 3000 rpm speed over 30 min and was used to test the separation performance of the membrane. The oil droplets in the feed were in the range of 0.2–5 with an average size of 2.1 . The experimental results showed that oil retention of the membrane was over 99% and oil concentration in the filtrate was below 10 mgL⁻¹, which met the requirement for discharge. Mohammadi et al. [95] used a tubular kaolin module that was calcined at 900°C with a maximum pore size of 10 in treating o/w emulsions. Oil-in-water emulsions were prepared by vigorous mixing of crude oil (obtained from Asaloyeh, Iran) and water with an addition of 0.2 g emulsifier (dodecyl sulphate sodium) to the mixture and the oil concentrations were kept at 500 - 3000 ppm. Results showed that good performance was obtained for oily wastewaters with concentrations lower than 2000 ppm, at temperatures lower than 40°C and a pressure of 2 bars.

The above review on separation of oil from oily water shows that a lot of efforts have been given by a number of researchers to bring down the oil content in the

water to be discharged below the allowable discharge limit of 10 mgL^{-1} . Some of them have become successful in doing so; however a very limited work has been reported on the use of PSf membrane in separating micron and submicron sized oil droplets from oily water.

1.3.3. Fouling mechanism

Though application of membrane technology such as MF and UF is offering a potential solution to the removal of low-diameter oil droplets, flux declination with time due to membrane fouling and concentration polarization is a major setback in such applications. Therefore, in order to scale up the systems, the flux decline mechanism should be thoroughly studied and analyzed. Fouling is a complex phenomenon depending on specific interactions between a particular membrane and a feed solution and also on a number of parameters. An extensive review was given by Fane and Fell [96] on fouling in UF processes. External fouling occurs on the top surface of the membrane due to deposition of larger oil particles (whose size is greater than the membrane pore size) that cannot enter the pores. Internal fouling occurs within the pores of the membrane due to deposition and adsorption of oil particles which are able to pass through the pores. Fouling can be sometimes irreversible i.e. resistant to cleaning; in such case, recovery of original flux is impossible.

A number of mathematical models are available in the literature that attempt to describe the mechanism of transport through membranes [2]. Membrane UF of macromolecular solutions is usually analyzed by the following models: (i) the gel polarization model, (ii) the osmotic pressure model and (iii) the resistance-in series

(RIS) model. All these models basically have resulted from Darcy's equation. In the gel polarization model, permeate flux is reduced by the hydraulic resistance of the gel layer. In the osmotic pressure model, permeate flux reduction results from the decrease in effective TMP that occurs as osmotic pressure of the retentate increases. In the RIS model, permeate flux decreases due to the resistances caused by fouling or solute adsorption and concentration polarization. The last model i.e. RIS model easily describes the relationships of permeate flux with operating parameters. Some workers have developed new modified models based on RIS model while some have used it to analyze the flux decline. Tansel et al. [97] developed a simple flux decline model based on the RIS approach. They carried out research work to characterize flux decline and to estimate the characteristic fouling times of membranes under specific operating conditions using their model. Rai et al. [98] quantified the flux decline during UF of mosambi juice using thin film composite polyamide membranes with the help of the RIS model. Dal-cin et al. [99] used the RIS model to evaluate the relative contributions of different fouling mechanisms during UF of pulp mill effluent. Jiraratananon and Chanachai [100] applied RIS model to evaluate the controlling resistance in UF of passion fruit juice using PSf hollow fiber membrane. Bhattacharjee and Bhattacharya [101] undertook a work to study and analyse the flux decline phenomena during UF of kraft black liquor. Further, they developed a model combining film theory, gel theory and filtration theory to predict permeate flux as a function of time. PEG 6000, a standard macromolecule, was used to compare the results obtained with a stirred batch cell. Bhattacharjee et al [102] developed a predictive model for flux prediction during batch cell UF unifying the osmotic pressure and gel layer models by performing experiments with polymeric solutes

(PEG, dextran and PVA) and a protein (BSA), ranging widely in molecular weights and physicochemical properties, under various operating conditions (TMP, solution pH, and stirrer speed).

Some models have been developed based on mass and momentum balance equations. Song [103] studied the mechanisms and physics behind the membrane fouling process and developed a mechanistic model for the time-dependent flux in cross-flow filtration mode. He also developed a mechanistic model for predicting the limiting flux in UF [104]. The limiting flux was calculated by considering mass balance in the concentration polarization layer. A procedure to correlate the model with experimental UF data was also presented. Lee and Clark [105] developed a step-wise pseudo steady-state model using the two-dimensional convective-diffusion equation to predict the flux decline due to concentration polarization during cross-flow UF of colloidal suspensions. A hydrophilic CA membrane with MWCO 100 KDa was used in this study, where variations in particle size, feed concentration, and CFV were also effectively modeled. Correlation equations for predicting the permeate flux of membrane UF in hollow-fiber modules were derived by Yeh et al. [106] from momentum and mass balances with the application of the RIS model, coupled with the considerations of declinations of flow rate and TMP along the tubes of hollow-fiber module made of PSf. It was concluded that the declination of permeate flux occurs mainly due to the decline of TMP and the increase of the thickness of concentration polarization layer along the membrane tube.

Several researchers have worked on fouling analysis using the classical models based on filtration laws. Jiraratananon et al. [107] made an attempt in describing the blocking phenomena by constant pressure filtration laws in cross-flow MF of a

colloidal suspension of bentonite with the presence of bovine serum albumin (BSA), dextran and PEG using the hydrophilic PVDF membranes. Huang and Morrissey [108] analyzed the experimental data of MF (by PSf membrane) of surimi wash water containing both soluble solids and suspended solids and showed that the development of membrane fouling was a dynamic process starting with pore blocking at the initial stage of filtration (modeled by the standard pore blocking law), and followed by a continuous cake layer formation (modeled by a newly proposed power law). Jaffrin et al. [109] made an attempt to identify the mechanisms responsible for the permeate flux reduction during UF of albumin-ethanol solutions using PSf hollow fiber membranes using the filtration models suitable for cross-flow filtration. Most of the works on membrane fouling based on the pore blocking and cake formation models [110, 111] are actually more applicable to the dead-end filtration process as they predict a zero flux at infinite time [111]. Models developed by De and Bhattacharya [112], Suki et al. [113], Fu and Dempsey [114], Sethi and Wiesner [115] are based on particle sizes. Purkait et al. [116] identified the flux decline mechanisms during nanofiltration (NF) of the pretreated leather plant effluent as well as during RO of the permeating solution which came out from NF using membranes of MWCO 200 and 400. The concept of particle adhesion was utilized by Stamatakis and Tien [117] to develop a model with which they could predict the time dependent flux and also estimate the amount of solute particles retained on the membrane surface. The characteristic permeate flux behaviour in UF, i.e., the existence of a limiting flux which is independent of applied pressure and membrane resistance is explained using the osmotic pressure model by Wijmans et al. [118]. Blanpain et al. [119] investigated mechanisms to determine permeate flux and protein rejection for the MF of a clarified

beer using a Cyclopore membrane. Experimental results were analyzed in terms of existing membrane filtration model equations and membrane resistance. Flux decay was found to follow the standard blocking model (SBM) assuming that pore volume decreases proportionally to filtrate volume.

In UF of o/w emulsions, it is believed that membrane fouling is a very complicated phenomenon caused by many chemical and physical interactions. Koltuniewicz et al. [120] investigated the MF performance of various ceramic and polymeric membranes in cross-flow and dead-end filtration modes with n-dodecane/water emulsion as feed. They found that initially the membranes fouled internally and after a certain time external fouling began to dominate. According to them, two major components contribute to the resistance to permeate flow. The first one is connected with the membrane and its structural property such as pore size and pore size distribution giving rise to pore blocking and the second one with the generation of a membrane boundary layer and a fouling layer at the membrane interface. Proper selection of membrane materials may solve problems related to the first category to a large extent while the problems related to second category may be regulated through process control and optimization. Bhattacharyya et. al [121] studied both internal and external fouling during UF of a lubricating oil-in-water solution using noncellulosic, tubular membranes from which they noted that membrane fouling depends on the type of oily water system as well as the type of membranes used. Lee et al. [122] reported the cause of concentration polarization and fouling during UF as the result of adsorption of oil on the membrane surface. They carried out the study with oil-surfactant-water emulsion system in a stirred filtration cell. Lipp et al. [69] studied the UF of o/w emulsions using various polymeric and cellulosic membranes and found the fouling

mechanism to follow the gel-polarization model behaviour. Mueller et al. [2] observed significant fouling and flux decline while testing MF of oily water and used different resistance models to characterize the type of fouling. Bhanumurthy et al. [86] proposed a model to predict the permeate flux which incorporates both droplet coalescence and shear rate while carrying out a UF study of cutting oil with PSf membranes. Arnot et al. [123] examined the applicability of three distinct forms of flux decline model proposed by Field [124], Wu et al. [125] and Koltuniewicz [126] for cross-flow and dead-end MF of oily water emulsions and found the Field model to be superior as it makes due allowance for different fouling mechanisms. Lobo et al. [85] applied the RIS model to interpret the data obtained by studying the effect of pH and CFV on the UF of a model metalworking o/w emulsion using tubular ceramic membranes and found that concentration polarization resistance was a major factor at CFV below 2.5 ms^{-1} while the adsorption resistance had increased drastically at pH less than 4.

From the above review that corresponds to membrane fouling, it is understood that different studies have been carried out on understanding the type of fouling occurring during the UF and MF processes and also a number of mathematical models have been proposed to explain the mechanisms of flux decline in those processes; but in practice, none of the models is able to give a complete insight into the fouling/blocking process for a system containing both particles and macromolecules. It is also seen that a limited number of study has been reported so far which has focused on membrane fouling by oil particles.

1.4. Objectives and plan of the present work

From the review of literature, it is evident that several attempts have been made by many investigators to explain the membrane-forming mechanism during the phase inversion process since many years. In order to get membrane with suitable structure and permeation property, introduction of a suitable additive to the casting solution is a convenient and efficient method. From the review regarding the studies on membrane synthesis reported so far, it is understood that synthesis of membranes with required morphological as well as performance properties is an important factor so that they can be used for a specific application. It is also apparent that studies related to the modification of morphological as well as permeation properties of PSf membrane through the use of wide range molecular weight PVP and PEG additives are very limited. Generation of oily water from different industries and its appropriate treatment is another serious issue which needs to be resolved urgently. Oily water with emulsion droplets of size less than 10 μm is considered to be highly stable and so is very difficult to separate, particularly when oil concentration is in lower range. Therefore, oil content in water collected from the effluent treatment plants of most of the industries is quite high and above the allowable discharge standard of 10 mgL^{-1} . From the review of the literatures, though a number of researchers appear to devote considerable attention on treatment of oily water using membrane based techniques, to the best of my knowledge, treatment of oily water having oil droplets below 5 μm size using PSf membranes have not been reported so far. The present research study has been undertaken based on these facts. The aim of this study is to synthesize polysulfone (PSf) membranes of suitable compositions and investigate their

performance for the treatment of oily wastewater generated mainly from the post treatment unit of oil industries. As mentioned before, every UF operation happens to be associated with certain degree of fouling. In view of this, this work has also attempted on understanding and characterization of the type of fouling occurring during the UF of synthesized oily water, based on the concept of the constant pressure filtration model and the resistance-in-series model.

The entire research work has been taken up with the following objectives:

- Synthesis of PSf membranes using two solvents (NMP and DMAc) and two additives (PVP and PEG) of wide range of molecular weights separately and characterization of those membranes for morphological and UF performance information.
- Conduction of dead-end (batch) experiments with bovine serum albumin (BSA) solution to verify the applicability of the prepared membranes for UF studies. Further experimentation with synthetic oily water using batch and cross-flow (continuous) UF mode. Selection of the most suitable membrane/membranes for separating oil from oily wastewater under the optimum operating conditions based on their performance (i.e. flux and rejection).
- Conduction of batch and cross-flow UF experiments with real oily wastewater collected from actual site to study the usability of the selected membranes.

The proposed research objectives have been met through the following work plan:

- Preparation of flat sheet PSf membranes by phase inversion method and study of effect of different additives and solvents on membrane morphology.

- Characterization of the synthesized membranes for morphological and UF performance information.
- Fabrication of dead-end (batch) flow and cross-flow membrane cells for conducting UF experiments.
- Selection of the suitable membranes for UF application of oily wastewater in batch mode of operation.
- Optimization of the process parameters in batch cell experiments using the selected membranes for separating oil from synthetic oily water.
- Development of flux decline mechanism based on the study with synthetic oily water.
- Conduction of cross-flow UF experiment using the optimized condition obtained in batch experiments.
- Batch and cross-flow experimental study with real oily wastewater collected from actual site with the most suitable membrane/membranes under optimum conditions.

Abbreviations

BSA	Bovine serum albumin
CA	Cellulose acetate
CFV	Cross flow velocity
CMC	Critical micelle concentration
COD	Chemical oxygen demand
DMAc	Dimethyl acetamide
DMF	Dimethyl formamide

DMSO	Dimethyl sulfoxide
GLC	Gas liquid chromatography
MD	Membrane distillation
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NMP	N- methyl pyrrolidone
PA	Polyamide
PAN	Polyacrylonitrile
PE	Polyethylene
PEG	Poly(ethylene glycol)
PEI	Polyetherimide
PES	Polyethersulfone
PP	Polypropylene
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
RIS	Resistance-in-series
RO	Reverse osmosis
SBM	Standard blocking model
TDS	Total dissolved solid

THF	Tetra-hydrofuran
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration

References

1. R. M. Bande, B. Prasad, I. M. Mishra and K L. Wasewar, Oil field effluent water treatment for safe disposal by electroflotation, Chem. Eng. J., 137, (2008), 503 - 509.
2. J. Mueller, Y. Cen and R. H. Davis, Crossflow microfiltration of oily water, J. Membr. Sci., 129 (1997), 221 - 235.
3. A. Bevis, The treatment of oily water by coalescing, Filtration and Separation, July/August (1992), 295 - 301.
4. M. Cheryan and N. Rajagopalan, Membrane processing of oily streams. Wastewater treatment and waste reduction, J. Membr. Sci., 151 (1998), 13 - 28.
5. C. L. Yang, Electrochemical coagulation for oily water demulsification, Sep. Purif. Technol., 54 (2007), 388 – 395.
6. A. A. Al - Shamrania, A. Jamesa and H. Xiao, Destabilisation of oil – water emulsions and separation by dissolved air flotation , Water Res., 36 (2002), 1503 - 1512.
7. A. El-Kayar, M. Hussein, A. A. Zatout, A. Y. Hosny and A. A. Amer, Removal of oil from stable oil-water emulsion by induced air floatation technique, Sep. Technol., 3 (1993), 25 - 31.

8. A.Y. Hosny, Separating oil from oil-water emulsions by electroflotation technique, *Sep. Technol.*, 6 (1996), 9 - 17.
9. Chen-Lu Yang, Electrochemical coagulation for oily water demulsification, *Sep. Purif. Technol.*, 54 (2007), 388 - 395.
10. J. M. Benito, G. Rios, E. Ortea, E. Fernhdez, A. Cambiella, C. Pazos and J. Coca, Design and construction of a modular pilot plant for the treatment of oil-containing waste waters, *Desalination*, 147 (2002), 5 - 10.
11. D. Abdessemed, G. Nezzal and R. Ben Aim, Coagulation-adsorption-ultrafiltration for wastewater treatment and reuse, *Desalination*, 131 (2000), 307 - 314.
12. C. Ratlege, Mini review compilation biodegradation and biotransformations of oils and fats, *J. Chem. Tech. Biotechnol.*, 55 (1992), 397 - 414.
13. M. Gryta, K. Karakulski and A. W. Morawski, Purification of oily wastewater by hybrid UF/MD, *Water Res.*, 35 (2001), 3665 – 3669.
14. M. Hlavacek, Break-up of oil-in-water emulsions induced by permeation through a microfiltration membrane, *J. Membr. Sci.*, 102 (1995), 1 - 7.
15. S. Deng, S. Sourirajan, K. Chan, B. Farnand, T. Okada and T. Matsuura, Dehydration of oil-water emulsion by pervaporation using porous hydrophilic membranes, *J. Colloid Interf. Sci.*, 141 (1991), 218 - 225.
16. T. Mohammadi, M. Kazemimoghadam and M. Saadabadi, Modeling of membrane fouling and flux decline in reverse osmosis during separation of oil in water emulsions, *Desalination*, 157 (2003), 369 – 375.

17. J. Zhong, X. Sun and C. Wang, Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration, *Sep. Purf. Technol.*, 32 (2003), 93 - 98.
18. H. Ohya, J. J. Kim, A. Chinen, M. Aihara, S. I. Semenova, Y. Negishi, O. Mori, and M. Yasuda, Effects of pore size on separation mechanisms of microfiltration of oily water using porous glass tubular membrane, *J. Membr. Sci.*, 145 (1998), 1 - 14.
19. M. Bodzek and K. Konieczny, The use of ultrafiltration membranes made of various polymers in the treatment of oil-emulsion wastewater. *Waste Management Res.*, 12 (1992), 75 - 84.
20. Simon Judd and Bruce Jeffers (Eds.), *Membranes for Industrial Wastewater Recovery and Re-use*, Published by Elsevier Advanced Technology, The Boulevard, Langford Lane, Kidlington Oxford OX5 1 GB, UK, 2003.
21. Munir Cheryan, *Ultrafiltration and Microfiltration Handbook*, Technomic Publishing Co. Inc. Lancaster, Pennsylvania, U.S.A, 1998.
22. M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, 1991.
23. S. P. Nunes and K.V. Peinemann (Eds.), *Membrane Technology in the Chemical Industry*, Wiley-VCH Verlag GmbH., 2001.
24. *Application of membrane technologies for liquid radioactive waste processing*, International Atomic Energy Agency, Vienna, Technical Reports Series No. 431, 2004.
25. W. J. Koros, Y. H. Ma and T. Shimidzu, Terminology for membranes and membrane processes; IUPAC recommendations, *J. Membr. Sci.*, 120 (1996),

- 149-159.
26. M. R. Wiesner and P. Aptel, Mass transport and permeate flux and fouling in pressure driven processes (Ch. 4). In: Water Treatment Membrane Processes. Mallevialle, J., Odendaal, P.E. and Wiesner, M.R. (eds.), McGraw-Hill, New York. 1996.
27. K. Parameshwaran, A. G. Fane, B. D. Cho and K. J. Kim, Analysis of microfiltration performance with constant flux processing of secondary effluent. *Water Res.*, 35 (18), (2001), 4349-4358.
28. Membrane fouling in waste water filtration. Causes, consequences and prevention. PhD thesis, UTwente, Enschede (the Netherlands), (1997).
29. A. G. Fane and C. J. D. Fell, A review of fouling and fouling control in ultrafiltration, *Desalination*, 62 (1987), 117-136.
30. L. J. Zeman and A. L. Zydney, Microfiltration and ultrafiltration: principles and applications. Marcel Dekker, New York, 1996.
31. X. Chai, T. Kobayashi and N. Fujii, Ultrasound-associated cleaning of polymeric membranes for water treatment, *Sep. Purif. Technol.*, 15 (1999), 139-146.
32. F. Vigo, C. Uliana, E. Ravina, A. Lucifredi and M. Gandoglia, The vibrating ultrafiltration module: Performance in the 50-1000 Hz frequency range, *Sep. Sci. Technol.*, 28 (4) (1993), 1063-1076.
33. T. Matsuura, Synthetic Membranes and Membrane Separation Processes, CRC Press. Inc., Corporate Blvd., N.W., Boca Raton, Florida 33431, 2000.
34. G. Pearce, Introduction to membranes: Membrane selection, Filtration and Separation, April 2007.

35. A. J. Gijsbertsen-Abrahamse, E. Cornelissen and J. A. M. Hofman, Fiber failure frequency and causes of hollow fiber integrity loss, *Desalination* 194, (2006), 251-258.
36. R. M. Boom, I. M. Wienk, T. van den Boomgaard and C. A. Smolders, Microstructures in phase inversion membranes Part 2. Role of polymeric additives, *J. Membr. Sci.*, 73, (1992), 277 - 292.
37. R. W. Baker, *Membrane Technology and Applications*, Second Edition, John Wiley & Sons Ltd., The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 2004.
38. H. Strathmann, P. Scheible and R.W. Baker, A Rationale for the Preparation of Loeb–Sourirajan-type Cellulose Acetate Membranes, *J. Appl. Polym. Sci.*, 15, (1971), 811 - 828.
39. M. C. Porter (Eds.), *Handbook of Industrial Membrane Technology*, Noyes Publications, Westwood, New Jersey, U.S.A., 1990.
40. F. R. Eirich, M. T. So, H. Strathmann and R. W. Baker, *Polymer Letters*, Vol. 11 (1973), 201 - 205.
41. A. J. Reuvers, J. W. A. van den Berg and C. A. Smolders, Formation of membranes by means of immersion precipitation. Part I A model to describe mass transfer during immersion precipitation, *J. Membr. Sci.*, 34 (1987), 45 - 65.
42. P. S. T. Machado, A. C. Habert and C. P. Borges, Membrane formation mechanism based on precipitation kinetics and membrane morphology: flat and hollow fiber polysulfone membranes, *J. Membr. Sci.*, 155 (1999), 171 –

183.

43. H. T. Yeo, S. T. Lee and M. J. Han, Role of Polymer Additive in Casting Solution in Preparation of Phase Inversion Polysulfone Membranes, *J. Chem. Eng. Japan*, 33 (2000), 180 - 185.
44. I. M. Wienk, R. M. Boom, M. A. M. Beerlage, A. M. W. Bulte and C. A. Smolders, Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, *J. Membr. Sci.*, 113 (1996), 361 - 371.
45. M. J. Han and S. T. Nam, Thermodynamic and rheological variation in polysulfone solution by PVP and its effect in the preparation of phase inversion membrane, *J. Membr. Sci.*, 202 (2002), 55 – 61.
46. M. J. Han, Effect of propionic acid in the casting solution on the characteristics of phase inversion polysulfone membranes, *Desalination*, 121 (1999), 31 - 39.
47. K. W. Lee, B. K. Seo, S. T. Nam and M. J. Han, Trade-off between thermodynamic enhancement and kinetic hindrance during phase inversion in the preparation of polysulfone membranes, *Desalination*, 159 (2003), 289 - 296.
48. Q. Z. Zheng, P. Wang and Y. N. Yang, Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process, *J. Membr. Sci.*, 279 (2006), 230 – 237.

49. T. P. Hou, S. H. Dong and L. Y. Zheng, The Study of Mechanism of organic additives action in the Polysulfone membrane casting solution, *Desalination*, 83 (1991), 343 - 360.
50. J. H. Kim and K. H. Lee, Effect of PEG additive on membrane formation by phase inversion, *J. Membr. Sci.*, 138 (1998), 153 - 163.
51. S. H. Chen, R. M. Liou, J. Y. Lai and C. L. Lai, Effect of the polarity of additional solvent on membrane formation in polysulfone/N-methyl-2-pyrrolidone/water ternary system, *Eur Polym J*, 43 (2007), 3997 – 4007.
52. N. A. Ochoa, P. Pradanos, L. Palacio, C. Pagliero, J. Marchese and A. Hernandez, Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes: Characterisation of polyethersulfone UF membranes with dopes containing different PVP, *J. Membr. Sci.*, 187 (2001), 227 - 237.
53. B. K. Chaturvedi, A. K. Ghosh, V. Ramachandran, M. K. Trivedi, M. S. Hanra and B. M. Misra, Preparation, characterization and performance of polyethersulfone ultrafiltration membranes, *Desalination*, 133 (2001), 31 – 40.
54. D. B. Mosqueda-Jimenez, R. M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier, J. P. Santerre, Influence of processing conditions on the properties of ultrafiltration membranes, *J. Membr. Sci.*, 231 (2004), 209 - 224.
55. B. T. Sanchez, R. I. Ortiz-Basurto and E. B. Fuente, Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes, *J. Membr. Sci.*, 152 (1999), 19 - 28.

56. J. J. Qin, M. H. Oo and Y. Li, Development of high flux polyethersulfone hollow fiber ultrafiltration membranes from a low critical solution temperature dope via hypochlorite treatment, *J. Membr. Sci.*, 247 (2004), 137 - 142.
57. B. Jung, J. K. Yoon, B. Kim and H. W. Rhee, Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes, *J. Membr. Sci.*, 243 (2004), 45 - 57.
58. S. Deniz, Characteristics of polycarbonate membranes with polyethylene glycol prepared via dry / wet - phase inversion methods, *Desalination*, 200 (2006), 42 - 43.
59. I. C. Kim and K. H. Lee, Effect of poly(ethylene glycol) 200 on the formation of a polyetherimide asymmetric membrane and its performance in aqueous solvent mixture permeation, *J. Membr. Sci.*, 230 (2004), 183 - 188.
60. J. J. Shieh, T. S. Chung, R. Wang, M. P. Srinivasan and D. R. Paul, Gas separation performance of poly(4-vinylpyridine)/polyetherimide composite hollow fibers, *J. Membr. Sci.*, 182 (2001), 111 - 123.
61. A. Idris, N. M. Zain and M. Y. Noordin, Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives, *Desalination*, 207 (2007), 324 – 339.
62. W. L. Chou, D. G. Yu, M. C. Yang and C. H. Jou, Effect of molecular weight and concentration of PEG additives on morphology and permeation

- performance of cellulose acetate hollow fibers, *Sep. Purif. Technol.*, 57 (2007), 207 – 217.
63. J. Marchese, M. Ponce, N. A. Ochoa, P. Pradanos, L. Palacio and A. Hernandez, Fouling behaviour of polyethersulfone UF membranes made with different PVP, *J. Membr. Sci.*, 211 (2003), 1 - 11.
64. R. Mahendran, R. Malaisamy and D. Mohan, Preparation, characterization and effect of annealing on performance of cellulose acetate / sulfonated polysulfone and cellulose acetate/epoxy resin blend ultrafiltration membranes, *Euro. Polym. J.*, 40 (2004), 623 - 633.
65. M. Sivakumar, R. Malaisamy, C. J. Sajitha, D. Mohan, V. Mohan and R. Rangarajan, Ultrafiltration application of cellulose acetate - polyurethane blend membranes, *Euro. Polym. J.*, 35 (1999), 1647 – 1651.
66. G. Arthanareeswaran, C. S. Latha, D. Mohan, M. Raajenthiren and K. Srinivasan, Studies on Cellulose Acetate/Low Cyclic Dimmer Polysulfone Blend Ultrafiltration Membranes and their Application, *Sep. Sci. Technol.*, 41 (2006), 2895 – 2912.
67. R. Malaisamy, R. M. Doraiswamy and R. Munnuswamy, Polyurethane and Sulfonated Polysulfone Blend Ultrafiltration Membranes, *J. Colloid Interf. Sci.*, 254, (2002), 129 – 140.
68. V. Simanzhenkov and R. Idem, *Crude Oil Chemistry*, Marcel Dekker, Inc., 270 Madison Avenue, New York, NY 10016, U.S.A, 2003.
69. P. Lipp, C. H. Lee, A. G. Fane and C. J. D. Fell, A fundamental study of the ultrafiltration of oil-water emulsions, *J. Membr. Sci.*, 36 (1988), 161-177.

70. K. Karakulski, A. Kozlowski and A. W. Morawski, Purification of oily wastewater by ultrafiltration, *Sep. Technol.*, 5 (1995), 197 - 205.
71. S. H. Lin and W. J. Lan, Treatment of waste oil/water emulsion by ultrafiltration and ion exchange, *Water Res.* 32 (1998), 2680 - 2688.
72. N. N. Nazal, and M. R. Wiesner, Microfiltration of oil-in-water emulsion, *Water Environ. Res.*, 68 (1996), 197 - 203.
73. U. Daiminger, W. Nitsch, P. Plucinski and S. Hoffmann, Novel techniques for oil/water separation, *J. Membr. Sci.*, 99 (1995), 197 - 203.
74. K. Ueyama, K. Fukuura and S. Furusaki, Oil-phase permeation behaviour of o/w emulsion through a porous polytetrafluoroethylene membrane, *J. Chem. Eng. Japan*, 20 (1987), 618 - 622.
75. J. Kong and K. Li, Oil removal from oil-in-water emulsions using PVDF membranes, *Sep. Purif. Technol.*, 16 (1999), 83 - 93.
76. R. Field, A. Hang and S. Arnot, The influence of surfactant on water flux through microfiltration membranes, *J. Membr. Sci.*, 86 (1994), 291 - 304.
77. A. B. Koltuniewicz and R. W. Field, Process factors during removal of oil-in-water emulsions with cross-flow microfiltration, *Desalination*, 105 (1996), 79 - 89.
78. I. W. Cumming, R. G. Holdich and I. D. Smith, The rejection of oil by microfiltration of a stabilised kerosene/water emulsion, *J. Membr. Sci.* 169 (2000), 147 - 155.

79. H. J. Li, Y. M. Cao, J. J. Qin, X. M. Jie, T. H. Wang, J. H. Liu and Q. Yuan, Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil–water separation, *J. Membr. Sci.*, 279 (2006), 328 - 335.
80. C. Wu, A. Li, L. Li, L. Zhang, H. Wang, X. Qi and Q. Zhang, Treatment of oily water by a poly(vinyl alcohol) ultrafiltration membrane, *Desalination*, 225 (2008), 312 – 321.
81. F. L. Hua, Y. F. Tsang, Y. J. Wang, S. Y. Chan, H. Chua and S. N. Sin, Performance study of ceramic microfiltration membrane for oily wastewater treatment, *Chem. Eng. J.*, 128 (2007), 169 – 175.
82. Y. Zhao, Y. Tan, F.S. Wong, A.G. Fane, and N. Xu, Formation of dynamic membranes for oily water separation by crossflow filtration, *Sep. Purif. Technol.*, 44 (2005), 212 - 220.
83. Jing Zhong, Xiaojuan Sun, Cheli Wang, Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration, *Sep. Purif. Technol.*, 32 (2003), 93 - 98.
84. T. Bhanumurthy, S. K. Gautam and S. Basu, Separation and recycling of oily industrial effluents: A study with cutting oil, ITT Bombay, personal communication, 1994.
85. A. Lobo, Á. Cambiella, J. M. Benito, C. Pazos and J. Coca, Ultrafiltration of oil-in-water emulsions with ceramic membranes: Influence of pH and crossflow velocity, *J. Membr. Sci.*, 278 (1-2) (2006), 328 - 334.

86. Y. S. Li, L. Yana, C. B. Xiang and L. J. Hong, Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes, *Desalination* 196 (2006), 76 – 83.
87. E. Gorouhi, M. Sadrzadeh and T. Mohammadi, Microfiltration of oily wastewater using PP hydrophobic membrane, *Desalination*, 200, (1-3) (2006), 319 - 321.
88. S. Elmaleh and N. Ghaffor, Cross-flow ultrafiltration of hydrocarbon and biological solid mixed suspensions , *J. Membr. Sci.*, 118 (1996), 111 - 120.
89. M. J. Um, S. H. Yoon, C. H. Lee, K. Y. Chung and J. J. Kim, Flux enhancement with gas injection in crossflow ultrafiltration of oily wastewater, *Water Res.*, 35 (2001), 4095 – 4101.
90. K. Scott, A. Adhamy, W. Atteck and C. Davidson, Crossflow microfiltration of organic/water suspensions, *Water Res.*, 28 (1994), 137 - 145.
91. W. Lin and B. E. Reed, Comparison of cross flow ultrafiltration and centrifugal membrane technology in treating and oil/ grease wastewater, in: A.S. Weber (Ed.), *Hazardous and Industrial Waste: Proceedings of the 28th Mid-Atlantic Industrial and Hazardous Waste Conference*, Technomic Publishing Company, USA, 1996, pp. 278 - 285.
92. Z. L. Xu, T. S. Chung, K. C. Loh and B. C. Lim, Polymeric asymmetric membranes made from Polyetherimide / polybenzimidazole / poly(ethylene glycol) (PEI/PBI/PEG) for oil–surfactant–water separation, *J. Membr. Sci.*, 158 (1999), 41 - 53.

93. J. Hao, B. D. McCloskey, A. C. Sagle, Y. H. Wu, V. A. Kusuma and B. D. Freeman, Crosslinked poly(ethylene oxide) fouling resistant coating materials for oil/water separation , J. Membr. Sci., 307 (2008), 260 – 267.
94. H. J. Li, Y. M. Cao, J. J. Qin, X. M. Jie, T. H. Wang, J. H. Liu and Q. Yuan, Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil–water separation, J. Membr. Sci. 279 (2006), 328 - 335.
95. T. Mohammadi, A. Pak, M. Karbassian and M. Golshan, Effect of operating conditions on microfiltration of an oil-water emulsion by a kaolin membrane, Desalination, 168 (2004), 201 - 205.
96. A. G. Fane and C. J. D. Fell, A review of fouling and fouling control in ultrafiltration, Desalination, 62 (1987), 117 - 136.
97. B. Tansel, W.Y. Bao and I. N. Tansel, Characterization of fouling kinetics in ultrafiltration systems by resistances in series model, Desalination 129 (2000), 7 - 14.
98. P. Rai , C. Rai, G. C. Majumdar, S. Das Gupta and S. De, Resistance in series model for ultrafiltration of mosambi (Citrus sinensis (L.) Osbeck) juice in a stirred continuous mode, J. Membr. Sci., 283 (2006), 116 – 122.
99. M. M. Dal-Cin , F. McLellan , C. N. Striez , C. M. Tam, T. A. Tweddle and A. Kumar, Membrane performance with a pulp mill effluent: Relative contributions of fouling mechanisms, J. Membr. Sci., 120 (1996), 273 - 285.
100. R. Jiraratananon and A. Chanachai, A study of fouling in the ultrafiltration of passion fruit juice, J. Membr. Sci., 111 (1996), 39 - 48.
101. C. Bhattacharjee and P. K. Bhattacharya, Prediction of limiting flux in

- ultrafiltration of kraft black liquor, *J. Membr. Sci.*, 72 (1992), 137 - 147.
102. S. Bhattacharjee, A. Sharma and P. K. Bhattacharya, A unified model for flux prediction during batch cell ultrafiltration, *J. Membr. Sci.*, 111 (1996), 243 - 258.
103. L. Song, Flux decline in cross flow microfiltration and ultrafiltration: mechanisms and modeling of membrane fouling, *J. Membr. Sci.*, 139 (1998), 183 – 200.
104. L. Song, A new model for the calculation of the limiting flux in ultrafiltration, *J. Membr. Sci.*, 144 (1998), 173 –185.
105. Y. Lee and M. M. Clark, Modeling of flux decline during crossflow ultrafiltration of colloidal suspensions, *J. Membr. Sci.*, 149 (1998), 181-202.
106. H. M. Yeh, H. P. Wu and J. F. Dong, Effects of design and operating parameters on the declination of permeate flux for membrane ultrafiltration along hollow- fiber modules, *J. Membr. Sci.*, 213 (2003), 33 – 44.
107. R. Jiraratananon, D. Uttapap and E. Sampranpiboon, Crossflow microfiltration of a colloidal suspension with the presence of macromolecules, *J. Membr. Sci.*, 140 (1998), 57 - 66.
108. L. Huang and M. T. Morrissey, Fouling of membranes during microfiltration of surimi wash water: Roles of pore blocking and surface cake formation, *J.*

- Membr. Sci., 144 (1998), 113 - 123.
109. M. Y. Jaffrin, L. H. Ding, C. Couvreur and P. Khari, Effect of ethanol on ultrafiltration of bovine albumin solutions with organic membranes, J. Membr. Sci., 124 (1997), 233 - 241.
110. J. Hermia, Constant pressure blocking filtration laws application to power-law non newtonian fluids, Trans. Inst. Chem.Eng., 60 (1982), 183-187.
111. P.H. Hermans and H.L. Bredee, Principles of the mathematical treatment of constant pressure filtration, J. Soc. Chem. Ind. 55 (1936), 1T.
112. S. De and P. K. Bhattacharya, Modeling of ultrafiltration process for a two-component aqueous solution of low and high (gel-forming) molecular weight solutes, J. Membr. Sci., 136 (1997), 57 - 69.
113. A. Suki, A. G. Fane and C. J. D. Fell, Modeling Fouling Mechanisms in Protein Ultrafiltration, J. Membr. Sci., 27 (1986), 181 - 193.
114. L. F. Fu and B. A. Dempsey, Modeling the effect of particle size and charge on the structure of the filter cake in ultrafiltration, J. Membr. Sci., 149 (1998), 221 - 240.
115. S. Sethi and M. R. Wiesner, Modeling of transient permeate flux in cross-flow membrane filtration incorporating multiple particle transport mechanisms, J. Membr. Sci., 136 (1997), 191 - 205.
116. M. K. Purkait, P. K. Bhattacharya and S. De, Membrane filtration of leather plant effluent: Flux decline mechanism, J. Membr. Sci., 258 (2005), 85 – 96.
117. K. Stamatakis and C. Tien, A simple model of cross-flow filtration based

- on particle adhesion, *AIChE* 39 (1993), 1292 - 1302.
118. J. G. Wijmans, S. Nakao and C. A. Smolders, Flux Limitation in Ultrafiltration : Osmotic pressure model and Gel layer model, *J. Membr. Sci.*, 20 (1984), 115 - 124.
119. P. Blanpain, J. Hermia and M. Lenoel, Mechanisms governing permeate flux and protein rejection in the microfiltration of beer with a Cyclopore membrane, *J. Membr. Sci.*, 84 (1993), 37 - 51.
120. A. B. Koltuniewicz, R.W. Field and T. C. Arnot, Cross-flow and dead-end microfiltration of oily-water emulsion. Part I: Experimental study and analysis of flux decline, *J. Membr. Sci.*, 102 (1995), 193 - 207.
121. D. Bhattacharyya, A. B. Jumawan and R. B. Grieves, Ultrafiltration characteristics of oil - detergent - water systems : Membrane fouling mechanisms, *Sep. Sci. Technol.*, 14 (1979), 529 - 549.
122. S. Lee, Y. Aurelle and H. Roques, Concentration polarization, membrane fouling and cleaning in ultrafiltration of soluble oil, *J. Membr. Sci.*, 19 (1984), 23 - 38.
123. T. C. Arnot, R. W. Field and A. B. Koltuniewicz, Cross-flow and dead-end microfiltration of oily-water emulsions Part II. Mechanisms and modeling of flux decline, *J. Membr. Sci.*, 169 (2000), 1–15.
124. R. W. Field, D. Wu, J. A. Howell and B. B. Gupta, Critical flux concept for microfiltration fouling, *J. Membr. Sci.* 100 (1995) 259 – 272.

125. D. Wu, J. A. Howell and N. M. Turner, A new method for modelling the time dependence of permeation flux in ultrafiltration, *Trans. IChemE* 69, Part C (1991) 77 – 82.
126. A. B. Koltuniewicz, Predicting permeate flux in ultrafiltration on the basis of surface renewal concept, *J. Membr. Sci.* 68 (1992) 107 – 118.

Chapter 2

Membrane Synthesis and Characterization: Experimental

This chapter gives a complete description of the experimentation involved in the preparation and characterization of polysulfone membranes. The chapter also gives information regarding the materials used for the preparation of polysulfone membranes along with their sources from where they are obtained. It further elaborates the characterizations of the prepared membranes through measurement of pure water flux (PWF), compaction factor (CF), equilibrium water content (EWC) and hydraulic resistance ().

2.1. Materials

Selection of materials and their appropriate compositions are some basic aspects that finally decide the morphological structure of a membrane so that the membrane can be used for specific application. Based on the facts given in Sections 1.2.4 and 1.2.5 in Chapter 1, the materials used for the synthesis of the membranes for this study are presented below:

- **Polymer:** Polysulfone (PSf) - Average molecular weight 30,000 Da
- **Solvents:** N-methyl-2-pyrrolidone (NMP) and Dimethyl Acetamide (DMAc)
- **Additives:** (1) Polyethylene Glycol (PEG) – Average molecular weights

of 400 Da, 6000 Da and 20,000 Da

(2) Polyvinylidene Pyrrolidone (PVP) – Average molecular weights of 24,000 Da, 40,000 Da and 3,60,000 Da

- **Nonsolvent:** Deionized water

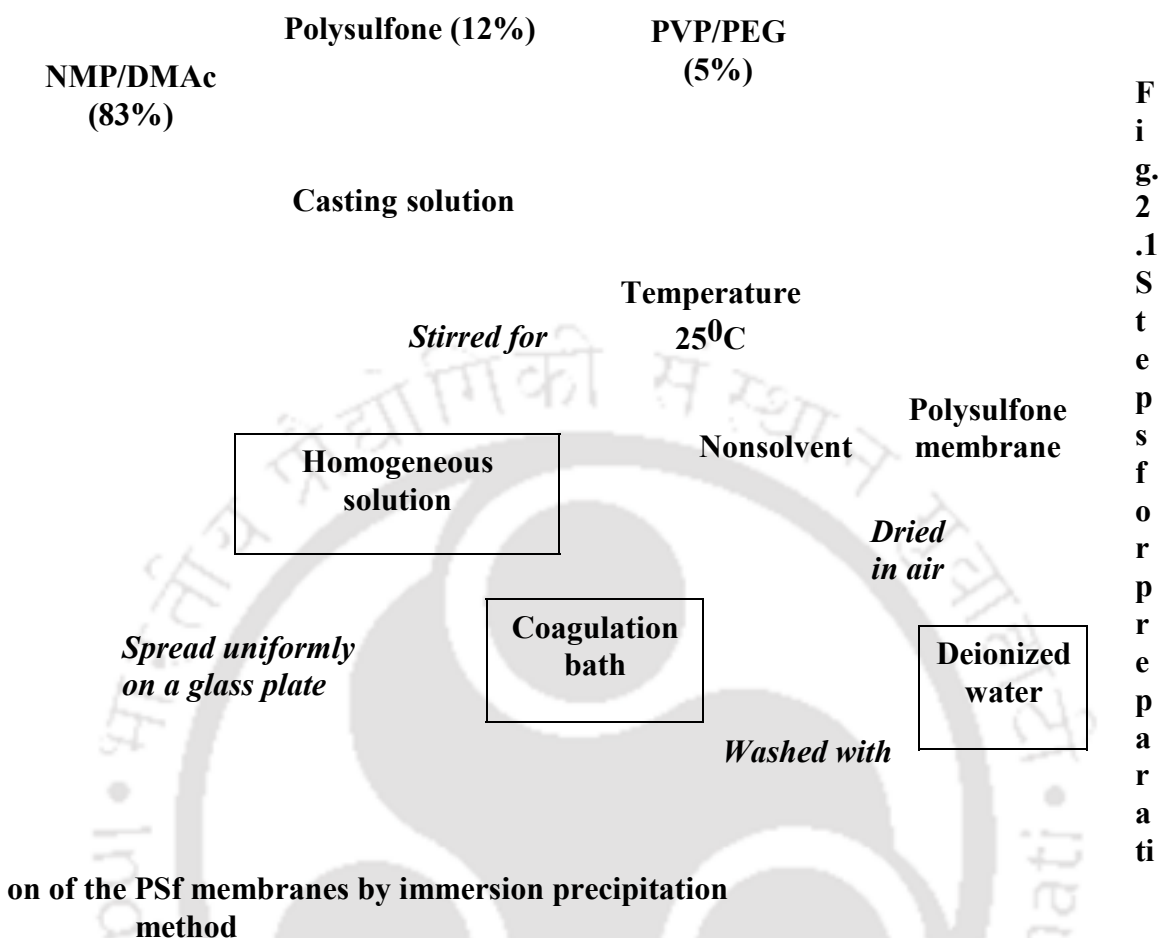
PSf (30000 Da) supplied by Sigma-Aldrich Co., USA, was used as the main polymer in the membrane casting solution. Reagent grade NMP (99.5 % purity) and DMAc (99 % purity) were used as solvents. Both the solvents were supplied by Central Drug House (CDH) Ltd., India and used without further purification. Reagent grade PEG (400 Da, 6000 Da and 20,000 Da) and PVP (24,000 Da, 40,000 Da and 3,60,000 Da) were used as the pore forming additives in the casting solution. Deionized water purified with Millipore system (Millipore, France) was used as the main nonsolvent in the coagulation bath.

2.2. Method of preparation

Flat sheet PSf membranes were prepared by the conventional immersion precipitation (i.e. phase inversion) method described in Chapter 1. As PSf is hydrophobic in nature, polymers like PEG and PVP are added as additives to the membrane casting solution to enhance its hydrophilicity in order to control the fouling of membrane [1, 2]. To make the casting solution, measured amount of polymer (PSf) along with either PVP or PEG was dissolved in the two solvents viz. NMP and DMAc, separately at room temperature

(25°C). **The steps for preparing the membranes are shown in Fig. 2.1 in the form of a block diagram.**

The polymer solution was stirred for about 6 hours at room temperature using a magnetic stirrer. When the solution (consisting of polymer, solvent and the additive) became homogeneous, it was kept at room temperature for 24 hours. Subsequently, the solution was spread uniformly on a glass plate ($0.01\text{ m} \times 0.01\text{ m}$) with the help of a casting knife maintaining a constant clearance gap between the knife and the plate in order to have membrane of uniform thickness. In this study, the gap was approximately 0.3 mm. The constant clearance gap could be maintained due to special design of the knife (doctor's knife). The resulting film was then exposed to the ambient for few seconds (not more



than 30 s) before immersion into coagulation bath containing deionized water at room temperature. Exposure of the cast film to the ambient is necessary in order to get asymmetric membrane with a somewhat denser skin to be able to perform ultrafiltration operation. Keeping the film in contact with the ambient for a long period will result in a completely dense membrane which would be applicable only for gas separation purpose [1]. The cast films changed their color from transparent to white immediately after immersion into the coagulation bath indicating the occurrence of precipitation (Fig. 1.8). After sometime, the film separated out of the glass plate as it attained the final membrane composition (i.e point D of Fig. 1.8). The prepared membrane sheets were washed under

running water and then kept overnight in a deionized water bath to remove the additional amount of additive and solvent. Finally, the sheets were air dried at room temperature. These membrane sheets were used for carrying out the subsequent studies.

2.3 Preliminary selection of composition

Selection of appropriate composition of membrane is the basic aspect as it finally decides the morphological structure of the membrane so that the membrane can be used for specific application. Initially, different compositions of membrane have been considered by changing the ratio of polymer, solvent and the additives in the casting solution in order to have a membrane with comparatively smooth surface and with a reasonable thickness. The effect of concentration of PSf on membrane formation was observed by taking three concentrations viz. 12 wt%, 15 wt% and 18 wt% keeping the solvent:additive ratio constant in the casting solution. Three concentrations of each solvent were considered viz. 75 wt%, 80 wt% and 85 wt% maintaining a constant ratio of PSf and the additives to see the effect of solvent concentration. Similarly, three concentrations of each of the additives of all the molecular weights were taken at 5 wt%, 10 wt% and 15 wt% maintaining the PSf:solvent ratio constant. Table 2.1 illustrates the different compositions considered initially to prepare the membranes together with the quality of the corresponding membranes formed. From the table it is seen that membranes prepared

Table 2.1 Preliminary compositions of membrane considered for selection

PSf (wt %)	Solvent (wt %)	Additive (wt %)	Quality of membranes
15	DMAc 80% NMP 80%	PVP 5% PEG 5%	Not good, surface is not smooth with all the membranes
14.2	DMAc 75.8% NMP 75.8%	PVP 10% PEG 10%	Lots of wrinkles on the surface of some of the membranes
13.4	DMAc 71.6% NMP 71.6%	PVP 15% PEG 15%	High degree of shrinkage for membranes prepared with high molecular weight additives
12	DMAc 82.8% NMP 82.8%	PVP 5.2% PEG 5.2%	Very fine and smooth membranes are formed for all the combinations
18	DMAc 77.2% NMP 77.2%	PVP 4.8% PEG 4.8%	Membranes are quite thicker
18.75	DMAc 75% NMP 75%	PVP 6.25% PEG 6.25%	Membranes are not formed
11.25	DMAc 85% NMP 85%	PVP 3.75% PEG 3.75%	Membranes formed are too weak to handle

with composition 12 : 82.8 : 5.2 (polymer : solvent : additive) are the most suitable membranes as the membranes are found to be of finer quality with both the solvents and

both the additives of different molecular weights. Based on these results, the following membrane composition was selected to carry out the further study:

Polymer (PSf) = 12%; solvent (NMP or DMAc) = 83%; and additive (PVP or PEG) = 5% (all on weight basis).

Finally, altogether twelve membranes were prepared considering the combinations of polymer, solvents and additives which were designated as M₁, M₂... M₁₁, M₁₂ as shown in Table 2.2.

Table 2.2 Composition of selected membranes (PSf: 12 wt%)

Membrane systems	Membranes	PVP (wt %)			PEG (wt %)			Solvent (wt%)	
		Mol.wt 24000	Mol.wt 40000	Mol.wt 360000	Mol.wt 400	Mol.wt 6000	Mol.wt 20000	NMP	DMAc
PSf/ NMP/ PVP	M ₁	5	-	-	-	-	-	83	-
	M ₂	-	5	-	-	-	-	83	-
	M ₃	-	-	5	-	-	-	83	-
PSf/ DMAc/ PVP	M ₄	5	-	-	-	-	-	-	83
	M ₅	-	5	-	-	-	-	-	83
	M ₆	-	-	5	-	-	-	-	83
	M ₇	-	-	-	5	-	-	83	-
PSf/ NMP/ PEG	M ₈	-	-	-	-	5	-	83	-
	M ₉	-	-	-	-	-	5	83	-
	M ₁₀	-	-	-	5	-	-	-	83
PSf/ DMAc/ PEG	M ₁₁	-	-	-	-	-	5	-	83

M₁₂

The M₁, M₂ and M₃ membranes belong to PSf/NMP/PVP system; M₄, M₅ and M₆ membranes to PSf/DMAc/PEG system; M₇, M₈ and M₉ membranes to PSf/NMP/PEG system and M₁₀, M₁₁ and M₁₂ membranes correspond to PSf/DMAc/PEG system.

2.4. Membrane characterization

Membrane characterization leads to the determination of structural and morphological properties of a given membrane [1]. The membranes so prepared in this work were expected to be of ultrafiltration types which were supposed to be used for separation of macromolecular solutes (e.g. protein and oil). Therefore, these membranes were characterized to ascertain their applicability in ultrafiltration (UF) operations. From the findings of the characterization, effects of different molecular weight of additives (i.e. PEG and PVP) and the nature of solvents (i.e. NMP and DMAc) on morphology and the permeation characteristics of the prepared membrane were explored.

2.4.1. Characterization by morphological study

The morphology of the prepared membranes was investigated by microscopic observations and performing other standard tests.

2.4.1.1. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is considered to be very convenient and simple method for investigating the structure of porous membranes. Microscopic observation was carried out by a high resolution scanning electron microscope (LEO 1430VP, U.K), which directly provides the visual information of the top surface as well as cross-sectional morphology of the membranes prepared. Various SEM images were taken at different magnifications so as to have clear sights of both top surface and cross section of the prepared membranes. Computerized analysis of SEM image (using ImageJ Launcher Broken Symmetry Software) is a standard and widely used method for the investigation of perforated materials [3, 4]. In the present study, ImageJ Launcher Broken Symmetry Software was used to measure the morphological parameters such as pore size and hence the pore size distribution of each membrane. For this, SEM photographs were taken at different locations of the same membrane sheet from which the pore sizes were measured. This gave the information regarding the number of pores in different pore size range within a known membrane area, from which the average pore size and the pore size distribution for a particular membrane was calculated.

The mean pore radius, $(\bar{r})$ was calculated as

(2.1)

where, r_i is the radius of the pores of different size (r_i) and N_i is the number of pores of radius r_i . Assuming similar pore size distribution for the entire membrane sheet, the

pore density, (i.e. total number of pores per unit membrane area) was calculated using the following equation:

$$= \quad (2.2)$$

where, is the total membrane area (μm^2) as calculated from the respective SEM image.

Assuming similar pore distribution for the entire membrane sheet, the surface porosity was calculated by taking summation of all the pore areas divided by the total area of the image as follows [5]:

$$(2.3)$$

However, SEM findings through Image analysis technique has got some limitations; because as almost all the pores are in the ultrafiltration range, this practice would only give rough approximation of the pore size by overestimating the smallest pores on the surface and also by considering dead end pores, which have no role in actual separation. Therefore, this technique has been applied to some of the membranes prepared such as M₇, M₈, M₉, M₁₀, M₁₁ and M₁₂.

Accordingly, the average pore sizes of the above membranes were found out through this analysis. This work is published in the Journal of Colloid and Interface Science [6]. In

fact, the resulted values of pore size were compared with those obtained by other methods discussed subsequently to understand the applicability of the software to such analysis. The details are discussed in section 3.1 of Chapter 3.

2.4.1.2. Gas permeation test

The gas permeation test is one of the standard techniques mentioned in literature [1] to determine the pore size of a membrane. The measurement of the gas permeability coefficient as a function of the mean pressure across a membrane can be used to determine a mean pore radius of the membrane. This method has been applied by several workers to characterize microporous and asymmetric ultrafiltration or hyperfiltration membranes. The method relates the gas permeation characteristics to membrane structural parameters such as average pore size and porosity. The average pore size as well as the effective porosity of the prepared membranes is determined by gas permeation test [6, 7]. Gas permeation experiments were conducted in a 70 ml capacity unstirred batch filtration cell made of Teflon, the details of the cell are given in the section 2.4.2.1. Inside the cell, the synthesized membrane sheet was placed over a base support. The effective membrane area was $3.14 \times 10^{-4} \text{ m}^2$. The cell was pressurized with air. The schematic of the experimental set up is shown in Fig. 2.2. The flow rate of air through the membrane was measured at various TMP ranging from 100 to 180 kPa at room temperature using a precalibrated air rotameter.

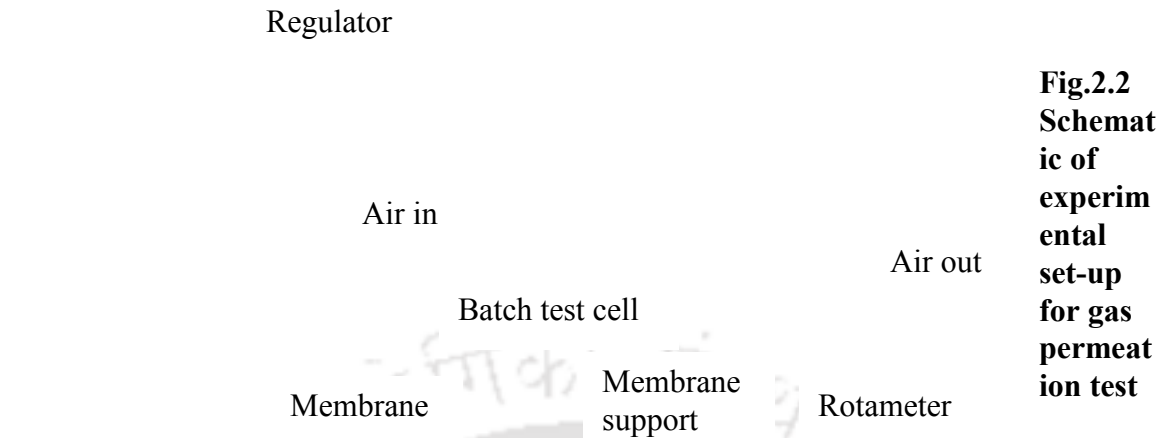


Fig.2.2
Schematic of experimental set-up for gas permeation test

Standard technique [7, 8] was used to

determine the mean pore radius of the membrane with the assumption that the pores in the skin layer are cylindrical in nature. The total gas flux through an asymmetric polymeric membrane is the sum of the diffusion flux through the dense (nonporous) skin of the membrane and the flux through the pores. The following assumptions were made for the mathematical description of gas transport in the membranes:

- (1) The pores in the skin layer are cylindrical pores of radius r and length l .
- (2) Additivity of the Fickian flow in the dense polymeric skin and the Knudsen and Poiseuille flows in the pores.
- (3) The permeability coefficients are independent of pressure.
- (4) A skin of uniform thickness rests on a porous support with a negligible flow

resistance.

The following equation is written for the total gas permeation rate $(\text{m}^3 \text{s}^{-1})$ [8]:

$$(2.4)$$

where, the first term of Eq. (2.4) relates to the the Fickian diffusion flow, the second term to the Knudsen molecular flow and the third term to the Poiseuille compressible flow. In Eq. (2.4), P is the permeability coefficient of the gas used in the polymeric membrane, r_p is the mean pore radius of the membrane (m), ϵ is the porosity, l_p is the pore length (m), R is the universal gas constant ($8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), M is the molecular weight of the gas (i.e. air), ΔP is the pressure drop across the membrane (Pa), A is the membrane area (m^2), P_a is the atmospheric pressure at which P is measured, P_m is the mean pressure (Pa) of the upstream and downstream of the membrane, η is the viscosity of the gas i.e. air (Pa.s), P_u is the applied pressure (Pa) and P_d is the downstream pressure (atmospheric pressure in the present case i.e.

). Neglecting the contribution of the Fickian diffusion flow through the nonporous

medium, the total gas permeation rate through an asymmetric membrane is expressed in

terms of Poiseuille flow and Knudsen flow in the porous medium. Then the total gas permeation rate will be of the following form [8]:

$$(2.5)$$

$$(2.6)$$

After rearranging, Eq. (2.5) can be written as

$$(2.7)$$

where

Since the pressure dependence of the gas viscosity is negligible, is a linear

function of the mean pressure, . The term is known as the “pressure normalized”

gas flux [8]. Thus, Eq. (2.7) is written as

$$(2.8)$$

where, (2.9)

(2.10)

(2.11)

Plotting values of $\frac{V_p}{V_t}$ against $\frac{V_p}{V_t}$, a straight line was obtained for each experiment according to Eq. (2.8). Constants $\frac{V_p}{V_t}$ and $\frac{V_p}{V_t}$ were calculated from the intercept and slope of the plot respectively. The mean pore radius was obtained from Eqs. (2.10) and (2.11) as shown below:

(2.12)

The effective porosity, ϵ , was evaluated from Eq. (2.11) i.e.

(2.13)

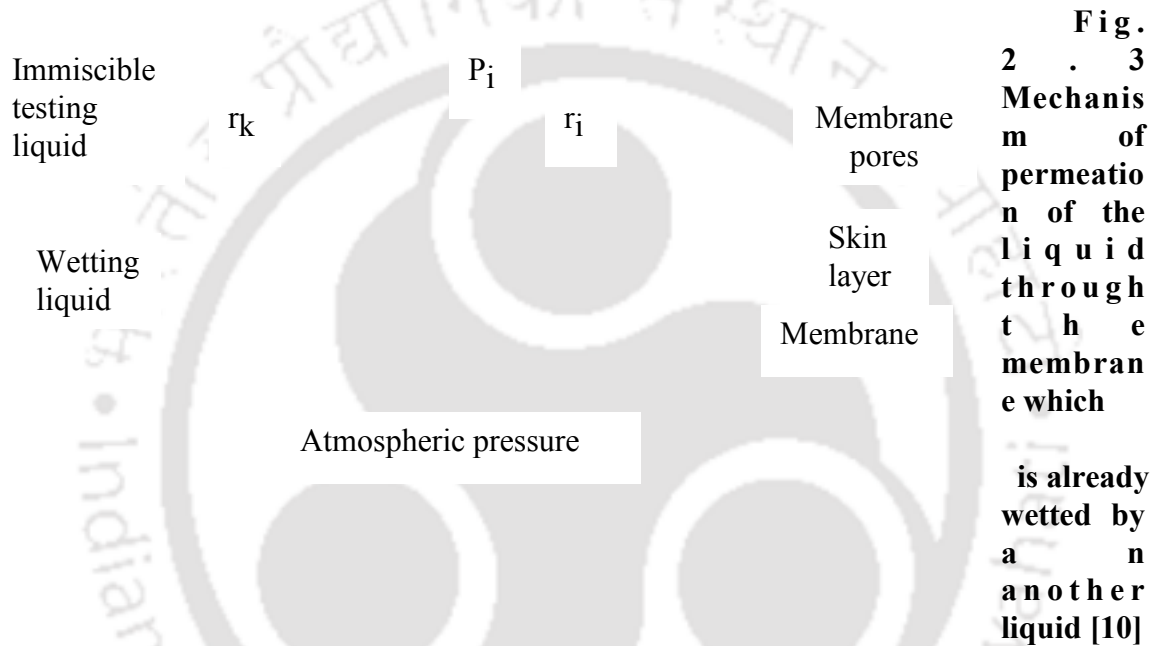
Absolute porosity, ϵ_a , was calculated from the effective porosity considering that the pore length, l_p , to be equivalent to the membrane thickness (l_m). The thickness of the prepared membranes was calculated from SEM photographs of cross-section of membranes with the help of ImageJ Software [9].

2.4.1.3. Liquid displacement test

The liquid displacement test helps us to evaluate the transmembrane pores of the membranes in wet state i.e. under the condition similar to that of UF operation. The average pore size as well as the pore number and pore area distribution of the prepared membranes were determined by this method [1], also known as combined bubble pressure and solvent permeability method [10]. In this method, the membrane is wetted previously with an appropriate penetrating liquid assuming that all the pores in the membrane are filled with that liquid. Then another liquid which is immiscible with the previous liquid and does not wet the membrane, is forced through the pores displacing the previous liquid which is already occupying the pores. As the two liquids are chosen to be immiscible, an interfacial tension arises at the interface between the two liquids so that the second liquid will displace the first liquid only when the pressure applied to the second liquid will reach the value given by the Cantor's equation:

$$(2.14)$$

where, ΔP is the TMP, γ is the interfacial tension between the two liquids and r is the pore radius. Based on the assumption that at the lowest pressure the largest pores are invaded by a liquid, and at the higher pressure the smaller pores are occupied, the mechanism of permeation can be explained as shown in Fig.2.3 [10].



Here, it is assumed that at pressure P_i the testing liquid permeates only through the pores with radius $r > r_i$ (r_i is the critical radius). Pores with smaller radius r_k become permeable at pressure $P_k (>P_i)$. By means of such a technique it is possible to obtain a plot of flux vs. pressure, which shows a trend as reported in Fig. 2.4. The flux, J_i corresponds to the pores for which $r > r_i$; while the flux J_k corresponds to the pores for which $r > r_k$. Therefore, $J_{i,k}$ calculated at $P_{i,k}$ is the contribution of the pores with radii between r_k

and r_i . Increasing the pressure will increase the flux until a pressure P_n is reached when all the pores are filled with the testing liquid; beyond this pressure, the liquid flux, J , through the membrane becomes directly proportional to the pressure [11, 12].

J

J_k

J_i

ΔJ_i

P_i $P_{i,k}$ P

P

P

Fig. 2.4

Typical flux

(J) vs.

pressure (P)

curve

One important criteria in this method is that the interfacial

tension, γ , between the two liquids should be low so that very small pores can be measured without applying high pressures. In fact, P_n depends on interfacial tension, besides the pore radius. In this work, water-isobutanol-methanol (25:15:7 v/v) mixture was taken as the penetrating (wetting) liquid. Deionized water was considered for the immiscible (testing liquid) liquid. The interfacial tension between this mixture and water is reported to be 0.35 mPa.m (dyne/cm) at 20°C [11, 12].

The pore size distribution was obtained from the data of variation of flow with pressure [11, 12]. The following equations were used to calculate the pore size distribution:

The total hydraulic permeability coefficient () was obtained by:

(2.15)

Where, is the flux at pressure and is the partial permeability coefficient of the pores with radius between and evaluated at , which corresponds to a mean radius i.e.

(2.16)

Combining Eqs. (2.14) and (2.15), flux versus pressure data gives the permeability versus pore radius curve. Again, the pore number versus pore radius and pore area versus pore radius curves is obtained using the following equations [11, 12]:

(2.17)

(2.18)

Where, is the pore density i.e., the number of pores having radii between and per unit area of the membrane surface, is the length of the pore that is assumed to be

the thickness of the skin layer and η is the viscosity of the alcohol rich mixture. ΔP is

the area of pores having radii between r and $r + dr$. Both the equations are derived from the

Cantor's equation (Eq. 2.14) and Hagen Poiseuille's permeation equation (Eq. 2.19)

assuming cylindrical pores and laminar flow as given below:

$$(2.19)$$

An average value of the thickness of the skin layer equal to δ is considered in the present work even though it is likely to vary along the surface of the membrane.

The total pore area A_p and the total number of pores per unit area of membrane N_p can be found as follows:

$$(2.20)$$

$$(2.21)$$

The mean pore radius $\bar{r}$ is calculated as follows [13]:

$$(2.22)$$

The limitation of this method is that the actual values of pore size and pore size distribution are likely to be marginally different in comparison to those measured by this

method. This is due to the assumption of cylindrical pores and uniform thickness of membrane skin layer in the analysis. However, the information is very useful in comparing the values of different membranes. This work has been published in the two volumes of Journal of Membrane Science [13, 14].

2.4.2. Characterization by permeation studies

The prepared membranes were subjected to UF characterizations such as measurement of compaction factor (CF), pure water flux (PWF), hydraulic resistance (R_m), and equilibrium water content (EWC) [13, 14].

2.4.2.1. Fabrication of the membrane cell

All the batch permeations experiments were conducted using the membrane cell mentioned before. Fig. 2.5 represents the schematic of the cell. The cell consists of two compartments with the provision of keeping the membrane sheet in between. Inside

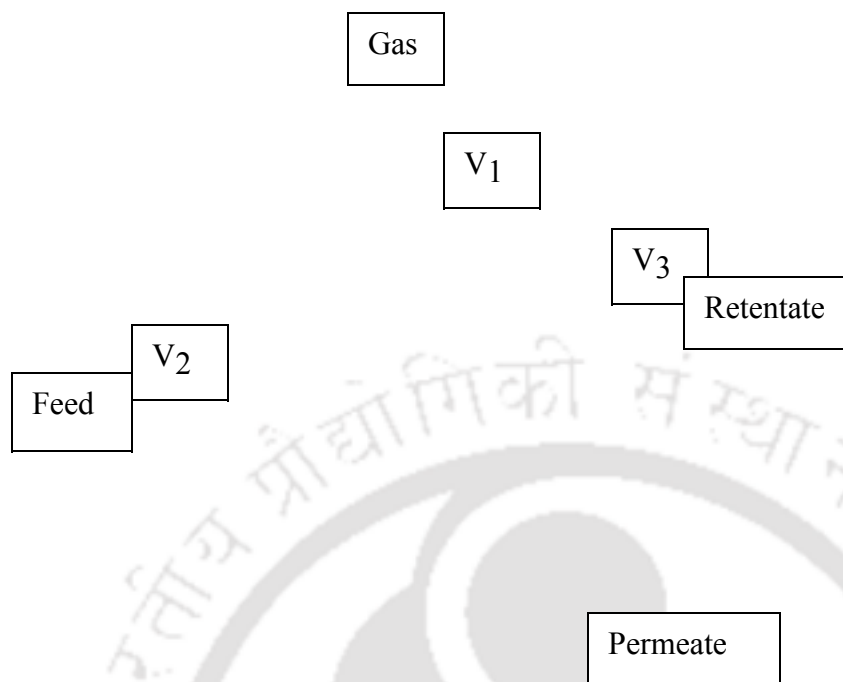


Fig. 2.5

Schematic of test cell

the cell, the flat circular membrane sheet was supported over a thin perforated Teflon plate.

The membrane diameter is 2×10^{-2} m and the effective area of the membrane is 3.14×10^{-4} m². The permeate solution was collected from the bottom of the cell.

There are two inlets viz. one for the gas to pressurize the cell and the other for the feed solution. There are two outlets to withdraw the permeate and the retentate solutions as shown in Fig. 2.5.

2.4.2.2. Membrane compaction

Before using a fresh membrane, it was compacted with deionized water for 4 hours at a transmembrane pressure (TMP) of 240 kPa which is higher than the maximum operating pressure in the present study. The water flux is calculated from the experimental permeate flow rate measured at every 30 minutes interval after attaining flow stabilization. The

compaction factor (CF) was calculated as the ratio of initial pure water flux () to steady state pure water flux () [14] i.e.

$$(2.23)$$

2.4.2.3. Pure water flux (PWF) and hydraulic resistance ()

Deionized water was allowed to pass through each compacted membrane at different TMP (ranging 0 - 240 kPa) and the water permeate was collected from the bottom of the cell (Fig. 2.5). Pure water flux (PWF) was determined by using the following equation:

$$(2.24)$$

where, is PWF ($Lm^{-2}h^{-1}$), is volume of water permeated (L), is effective membrane area (m^2) and is permeation time (h).

The term, (), also known as permeability, was determined from the slope of the linear relationship between the PWF () and corresponding TMP (). Hydraulic resistance () (m^2hkPaL^{-1}) was obtained from the inverse of the value of permeability.

Hydraulic resistance, *has got significance particularly for membranes used in*

pressure-driven separation processes. Higher the *for a particular membrane, lower is* the PWF, indicating generation of less amount of permeate. The high values of PWF indicate that either the membrane is more hydrophilic or more porous or both [13, 14].

2.4.2.4. Equilibrium water content (EWC)

Equilibrium water content (EWC) is considered to be an important characterization parameter as it indirectly indicates the degree of hydrophilicity or hydrophobicity of a membrane [15]. Also it is related to the porosity of a membrane. Membranes were weighed in an electronic balance in wet state after mopping the surface water with a clean tissue paper. The wet membranes were dried by putting in a vacuum oven for 24 hours at a temperature of 50 - 60 °C and again they were weighed in dry state. Then EWC at room temperature was calculated as follows [14]:

$$\text{EWC (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2.25)$$

where, W_w is weight of wet membranes (g) and W_d is weight of dry membranes (g).

All the experiments for characterization of the membranes and all the batch permeation experiments for UF separation of solutes were carried out in the same batch test cell mentioned in the previous section (Fig. 2.5). In those characterization experiments, the retentate line (i.e. valve V₃) was kept close; however the valve was kept open for the separation experiments. The schematic of the batch

experimental set up used for both the purposes i.e. membrane characterization and solute separation experiments is presented in Fig. 2.6 (a) while the photograph of the set up is shown in Fig. 2.6 (b).

The feed is pumped from the feed tank into the upper compartment of the cell which

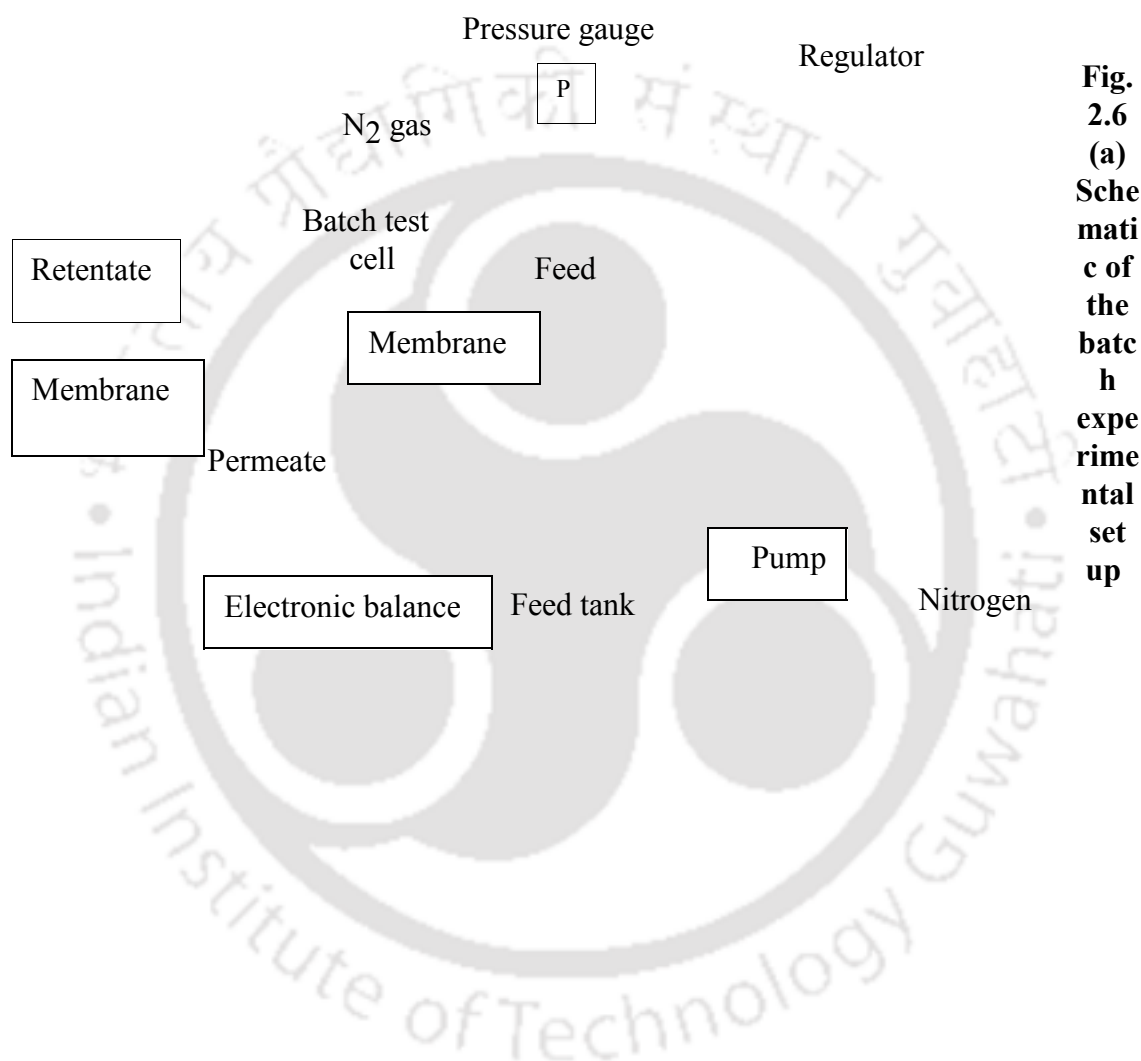




Fig. 2.6 (b) Photograph of the batch experimental set up

was then pressurized by nitrogen gas. As mentioned before, the permeate was collected from the bottom of the lower compartment continuously while the retentate was collected once only after the completion of the experiment.

Abbreviations

CF	Compaction factor
DMAc	Dimethyl acetamide
EWC	Equilibrium water content
NMP	N- methyl pyrrolidone
PEG	Poly(ethylene glycol)
PSf	Polysulfone
PVP	Polyvinylpyrrolidone
PWF	Pure water flux
SEM	Scanning electron microscopy
TMP	Transmembrane pressure
UF	Ultrafiltration

Notations

Effective Membrane area (m^2)

Area of pores having radii between and (cm^2) (as defined in Eq.2.18)

Total membrane area (μm^2) (as defined in Eq.2.2)

Total pore area of membrane (cm^2) (as defined in Eq.2.20)

Thickness of the skin layer (μm) (as defined in Eq.2.17)

Flux at pressure (ms^{-1})

PWF ($\text{Lm}^{-2}\text{h}^{-1}$)

Permeability coefficient of the gas ($\text{m}^2\text{Pa}^{-1}\text{s}^{-1}$)

Partial permeability coefficient of the pores with radius between and
($\text{ms}^{-1}\text{MPa}^{-1}$) (as defined in Eq.2.15)

Total hydraulic permeability coefficient ($\text{ms}^{-1}\text{MPa}^{-1}$)

Pore length (m) (as defined in Eq.2.4)

Molecular weight of the gas (i.e. air)

Pore density () (as defined in Eq.2.2)

Pore density i.e., the number of pores having radii between and per
unit area of the membrane surface (cm^{-2}) (as defined in Eq. 2.17)

Total number of pores per unit area of membrane (cm^{-2}) (as defined in
Eq. 2.21)

Number of pores of radius

TMP (Pa) (as defined in Eq. 2.14)

Atmospheric pressure (Pa)

Mean pressure (Pa) of the upstream and downstream of the membrane

Applied pressure (Pa)

Downstream pressure (Pa)

Pressure drop across the membrane (Pa) (as defined in Eq.2.4)

Total gas permeation rate (m^3s^{-1})

Volume of water permeated (L)

Universal gas constant ($8.314 \text{ m}^3 \text{ Pa mol}^{-1} \cdot \text{K}^{-1}$)

Hydraulic resistance ($\text{m}^2 \text{ h kPa L}^{-1}$)

Mean pore radius (obtained from SEM) ()

Mean pore radius (obtained from gas permeation test) ()

Mean pore radius (obtained from liquid displacement test) (nm)

Radius of the i^{th} pore (nm)

The absolute temperature (K)

Permeation time (h)

Weight of wet membranes (g)

Weight of dry membranes (g)

Greek symbols

Absolute porosity (as defined in Eq. 2.4)

Surface porosity (as defined in Eq. 2.3)

Viscosity of the gas (Pa.s) (as defined in Eq. 2.4)

Viscosity of the alcohol rich mixture (Pa.s) (as defined in Eq. 2.17)

Interfacial tension between the two liquids (Pa.m)

References

1. M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, 1991.
2. Munir Cheryan, Ultrafiltration and Microfiltration Handbook, Technomic Publishing Co. Inc. Lancaster, Pennsylvania, U.S.A, 1998.

3. K. J. Kim, A. G. Fane, C. J. D. Fell, T. Suzuki and M. R. Dickson, Quantitative microscopic study of surface characterization of ultrafiltration membranes, *J. Membr. Sci.*, 54 (1990), 89 - 102.
4. L. Palacio, P. Pradanos, J. I. Calvo and A. Hernandez, Porosity measurements by a gas penetration method and other techniques applied to membrane characterization, *Thin Solid Films*, 348 (1999), 22 - 29.
5. A. G. Fane, C. J. D. Fell and A. G. Waters, The relationship between membrane surface pore characteristics and flux for ultrafiltration membranes, *J. Membr. Sci.*, 9 (1981), 245 - 262.
6. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "SEM analysis and gas permeability test to characterize polysulfone membrane prepared with polyethylene glycol as additive", *J. Colloid. Interf. Sci.*, 320 (2008), 245 - 253.
7. H. Yasuda and J. T. Tsai, Pore size of microporous polymer membranes, *J. Appl. Polym. Sci.*, 18 (1974), 805 - 819.
8. P. Uchytil, X. Q. Nguyen and Z. Broz, Characterization of membrane skin defects by gas permeation method, *J. Membr. Sci.*, 73 (1992), 47 - 53.
9. J. Marchese and C. L. Pagliero, Characterization of asymmetric polysulfone membranes for gas separation, *Gas Sep. & Purif.*, 5 (1991), 215 - 221.
10. G. Capannelli, I. Becchi, A. Bottino, P. Moretti and S. Munari, in: K. K. Unger, J. Rouquesol, K.S.W. Sing (Eds.), *Characterization of porous solids*, Elsevier, Amsterdam, Holland, (1988), 283 - 294.

11. G. Capannelli, F. Vigo and S. Munari, Ultrafiltration Membranes-Characterization methods, J. Membr. Sci., 15 (1983), 289 - 313.
12. P. Abaticchio, A. Bottino, G. Capannelli and S. Munari, Characterization of Ultrafiltration Polymeric Membranes, Desalination, 78 (1990), 235 - 255.
13. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Effect of Molecular weight of PEG on Membrane Morphology and Transport Properties", J. Membr. Sci., 309 (2008), 209 - 221.
14. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive", J. Membr. Sci., 315 (2008), 36 - 47.
15. G. Arthanareeswaran, C. S. Latha, D. Mohan, M. Raajenthiren and K. Srinivasan, Studies on Cellulose Acetate / Low Cyclic Dimmer Polysulfone Blend Ultrafiltration Membranes and their Application, Sep. Sci. Technol., 41 (2006), 2895 - 2912.

Chapter 3

Membrane Synthesis and Characterization: Results and Discussion

This chapter presents the results and discussion of the experimental studies on Polysulfone (PSf) membrane synthesis and characterization. It discusses individually the effect of addition of different molecular weights of PVP and PEG additives into the membrane casting solution consisting of PSf as membrane forming polymer and NMP and DMAc as solvents. The results of different characterization methods carried out in this work e.g. scanning electron microscopy (SEM), gas permeation test and liquid displacement method to find out the membrane morphology are presented here. Also, the chapter gives an insight into the findings of the ultrafiltration (UF) characterizations of the membranes such as measurement of pure water flux (PWF), hydraulic resistance (), compaction factor (CF) and equilibrium water content (EWC). The consequences of addition of increasing molecular weights of the two additives i.e. PVP and PEG on membrane morphology and permeation performance are highlighted.

3.1. Morphological parameters

The membranes prepared with the two solvents and PVP and PEG as additives are designated as M₁, M₂... M₁₀, M₁₁ and M₁₂ as mentioned in Section 2.3 of Chapter 2.

The compositions of all the membranes are given in Table 2.2. To study the effect of increasing molecular weight of the two additives on membrane morphology, these

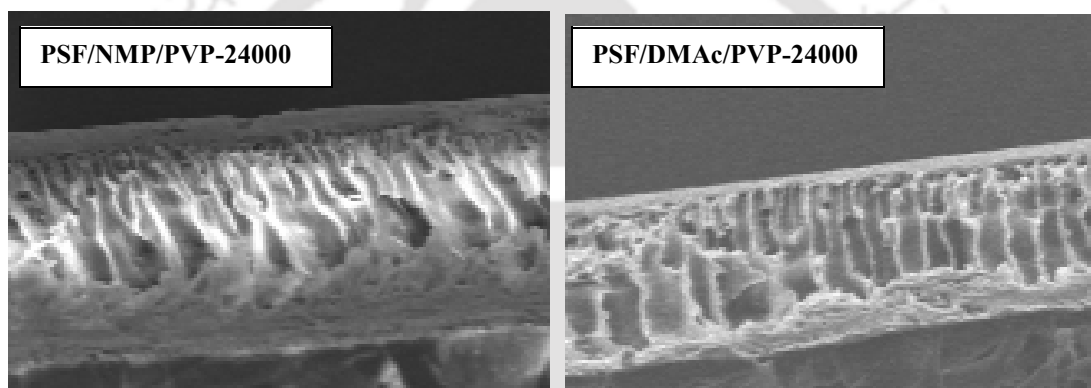
membranes were characterized by different methods mentioned in the previous chapter i.e. scanning electron microscopy (SEM), gas permeation test and liquid displacement method to quantify the membrane morphology in terms of average pore size and porosity.

3.1.1. SEM observations

3.1.1.1. Qualitative analysis

The morphology of the prepared membranes at different compositions was examined using a high resolution scanning electron microscope. SEM photographs of cross-sectional images of the prepared membranes are shown in Figs. 3.1(a) and 3.1 (b) for PSf/NMP and PSf/DMAc systems respectively with PVP as additive and in Figs. 3.2 (a) and 3.2 (b) for PSf/NMP and PSf/DMAc systems respectively with PEG as additive. From the figures it is seen that the membranes so formed are having asymmetric structure consisting of a dense top layer and a porous sub-layer. The sub-layer seems to have finger-like cavities as well as macrovoid structure. Similar observations were also found by Strathmann et al. [1] for the systems of polyamide as the polymer using dimethylsulfoxide (DMSO), DMF, DMAc and NMP as solvents, separately with lithium chloride (LiCl) as the additive. This phenomenon can be explained from the concept of the types of liquid-liquid demixing which may result in a membrane sub-layer either with macrovoids or without any macrovoids. Due to high mutual affinity of NMP and DMAc for water (used as nonsolvent during the phase inversion), instantaneous demixing results leading to the formation of finger like cavities in the sub-layer of the prepared membranes which has already been discussed

in Chapter 1. However, in this case, the occurrence of instantaneous demixing does not exclusively depends on the solvent-nonsolvent exchange as explained with the ternary phase diagram (Chapter 1); because in this study with the addition of the additive, the system has become a quaternary system, where the binodal and the spinodal are surfaces instead of two lines as seen in the ternary phase diagram and they intercept at a critical curve. Due to complexity, it is customary to analyze such quaternary system



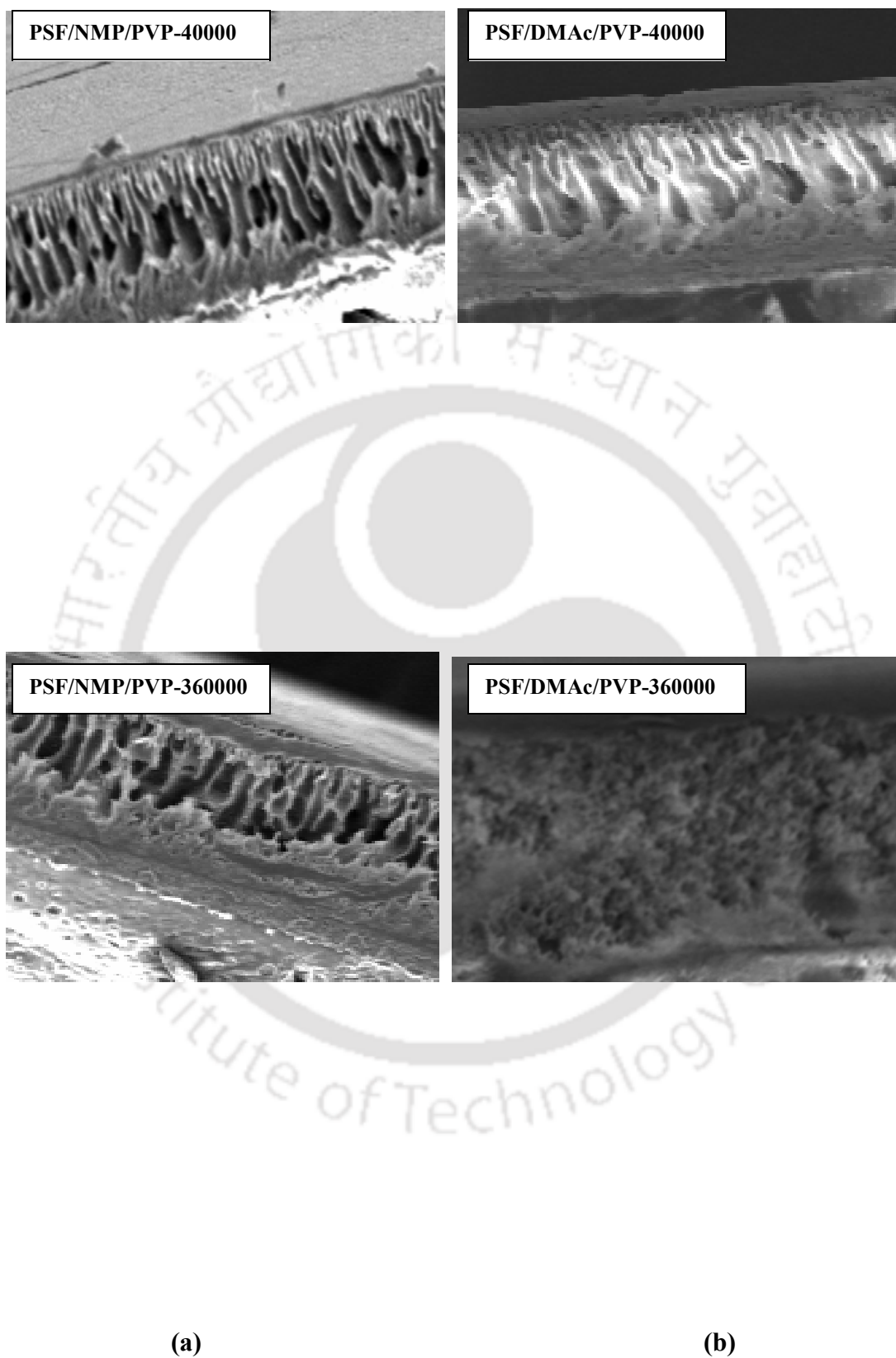
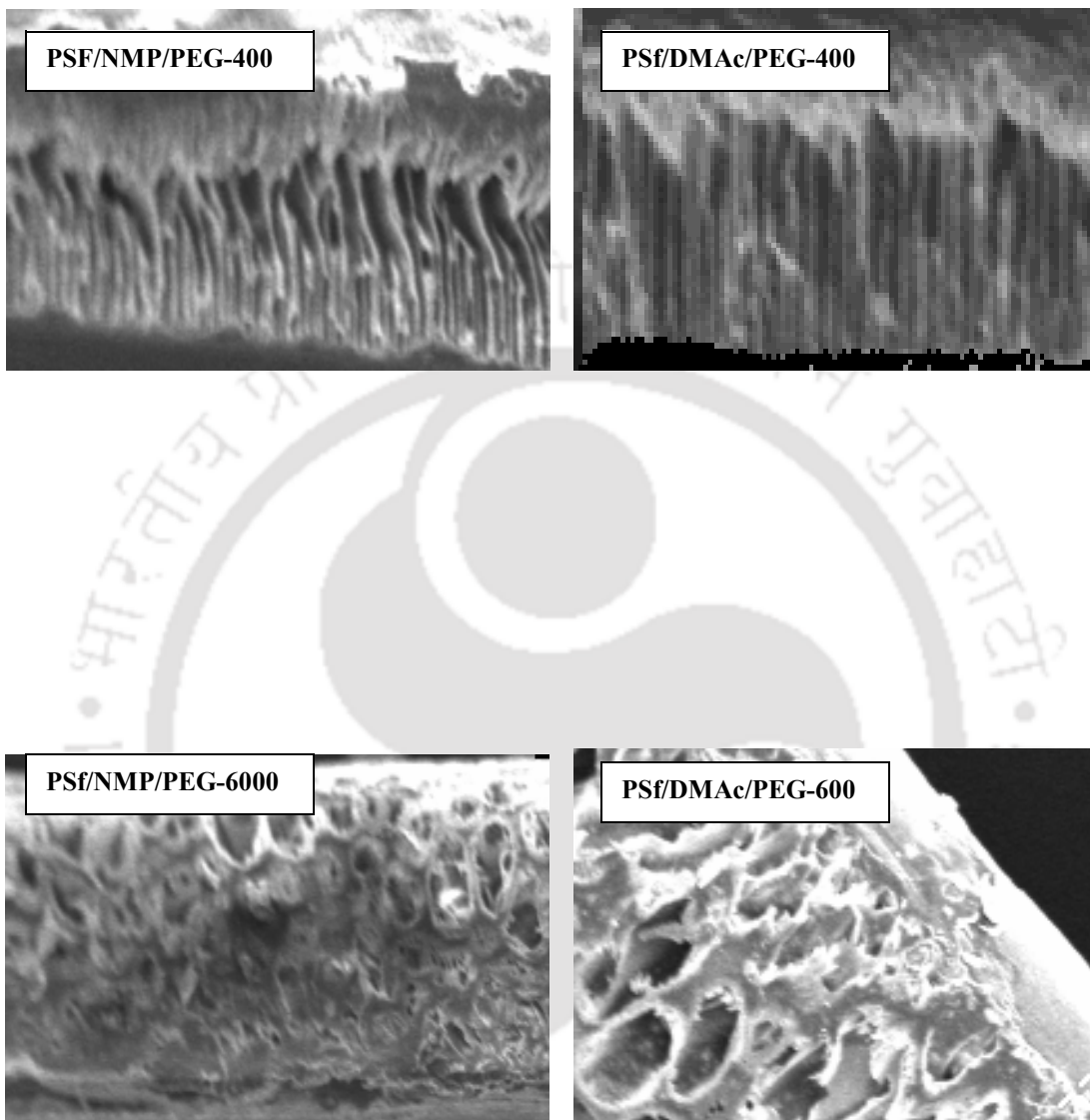


Fig. 3.1 SEM picture of the cross-section of the prepared membranes with

different molecular weight of PVP for (a) PSf/NMP system and for (b) PSf/DMAc system



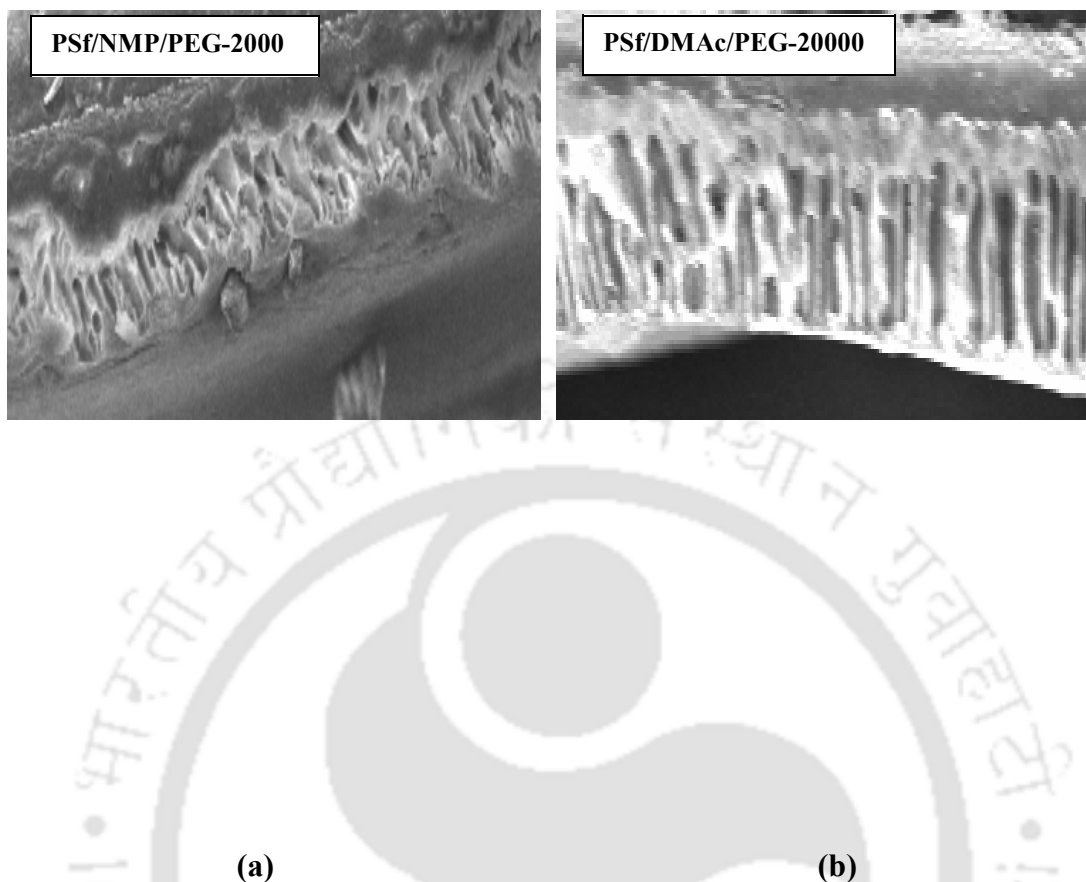


Fig. 3.2 SEM picture of the cross-section of the prepared membranes with different molecular weight of PEG for (a) PSf/NMP system and for (b) PSf/DMAc system.

in a pseudo-ternary diagram, where the additive is considered with the polymer as one single component [2]. According to Boom et al. [3] phase separation in a quaternary system (i.e. a system containing polymer / solvent / nonsolvent / additive) involves demixing of the intertwined polymers. In equilibrium, the polymeric additive has moved to the membrane forming polymer lean phase. This process is considerably slower than the exchange processes of solvent and non solvent between the casting solution and the coagulation bath occurring directly upon immersion. From the phase separation of such quaternary system, two phases arise - one consists of the membrane

forming polymer (i.e. PSf), solvent (i.e. NMP or DMAc) and nonsolvent (i.e. water) and the other consists of the polymeric additive (i.e. PVP or PEG), solvent (i.e. NMP or DMAc) and nonsolvent (i.e. water). The two polymers have a driving force to separate completely into a PSf-rich and a PVP or PEG-rich phase. Thus the demixing process is mainly determined by the diffusion of the two polymers with respect to each other. However, as the diffusional exchange between the solvent and the nonsolvent is much faster than the demixing process, there can be a large super saturation which results in a highly unstable polymer solution [3, 4]. Such condition favours occurrence of instantaneous demixing. It is clearly evident from the figures that the finger-like cavities in the sub-layer are significantly suppressed with the addition of PVP or PEG of increasing molecular weight for both types of solvents. Specially, for PSf/DMAc/PVP system, the membrane formed with PVP 360000 (M_6) is found to have almost cavity-free cross-section. These observations lead to the inference that though instantaneous demixing is maintained, the molecular weight of both PVP and PEG might have substantial role on the precipitation process. It appears that the macromolecular nature of the additive is responsible for the suppression of formation of macrovoids. Addition of higher molecular weight additives possibly encourages the delayed onset of liquid-liquid demixing to some extent, which results in formation of a membrane sub-layer with suppressed finger-like structure. Observing Figs 3.1 and 3.2, it is also noted that for both the polymer-solvent cases (i.e. PSf/NMP and PSf/DMAc) the top layers are becoming thicker with the increase in molecular weight of both PVP and PEG. Similar kind of observations has been reported by Jung et al. [5] for PAN /

DMSO system with PVP of different molecular weights. The effect of molecular weight on the growth of the top layer is however quite noticeable particularly for the higher range of molecular weight. The thickness of the top layer and the structure of the sub-layer seem to depend upon the solubility as well as relative diffusivity of the additives. The relatively high diffusivity of lower molecular weight PVP and PEG gives very less time for polymer molecules to aggregate on the top surface, which leads to the formation of a thin and smooth top layer. Again the high molecular weight polymeric additive because of low diffusivity relative to the solvent takes more time to come to the top surface giving the polymer molecules enough time to agglomerate and rearrange and thus form a comparatively denser and thicker top layer with bead-like structures. Similar kinds of analysis have been reported by Reverchon et al. [6] and Idris et al. [7] in their study with cellulose acetate membranes.

SEM images for the top surface (air side) of different membranes are presented in Figs. 3.3 and 3.4. These photographs provide the information regarding the surface morphology of each membrane. It is observed that the top surface of the membranes prepared with PEG has gradually become uneven due to the occurrence of some irregular sized nodules as the molecular weight of PEG increases. However, in case of PVP added membranes, such irregularities are not so clearly visible from the SEM image, except with PSf/NMP/PVP membranes where some amount of surface roughness is seen to exist for higher molecular weight of PVP. Such structures on the membrane top surface may be attributed to the result of spinodal demixing which according to Boom et al [3], is

likely to occur for systems with high molecular weight additives because of their lower mobility in the initial stage of immersion in the coagulation bath. In such cases, the

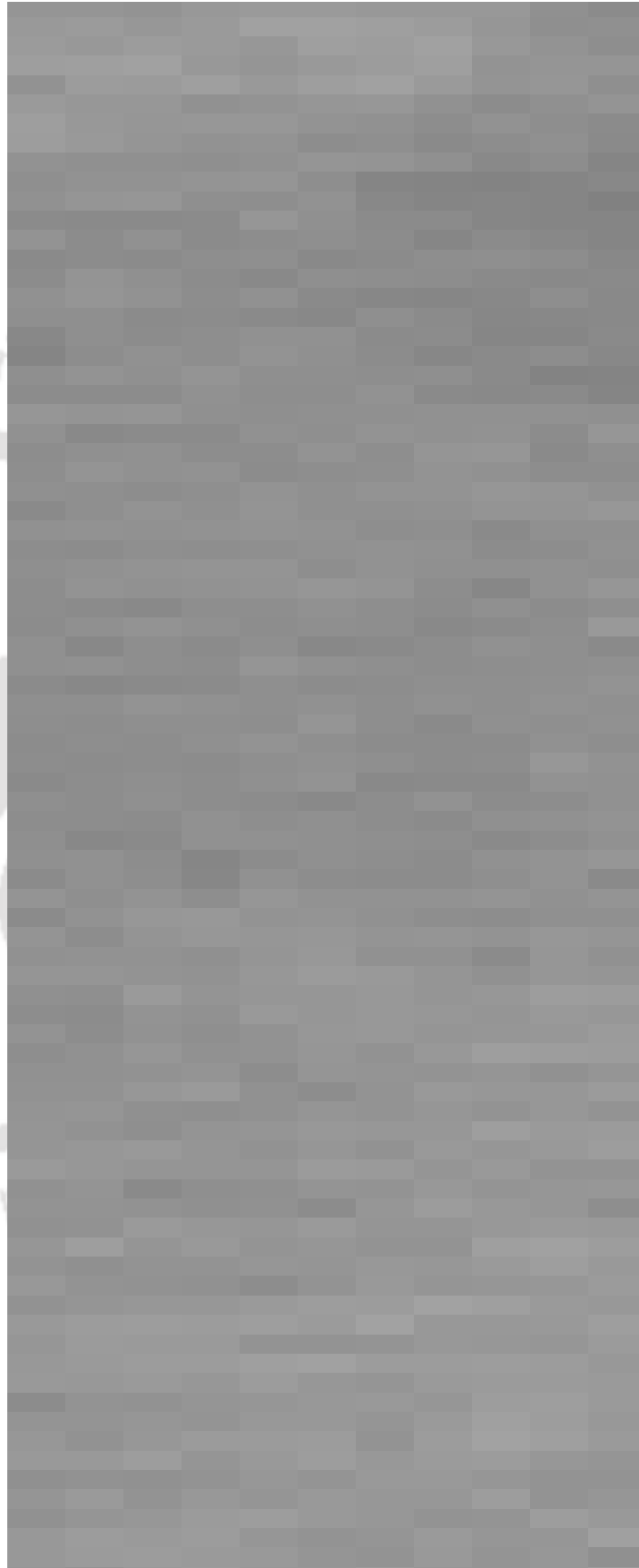


PSf/NMP/PVP-24000

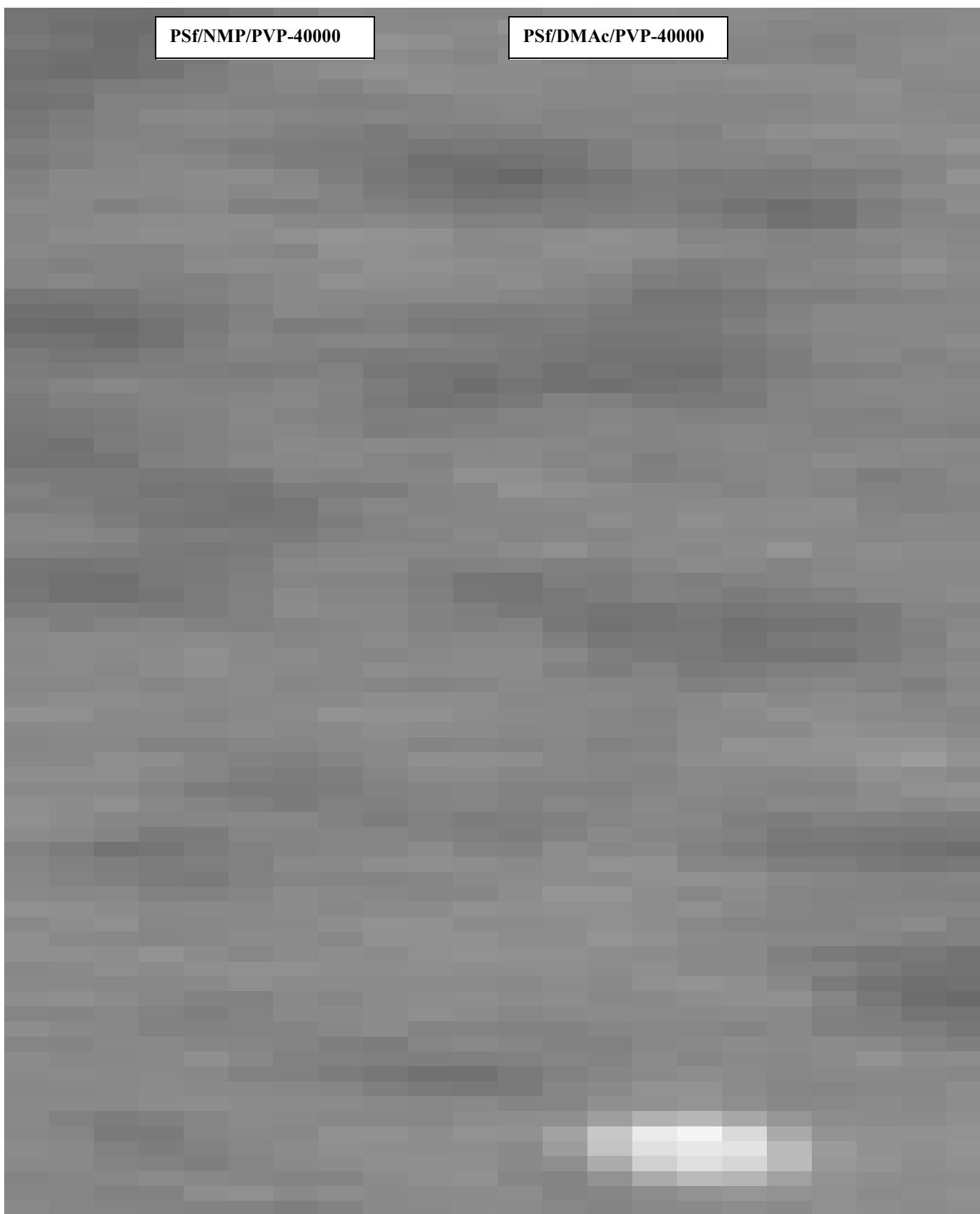
PSf/DMAc/PVP-24000

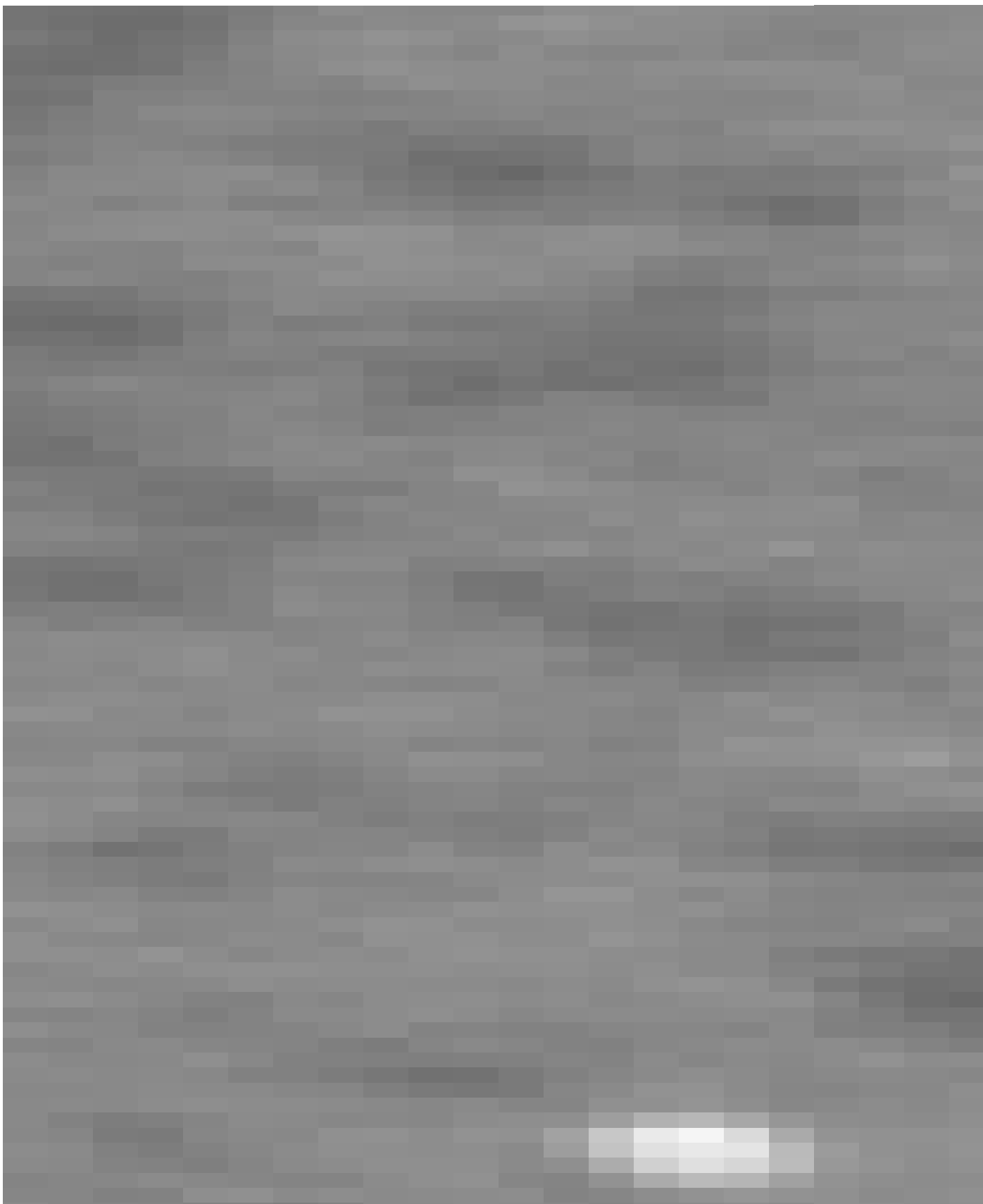


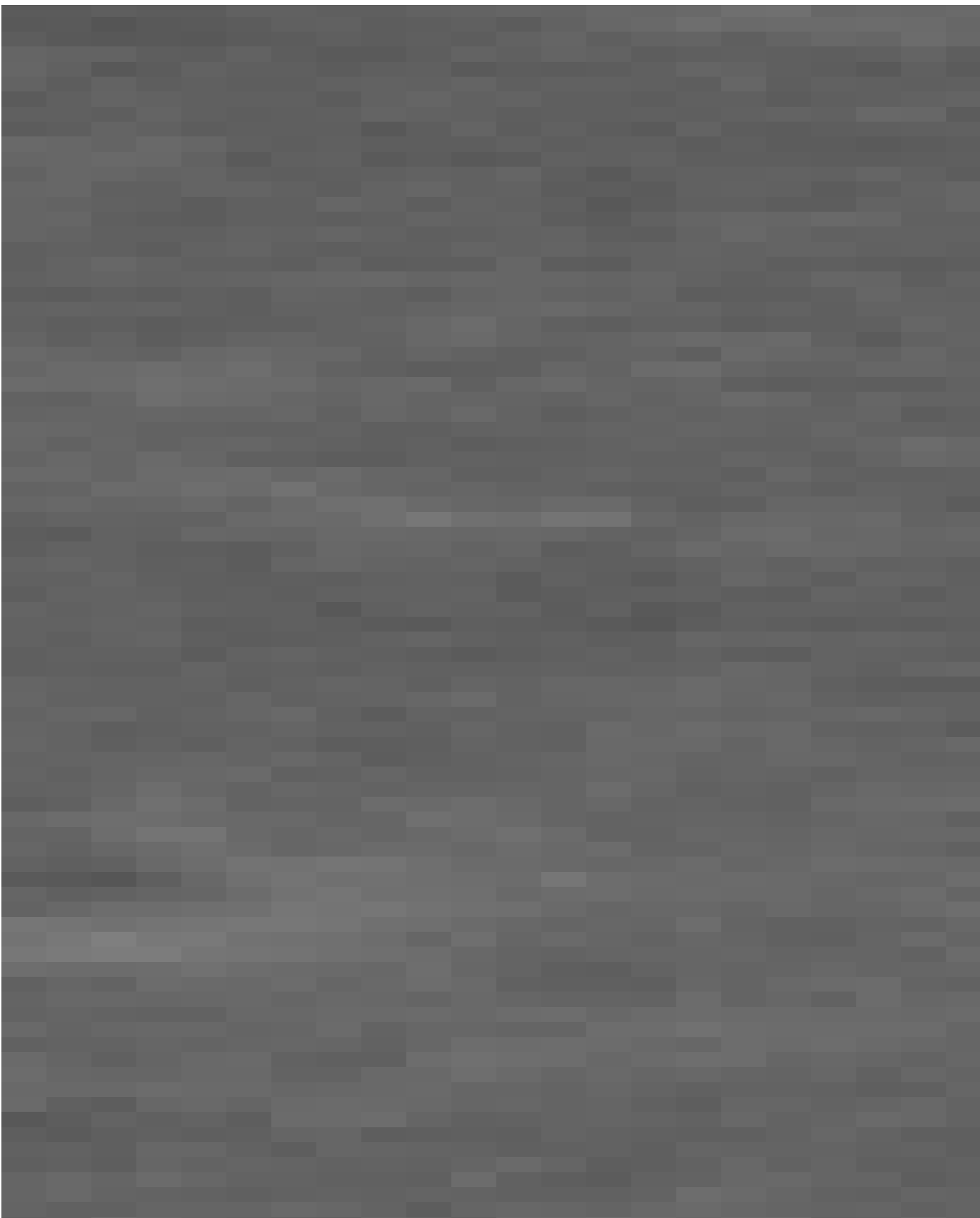


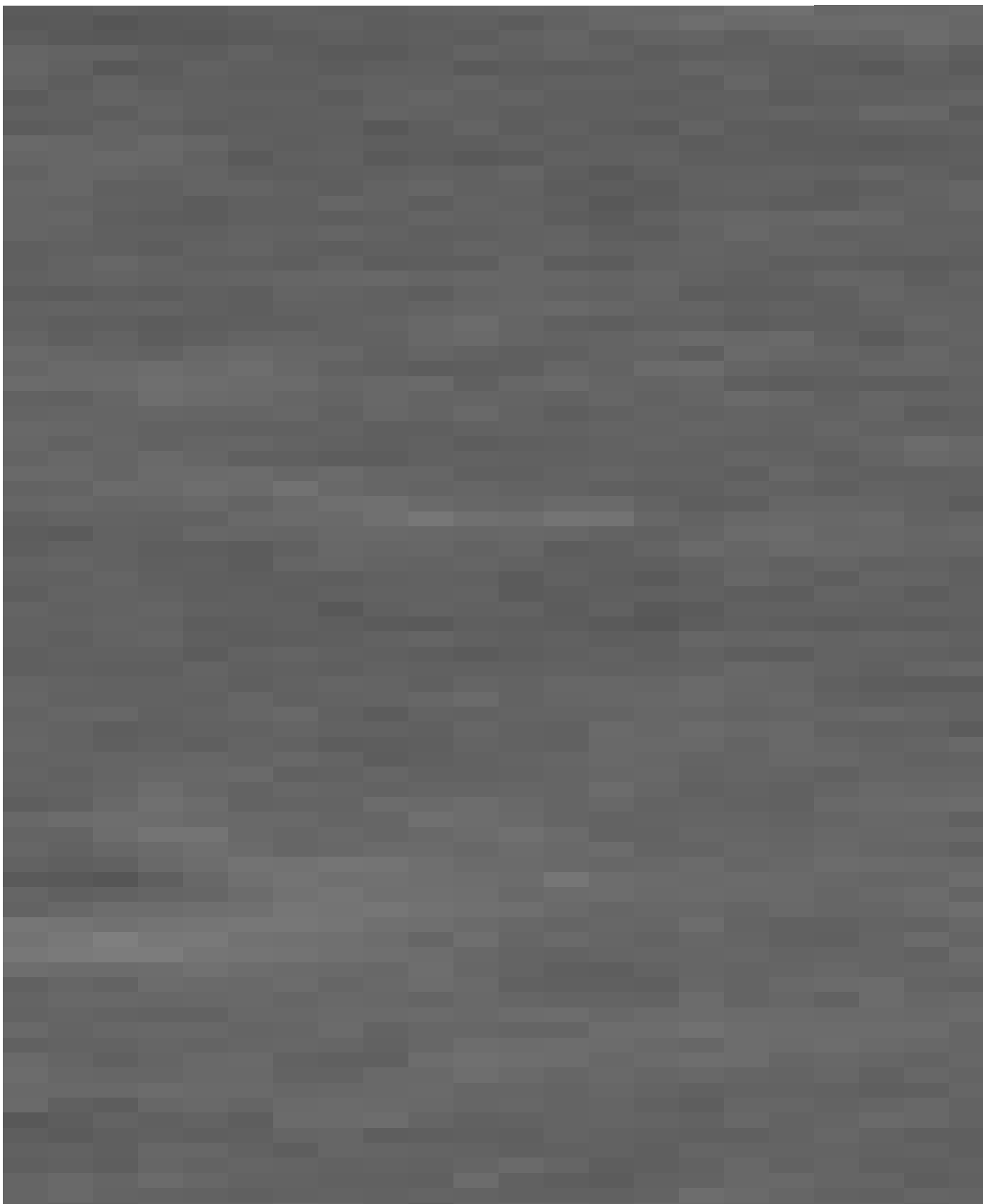










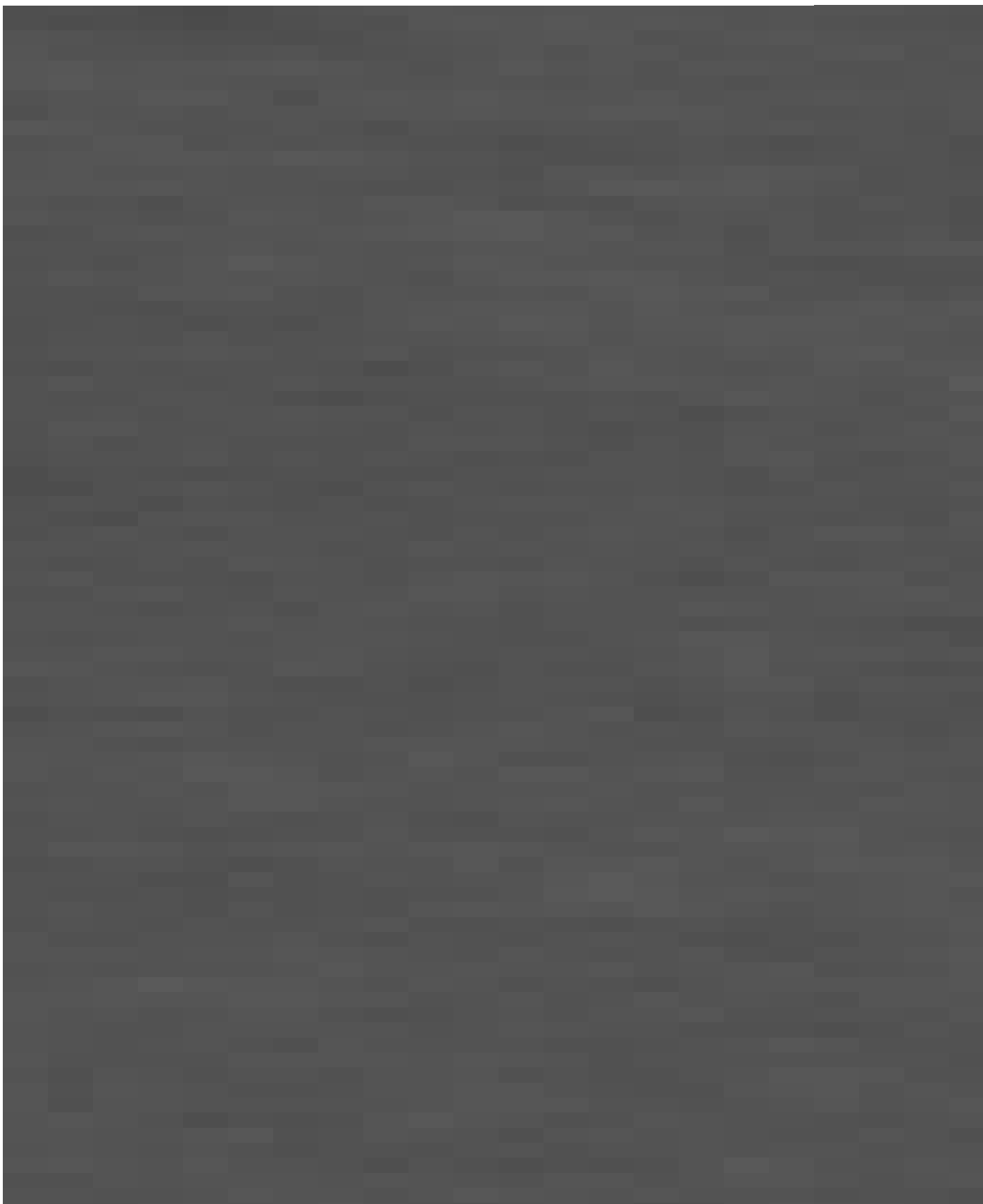


PSf/NMP/PVP-360000

PSf/DMAc/PVP-36000

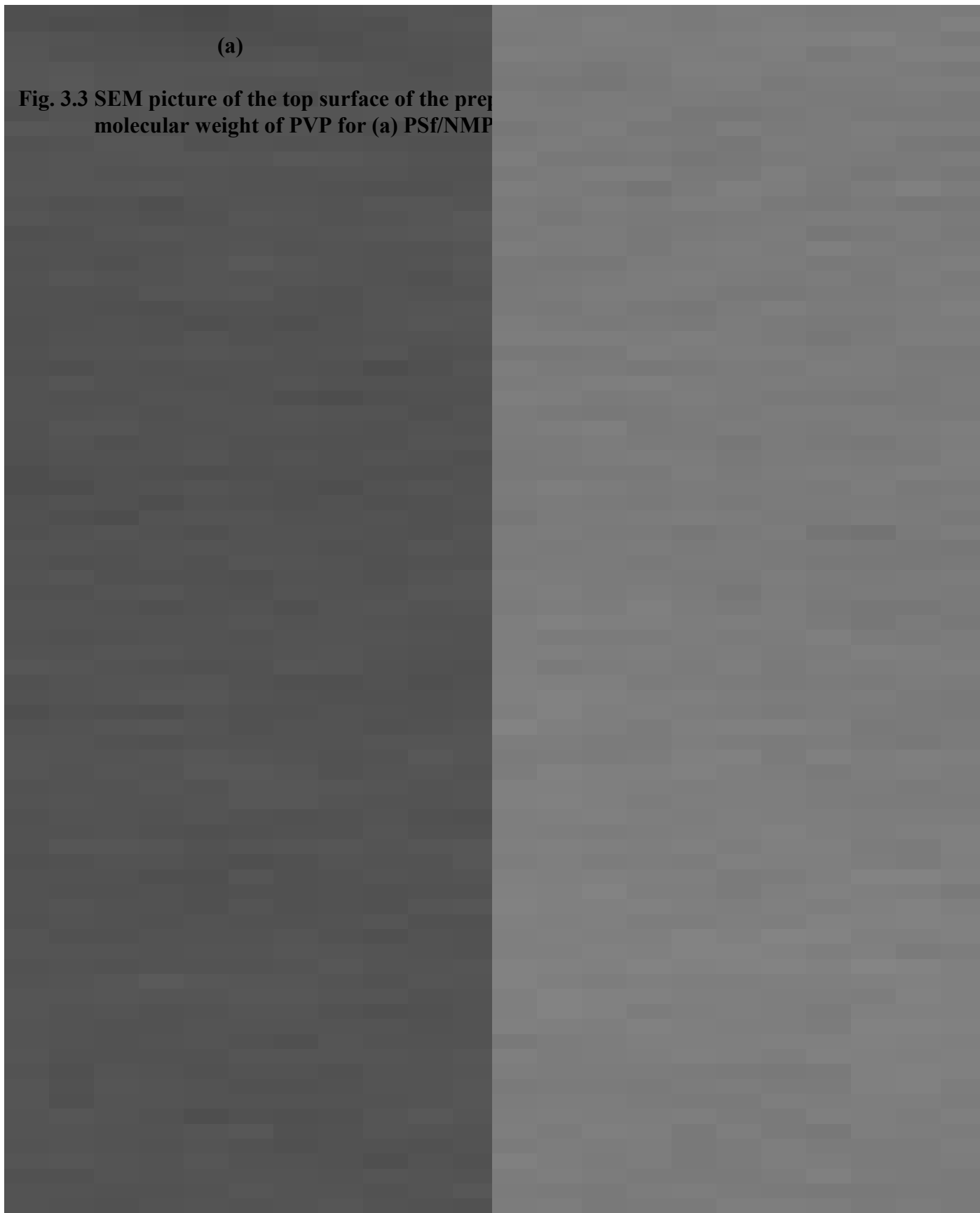






(a)

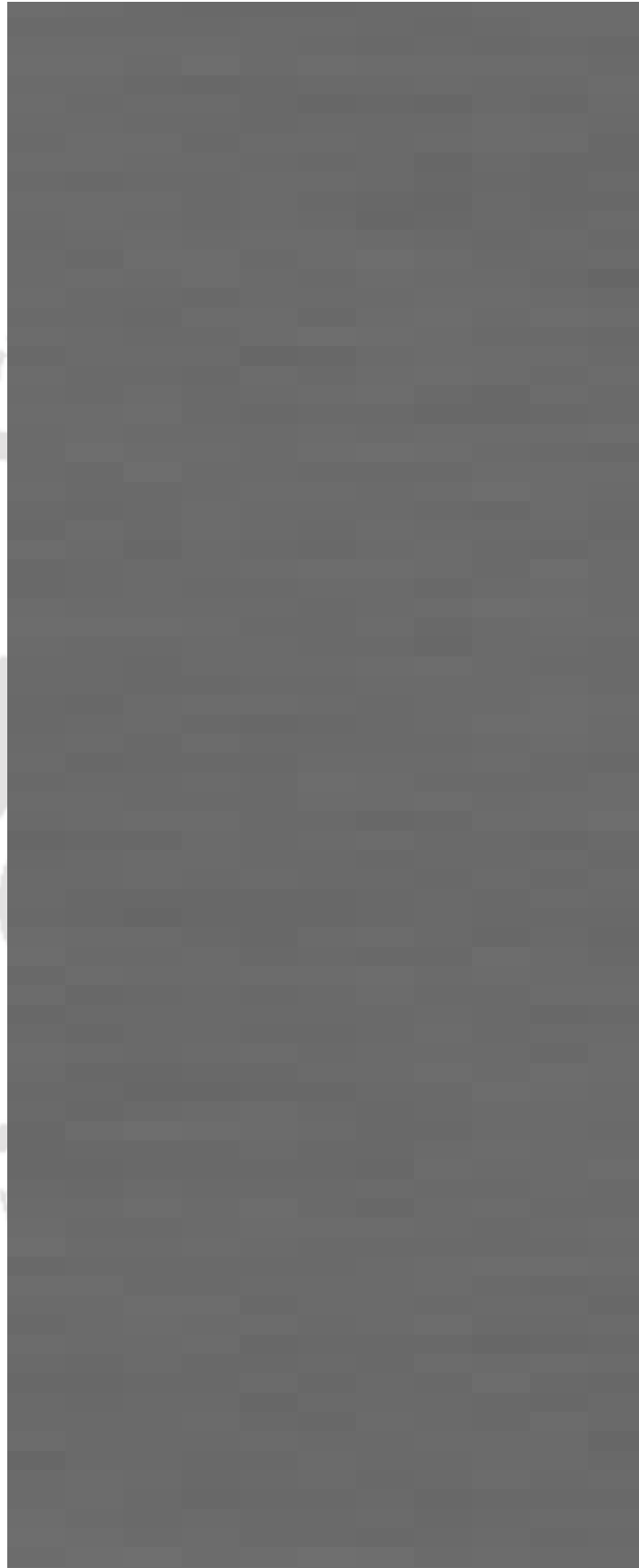
Fig. 3.3 SEM picture of the top surface of the prepolymer film of molecular weight of PVP for (a) PSf/NMP



PSf/NMP/PEG-400

PSf/DMAc/PEG-400





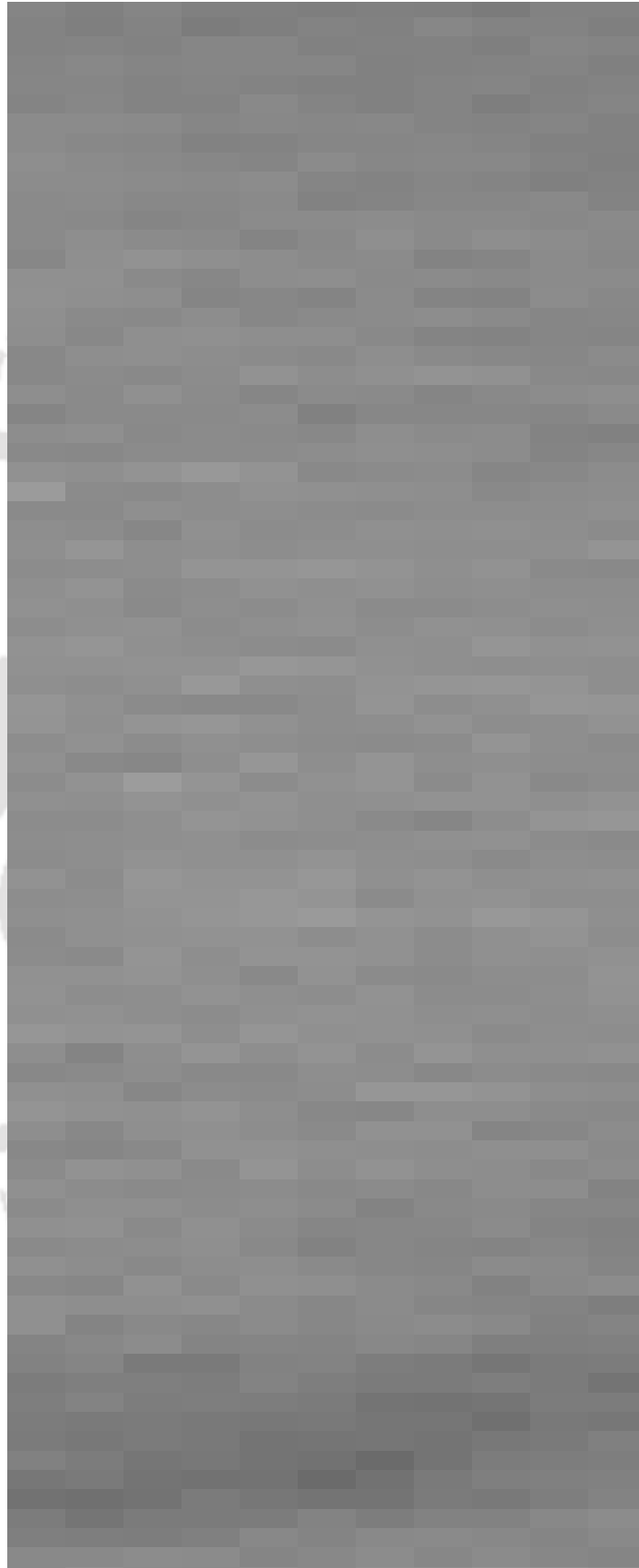


PSf/NMP/PEG-6000

PSf/DMAc/PEG-6000

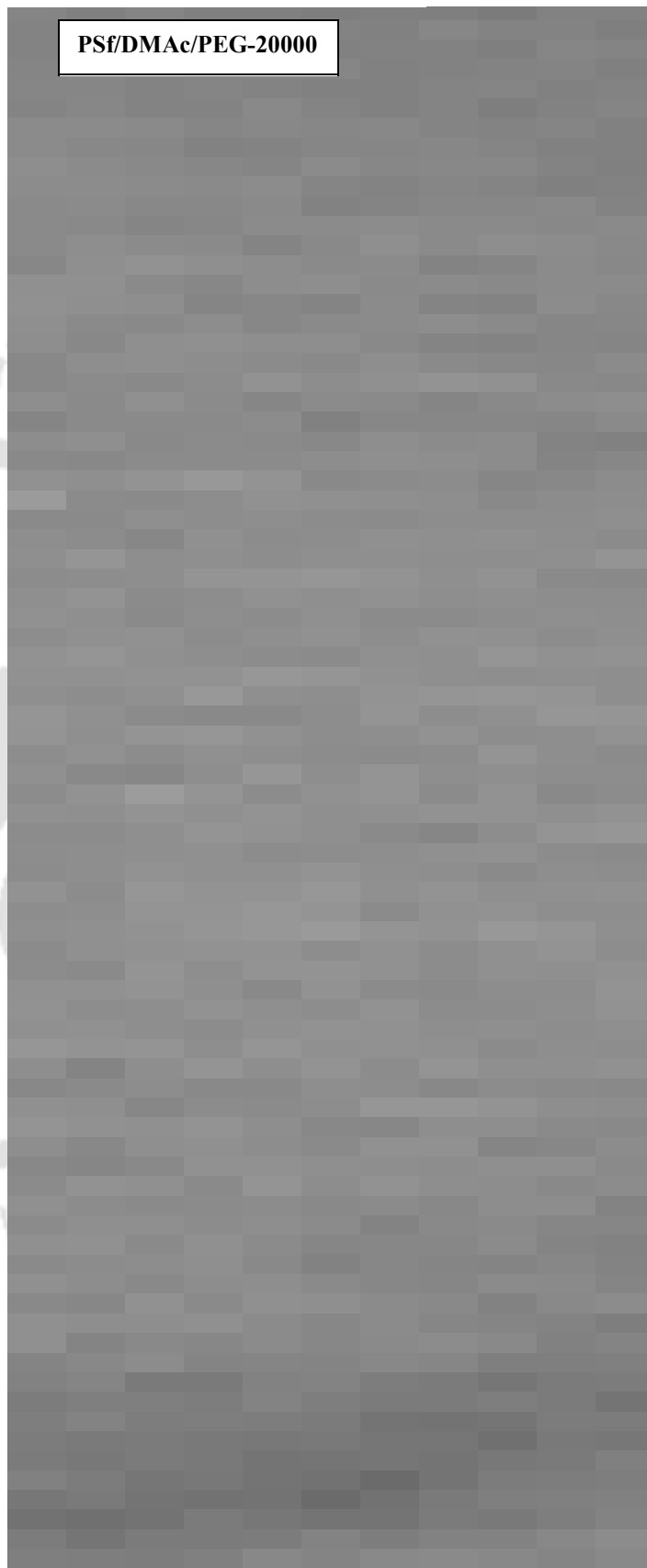


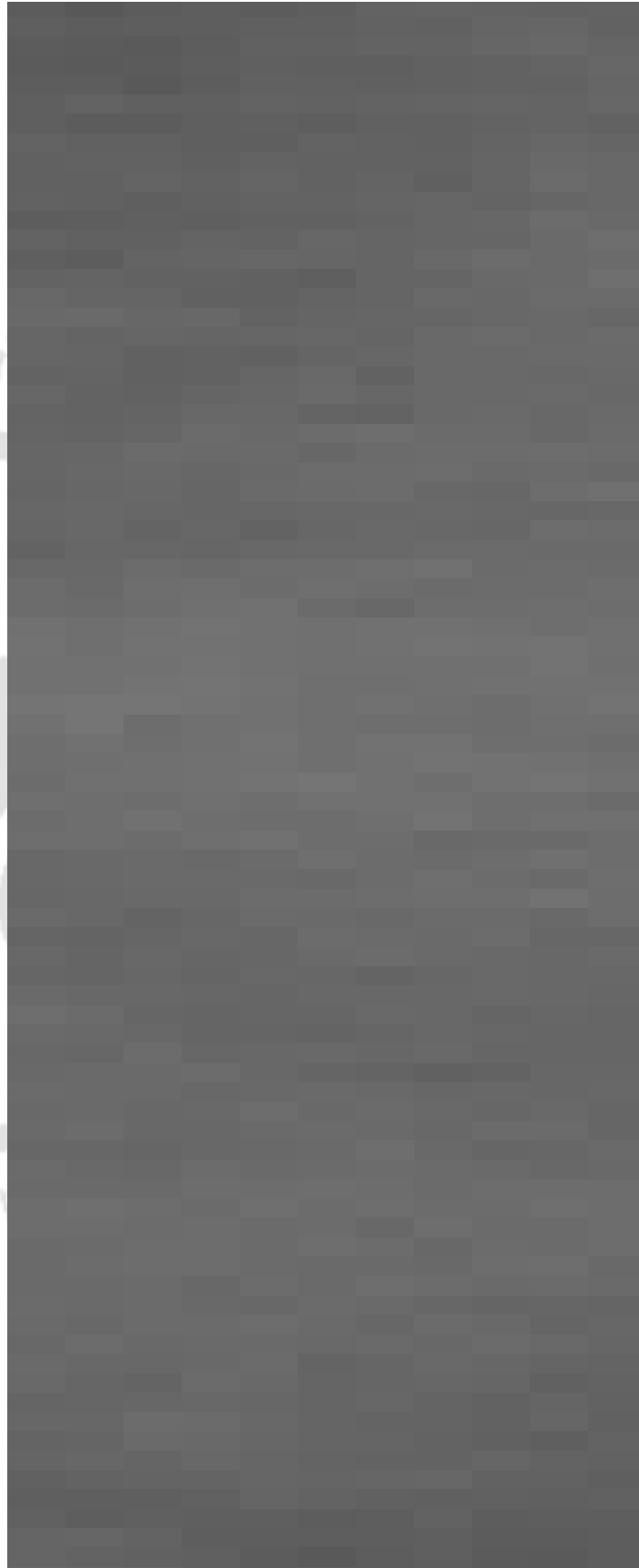




PSf/NMP/PEG-2000

PSf/DMAc/PEG-20000







(a)

(b)

Fig. 3.4 SEM picture of the top surface of the prepared membranes with different molecular weight of PEG for (a) PSf/NMP and (b) PSf/DMAc membranes

diffusion processes during formation of the top layer are fast enough for the polymer solution to become highly unstable and cross the spinodal curve [3, 8, 9]. Usually, much better interconnectivity of pores in the membranes is achieved due to spinodal decomposition [8, 9]. The interconnected pores can be considered as a continuous PSf lean (i.e. PVP/PEG rich) phase entangled by a continuous PSf rich (i.e. PVP/PEG lean) phase which forms the membrane matrix. This study is published in the Journal of Membrane Science [10, 11].

3.1.1.2. Quantitative analysis

Computerized analysis of SEM image (using ImageJ Launcher Broken Symmetry Software) is a standard and widely used method for the investigation of perforated materials [12, 13]. However, as almost all the pores are in the ultrafiltration (UF) range, this practice would only give first hand estimate or preliminary estimate of the pore size by overestimating the smallest pores on the surface and also by considering dead end pores which have no role in actual separation. So, use of this technique was carried out with only some of the membranes i.e. the PSf/NMP and PSf/DMAc membranes with PEG as additive (M₇, M₈, M₉, M₁₀, M₁₁ and M₁₂) to find out their average pore size and other morphological parameters and compares them with those obtained from other

standard methods. This work is published in Journal of Colloid and Interface Science [14].

Porosity, mean pore size and pore size distribution

From the Figs. 3.4 (a) and 3.4 (b), that represent the SEM photographs of the top surface of the PSf/NMP/PEG and PSf/DMAc/PEG membranes, respectively, the diameter of the pores is measured using the 'ImageJ Launcher Broken Symmetry Software package', under the assumption that the shapes of the pores are circular. From this, pores of different size range are found and thus the corresponding pore size distribution based on identical membrane area for each type of membranes is developed. Figs. 3.5 (a) and 3.5 (b) represent the pore size distributions of two types of membrane viz. PSf/NMP/PEG and PSf/DMAc/PEG respectively, prepared in the present work [14].



Fig. 3.5 Pore size distribution with increasing molecular weight of PEG as observed from SEM of (a) PSf / NMP membranes and (b) PSF/DMAc membranes [14]

In all the cases, it is observed that with increase in molecular weight of PEG, the pore size of the corresponding membranes decreases and the pore size distribution becomes narrower. The mean pore radii for all the membranes are calculated using Eq. (2.1) and shown in Table 3.1. It can be found from the table that the mean pore radius decreases from 0.11 to 0.04 for PSf/NMP membranes and 0.08 to 0.04 for

PSf/DMAc membranes when the molecular weight of PEG increases from 400 Da to 20,000 Da. The pore density, $\left(\frac{1}{\mu m^2} \right)$ is found by using Eq. (2.2) and is shown in Table 3.1. The values of surface porosity, $\left(\frac{1}{\mu m^2} \right)$ calculated by Eq. (2.3) are also reported in Table 3.1. From the table, it is seen that both $\left(\frac{1}{\mu m^2} \right)$ and $\left(\frac{1}{\mu m^2} \right)$ increase with increase in

Table 3.1 Pore structure parameters of the prepared PSf membranes with different solvents and different molecular weight PEG obtained from SEM [14]

Solvent	Molecular weight of PEG (Da)	Mean pore radius (μm)	Pore density ($\frac{1}{\mu m^2}$)	Surface porosity ($\frac{1}{\mu m^2}$)
NMP	400	0.11	0.03	0.20
	6000	0.09	0.05	0.29
	20000	0.04	0.19	0.37
DMAc	400	0.08	0.015	0.029
	6000	0.05	0.024	0.034
	20000	0.04	0.033	0.045

molecular weight of PEG. The pore density increases significantly from 0.03 to 0.19 $\frac{1}{\mu m^2}$ for PSf/NMP membranes and from 0.015 to 0.033 $\frac{1}{\mu m^2}$ for PSf/DMAc membranes) while $\left(\frac{1}{\mu m^2} \right)$ increases from 0.2 to 0.37 for PSf/NMP system and from 0.03 to

0.045 for PSf/DMAc system. The increase in porosity with increase in molecular weight of PEG is mainly due to the generation of large number of pores for both the systems.

3.1.1.3. Summary of SEM observation and analysis [10, 11]

- All the membranes so formed are having asymmetric structure consisting of a dense top layer and a porous sub layer.
- The sub layer seems to have finger-like cavities as well as macrovoid structure. This phenomenon can be attributed to the fact that NMP and DMAc have high mutual affinity for water which results in instantaneous demixing, leading to the formation of finger like cavities in the sub layer of the prepared membranes.
- The finger-like cavities in the sub layer are gradually suppressed with the increase of molecular weight of both the additives irrespective of the solvents.
- The top layers are becoming thicker with the increase in molecular weight of PVP and PEG for both PSf/NMP and PSf/DMAc systems.
- The membrane surfaces are smooth and even in case of lower molecular weight of additives. With increase in molecular weight of additives, the top layers of the membranes appear to have a nodular or bead-like structure with certain amount of roughness.
- The results of the analysis of Image J software for M₇, M₈,..., M₁₂ membranes are [14]:
- The average pore size calculated is found to be in the UF range.

- It is observed that with increase in molecular weight of PEG, the mean pore size of the corresponding membranes decreases and the pore size distribution becomes narrow.
- Both pore density, N () and surface porosity, increase with increase in molecular weight of PEG. The increase in porosity with increase in molecular weight of PEG is mainly due to the generation of large number of pores for both the systems.

3.1.2. Gas permeation test

The gas permeation test is one of the standard techniques mentioned in literature [15] to determine the pore size of a membrane. However, this test has got much physical significance when the asymmetric membranes have dense skin and applicable for reverse osmosis or gas separation. In the present study, this test is being carried out with some of the synthesized membranes to see their applicability in those applications by estimating their pore size. The test is based on the measurement of the flow rate of a gas through a porous medium which provides a means of determining the mean pore radius of the porous material. The flow rate of the gas can be converted to a gas permeability coefficient, which is a linear function of the mean pressure across the membrane. The mean pore radius is calculated from the coefficients of this functional dependence, using theoretical equations originally given by Carman [16]. In this study, the method is applied to find out the pore morphology of some of the membranes e.g. the PSf/NMP and

PSf/DMAc membranes with PEG additive just to have an approximate assessment about the deviation of the pore size estimated by this method from the results of SEM analysis.

3.1.2.1. Pressure normalized gas flux

The pressure normalized gas flux, J_p for air are calculated by using Eq. (2.8) for all the membranes and plotted against mean pressure (P_m), which are shown in Figs. 3.6 (a) and 3.6 (b). These figures also depict the variation of normalized gas flux, J_p with increase in molecular weight of PEG. It is seen that the normalized flux for air through the membranes increases significantly with the increase in the molecular weight of PEG at constant mean pressure (P_m), when the molecular weight is very high. For example, in case of PSf/NMP system, the J_p value for PEG 400 is 0.73 ms^{-1} , for PEG 6000 is 0.78 ms^{-1} while for PEG 20000, it is 2.39 ms^{-1} when the mean pressure P_m is maintained at 153 kPa. From the figures, it is also observed that for both the systems considered here, the difference in J_p values for lower range of molecular weight of PEG (i.e. for PEG 400



Fig. 3.6 Variation of pressure normalized gas flux (y) with mean pressure (P_m) of air through PSf membranes cast from solution consisting of 5 wt% of PEG of different molecular weight for (a) PSf/NMP membranes and for (b) PSf/DMAc membranes [14].

and PEG 6000) at a particular pressure is not so significant; however for higher molecular weight PEG (i.e. PEG 20000), the difference becomes distinct. So it can be said that PEG

of very high molecular weight has a great effect on normalized gas flux for air through the membranes. The result is also supported by the distinctly higher value of pore density for PEG 20000 in both PSf/NMP and PSf/DMAc systems (Table 3.1) [14].

3.1.2.2. Mean pore size and effective porosity

The effective porosity ϵ is an important kinetic parameter that accounts for open-end

pores contributing to gas permeation. The mean pore radius (r_m) and the effective porosity (ϵ) are calculated using Eqs. (2.12) and (2.13), respectively, and are reported in

Table 3.2. The two constants, ϵ/l_r and r_m of Eqs. (2.10) and (2.11) are determined from the intercept and slope of the plots of Figs. 3.6 (a) and 3.6 (b) for the two systems. It is

Table 3.2 Pore structure parameters of the prepared PSf membranes with different solvents and different molecular weight PEG obtained from gas permeation tests

Solvent	Molecular weight of PEG (Da)	Mean pore radius $r_m \times 10^2$ (μm)	Effective porosity $\epsilon/l_r \times 10^{-5}$ (m^{-1})	Absolute porosity,
NMP	400	5.23	2.11	0.02
	6000	1.65	17.3	0.17
	20000	1.10	102.0	1.0
DMAc	400	2.28	9.11	0.09

6000	1.41	22.4	0.22
20000	1.36	42.6	0.43

seen from Table 3.2 that for the two systems i.e. PSf/NMP and PSf/DMAc, the mean pore radius is decreasing and effective porosity is increasing with the increase in molecular weight of PEG. The mean pore radius decreases from 0.052 to 0.011 μm and from 0.023 to 0.013 μm while the effective porosity is seen to increase from 2.11 to 102.0 m^{-1} and from 9.11 to 42.6 m^{-1} for PSf/NMP and PSf/DMAc systems respectively. The absolute porosity calculated from effective porosity and membrane thickness is reported in Table 3.2 which also shows similar trend as the surface porosity shown in Table 3.1 [14].

3.1.2.3. Summary of gas permeation test [14]

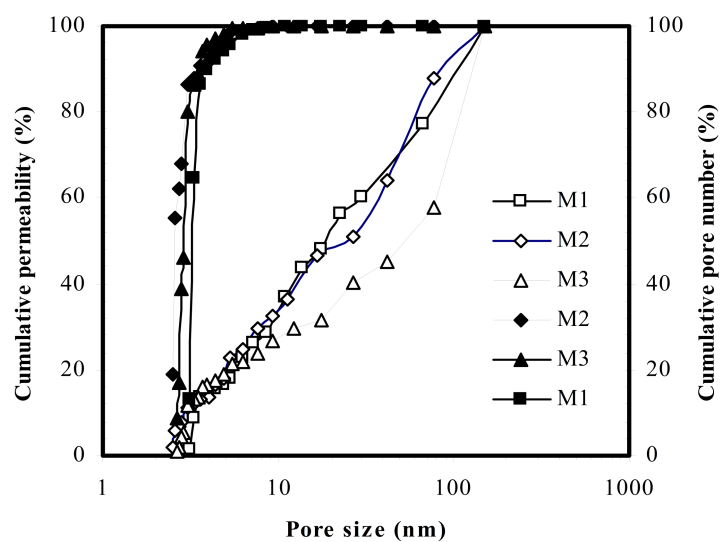
- The mean pore size values obtained are found to be within the MF/UF range which indicates disability of the membranes for selective gas separation.
- For the two systems i.e. PSf/NMP and PSf/DMAc, the mean pore radius is decreasing and effective porosity is increasing with the increase in molecular weight of PEG.
- The absolute porosity calculated from effective porosity and membrane thickness also shows similar trend.

- The molecular weight of PEG seems to have significant impact on normalized gas flux which is greatly enhanced for PEG 20000 for both PSf/NMP and PSf/DMAc systems. The normalized gas flux for air through the membranes increases significantly with the increase in the molecular weight of PEG at constant mean pressure (), when the molecular weight is very high. For example, in case of PSf/NMP system, the value for PEG 400 is 0.73 ms^{-1} , for PEG 6000 is 0.78 ms^{-1} while for PEG 20000, it is 2.39 ms^{-1} when the mean pressure is maintained at 153 kPa.

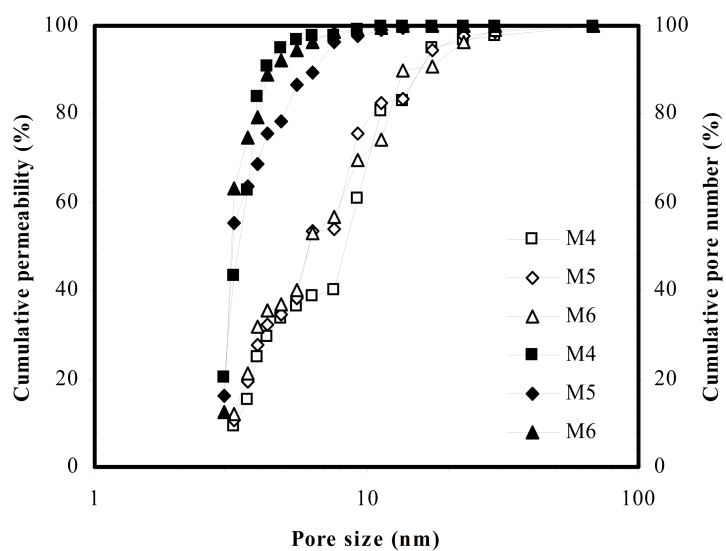
3.1.3. Liquid displacement method

This method helps us to evaluate the transmembrane pores of the membranes in wet state i.e. under the condition similar to that of UF operation. The membrane pore permeability, pore number and pore area for each membrane were determined using Eqs. (2.15), (2.17) and (2.18). Membrane permeability and pore number are plotted against pore radius as cumulative curves and presented in Figs. 3.7 (a) and 3.7 (b) for the PSf/NMP/PVP and PSf/DMAc/PVP systems and in Figs. 3.8 (a) and 3.8 (b) for the PSf/NMP/PEG and PSf/DMAc/PEG systems. From the figures it is observed that majority of the pores (approx. 90%) for PSf/PVP membranes while for PSf/PEG system, majority (approx. 80%) are in the 2 - 5 nm range for PEG, which indicates that the prepared membranes are suitable for UF purpose. However, the exact fraction of the larger pores ($>100 \text{ nm}$) as well as smaller pores ($< 2 \text{ nm}$) cannot be determined due to the

pressure limitation of the experimental set-up. For all the membranes, though the majority of pores (approx. 80%) are having radii in the range of 2 - 5 nm, these pores contribute not more than 20% to the overall permeability. The small number of larger pores actually determines the overall membrane performance by increasing the overall permeability. Similar type of result was observed by Munari et al. [17] with PVDF/PVP system. This fact can be explained from the Hagen-Poiseuille equation which says that transport through membranes (i.e. permeability) is directly proportional to the fourth power of pore radius i.e. r_p^4 (Eq. 2.19). Table 3.3 reports the results of liquid displacement method. It is seen that for both type of solvents, with increase in molecular weight of PVP and PEG, the pore number of all the membranes increases resulting in more porous membranes. The pore number per unit area (N_t) for PSf/NMP/PVP system is found to increase from 2.6×10^9 to 9.8×10^9 , while for PSf/DMAc/PVP system it is from 5.5×10^9 to 10.5×10^9 . That is the number of pores for PSf/DMAc/PVP system is relatively higher than those of PSf/NMP/PVP system. Again, the pore number per unit area () for PSf/NMP/PEG system is found to increase from 5.8×10^8 to 2.1×10^9 , while for PSf/DMAc/PEG system it is from 4.8×10^8 to 2.2×10^9 . The mean pore size () of the membranes for each membrane system calculated



(a)



(b)

Fig. 3.7 Variation of cumulative permeability (%) and cumulative pore number (%) with pore size for (a) PSf/NMP/PVP membranes and for (b) PSf/DMAc/PVP membranes [10]

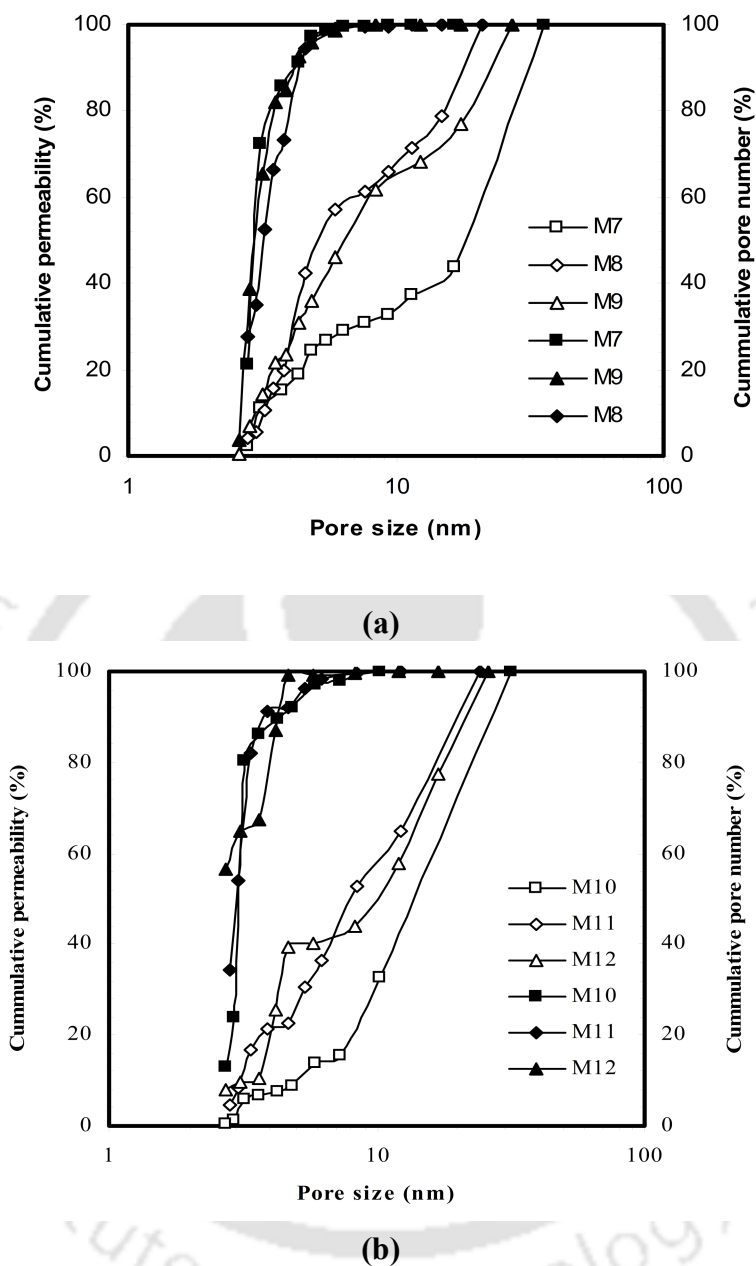


Fig. 3.8 Variation of cumulative permeability (%) and cumulative pore number (%) with pore size for (a) PSf/NMP/PEG membranes and for (b) PSf/DMAc/PEG membranes [11]

using Eq. (2.22) is seen to decrease though marginally with increase in molecular

weight of the respective additives. The total hydraulic permeability coefficient ()

is also affected by the molecular weight of both PVP and PEG. The values for

Table 3.3 Morphological Parameters of all membranes obtained from liquid displacement method

Membranes	r_m (nm)	N_t 10 ⁻⁹ (cm ⁻²)	102 (ms ⁻¹ MPa ⁻¹)	$A_{t,p}$ 10 ³ (cm ²)
M ₁	3.62	2.6	1.87	1.17
M ₂	3.1	4.1	2.24	1.23
M ₃	3.0	9.8	2.46	3.1
M ₄	3.88	5.5	3.52	2.83
M ₅	3.72	6.8	4.02	2.97
M ₆	3.21	10.5	4.54	3.6
M ₇	3.44	0.58	0.4	0.23
M ₈	3.44	0.66	0.3	0.3
M ₉	3.42	2.1	0.9	0.85
M ₁₀	3.57	0.48	0.7	0.23
M ₁₁	3.43	1.2	0.6	0.49
M ₁₂	3.39	2.2	1.0	0.87

PSf/NMP/PVP membranes are found to be 0.019 ms⁻¹MPa⁻¹ for PVP 24000, 0.022

$\text{ms}^{-1}\text{MPa}^{-1}$ for PVP 40000 and $0.025 \text{ ms}^{-1}\text{MPa}^{-1}$ for PVP 360000 while for PSf/DMAc/PVP system, the values of τ are found to be $0.035 \text{ ms}^{-1}\text{MPa}^{-1}$ for PVP 24000, $0.04 \text{ ms}^{-1}\text{MPa}^{-1}$ for PVP 40000 and $0.045 \text{ ms}^{-1}\text{MPa}^{-1}$ for PVP 360000. Similarly, For PSf/NMP/PEG membranes, the value of τ is found to be $0.004 \text{ ms}^{-1}\text{MPa}^{-1}$ for PEG 400, $0.003 \text{ ms}^{-1}\text{MPa}^{-1}$ for PEG 6000 and $0.009 \text{ ms}^{-1}\text{MPa}^{-1}$ for PEG 20000 while for PSf/DMAc/PEG system, the value of τ is found to be $0.007 \text{ ms}^{-1}\text{MPa}^{-1}$ for PEG 400, $0.006 \text{ ms}^{-1}\text{MPa}^{-1}$ for PEG 6000 and $0.01 \text{ ms}^{-1}\text{MPa}^{-1}$ for PEG 20000. So, compared to membranes with PEG, membranes with PVP have much higher values of τ [10, 11]. A sample calculation for determining τ for M_1 membrane by this method is given in Appendix II.

3.1.3.1. Summary of the liquid displacement test [10, 11]

- The average pore size is found to decrease marginally with increase in molecular weight of the additives i.e. PEG and PVP
- With increase in molecular weight of PEG and PVP, the pore number as well as pore area per unit surface area i.e. porosity of the prepared membrane is increased.

3.1.4. Analysis of the results obtained from the three methods

From Tables 3.1 and 3.2, it is seen that the average pore size calculated by SEM and gas permeability method shows a decreasing trend with increase in molecular weight of the

additive. However, the average pore size obtained by the third method i.e. liquid displacement method (Table 3.3) is found to be not much affected by the molecular weight of PVP and PEG though it is marginally decreasing. The decreasing trend of pore size with increase in molecular weight of additive, irrespective of the type of the solvents used, is due to the relatively lower rate of diffusion of polymer molecules compared to the solvent. When the casting solution comes into contact with the nonsolvent in the coagulation bath, there is a rapid outflow of the solvent from the casting solution to the coagulation bath causing the higher concentration polymer molecules to aggregate at the top layer [18]. Smaller molecular weight additives having comparatively higher diffusivity rates can diffuse out during immersion along with the solvent. In contrast to that, the diffusion rates of higher molecular weight additives (e.g. PVP 360000 and PEG 20000) are much lower than the solvent and so according to Idris et al. [19], they take more time to reach the surface. This gives the polymer molecules ample time to agglomerate resulting in a membrane with comparatively thicker top layer with reduced pore size. So it may be inferred that both PVP and PEG act as a pore former in membrane formation and with increase in molecular weight their capacity to form pores increases. However, the increase in pore density and porosity (both surface and absolute) with increase in molecular weight of additive can also be explained from the analysis given by Strathmann et al. [1]. According to them, addition of an additive into the casting solution produces two opposite effects. Depending on the molecular weight, additives may reduce the miscibility of the casting solution with water, which causes the thermodynamic enhancement of the phase separation (thermodynamic factor). At the same time, they may

increase the viscosity of the casting solution to a certain extent which causes kinetic hindrance against phase separation (rheological factor) [1, 8, 15]. So impact of thermodynamic or rheological factors on membrane morphology depends on the molecular weight of additives. In the present case, with increase in molecular weight of PEG or PVP, the rheological factor possibly becomes more significant than the thermodynamic one. The addition of high molecular weight PVP and PEG (e.g PVP 360000 and PEG 20000 in the present case) increases the ratio of nonsolvent inflow to solvent outflow by increasing the viscosity of the casting solution, which according to the theory proposed by Young et al. [20], results in more porous membranes. So membranes prepared with higher molecular weight additives are found to be more porous in terms of pore density or porosity.

Comparing Tables 3.1 - 3.3 for the membranes prepared with PEG, it is seen that the mean pore size values calculated by the ImageJ software from SEM photographs are higher than those obtained from the other two methods. It is because of the fact that in SEM analysis, there is a possibility of overestimating the mean pore size by considering the wider pores on the surface which may not even continue till the end of the membrane sheet. Mean pore radii obtained by gas permeation test and liquid displacement test correspond to the pores through which the gas or liquid permeates. It is also seen that though there are differences between the values, the decreasing trend of mean pore size and increasing trend of porosity and pore density with increasing molecular weight of PEG are agreed by all the three methods. It is to be noted here that all of them do represent the porous structure of the membranes.

Thus from the above study, it may be inferred that though SEM analysis predicts a reasonable trend of membrane morphology in terms of pore density and pore size distribution; but for actual separation application, gas permeation test and liquid permeation test may be considered to have more significance in assessing the mean pore size and porosity or pore density of the prepared membranes quantitatively. So, it can be concluded that SEM analysis is mostly suitable to estimate membrane morphology qualitatively i.e. to have the idea regarding the structure of the membrane. However, since the present study is associated with liquid stream, the subsequent sections analyzing the membrane performance consider the morphological properties (e.g. mean pore size, porosity and pore size distribution) obtained from the liquid displacement method.

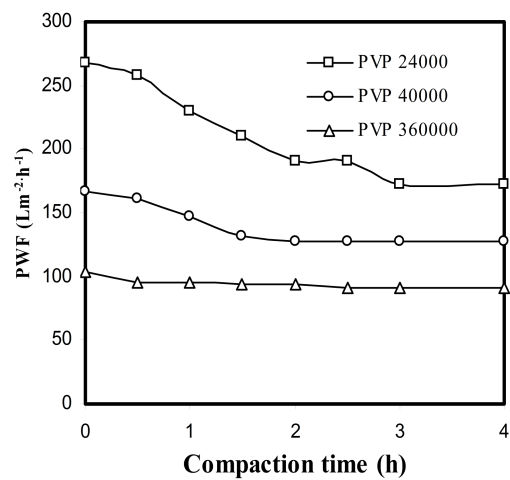
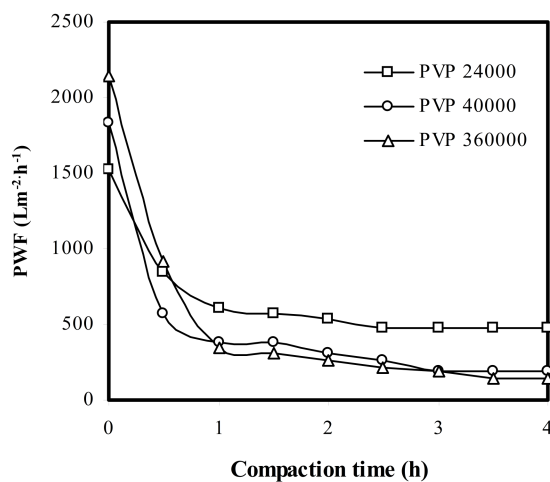
3.2. Performance parameters

Membranes that have been prepared separately with NMP and DMAc as solvents and PVP and PEG as additives are examined to see the effect of addition of PVP and PEG of different molecular weight on their permeation behaviour. The membranes are characterized in terms of compaction factor (CF), pure water flux (PWF), hydraulic resistance (R_m) and equilibrium water content (EWC).

3.2.1. Effect on CF

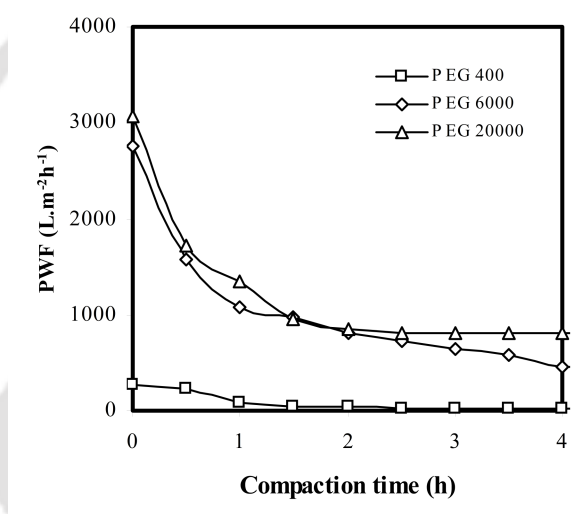
Compaction factor (CF) relates to the structure of the membrane specially membrane substructure. Higher the CF, more likely the membrane compacts due to presence of large

number of macrovoids in the sub layer. The effect of compaction time on PWF for all the membranes is shown in Fig. 3.9 for PVP and PEG, respectively. For all the types of membranes, the PWF is seen to decline gradually with time due to compaction and finally attain a steady state after 3 – 4 hrs. This is due to the fact that the walls of the pores become closer and denser resulting in reduction in pore size as well as the flux during compaction [15]. However, the degree of compaction is different for different membranes. Another fact which can be noticed from these figures is that the steady state values of PWF decrease with increase in molecular weight of PVP irrespective of the solvents used while with increase in molecular weight of PEG, the effect is just reverse. The steady state value of PWF for each membrane corresponding to the applied pressure (240 kPa) is found to increase with molecular weight of PEG for both the solvents. The CF values for the membranes are presented in Table 3.4. It is seen that for PSf/NMP/PVP membranes (i.e. M₁, M₂ and M₃), the CF increases from



(a)

(b)



(c)

(d)

Fig. 3.9 Flux profile during compaction for (a) PSf/NMP/PVP membranes; (b) PSf / DMAc /PVP membranes; (c) PSf/NMP/PEG membranes and (d) PSf/DMAc/ PEG membranes.

1.76 to 6.67 with increase in molecular weight of PVP while for PSf / DMAc / PVP membranes (i.e. M₄, M₅ and M₆), it decreases from 1.55 to 1.12. Again for PSf / NMP / PEG membranes (i.e. M₇, M₈ and M₉), the CF decreases from 6.67 to 1.27 while

for PSf / DMAc / PEG membranes (i.e. M_{10} , M_{11} and M_{12}), it decreases from 8.75 to 3.8. The increasing or decreasing trend of CF with different additives with various molecular weight can be explained from the fact that addition of additives into the casting solution can either enlarge or suppress the macrovoids in the membrane sub layer depending on their molecular weight as well as the type of solvent used [3]. In the present case, it is possible that with increase in molecular weight of PVP for PSf/DMAc system and with increase in molecular weight of PEG for both PSf/NMP and PSf/DMAc systems, the tendency of the casting solution to form macrovoids in the sub layer of the membrane decreases; on the other hand for the PSf/NMP system, increase in molecular weight of PVP has resulted in a membrane with a highly porous substructure due to presence of higher number of macrovoids [10, 11].

3.2.2. Effect on PWF and hydraulic resistance ()

Fig. 3.10 shows the effect of molecular weight of PVP and PEG on PWF at various values of TMP. It is seen that within the range of 0 - 240 kPa, with increase in TMP, PWF (calculated using Eq. (2.1)) increases almost linearly for all the membranes. It is also seen from the Figs. 3.10 (a) and (b) that the PWF decreases with increase in molecular weight of PVP at a particular pressure irrespective of the solvent used which agrees with the findings of the compaction study (Figs. 3.9 (a) and (b)). For example, at 173 kPa, the PWF decreases from 355.4 to 118.5 $\text{Lm}^{-2}\text{h}^{-1}$ for PSf/NMP and from 149.0 to 68.8 $\text{Lm}^{-2}\text{h}^{-1}$ for PSf/DMAc systems, respectively, when molecular weight of PVP increases from 24000 Da to 360000 Da. This result contradicts with the findings with

PEG which can be seen in Figs. 3.10 (c) and (d) where PWF is seen to increase with increase in molecular weight of PEG.

Hydraulic resistance () is determined from the inverse of the slope of the plots of

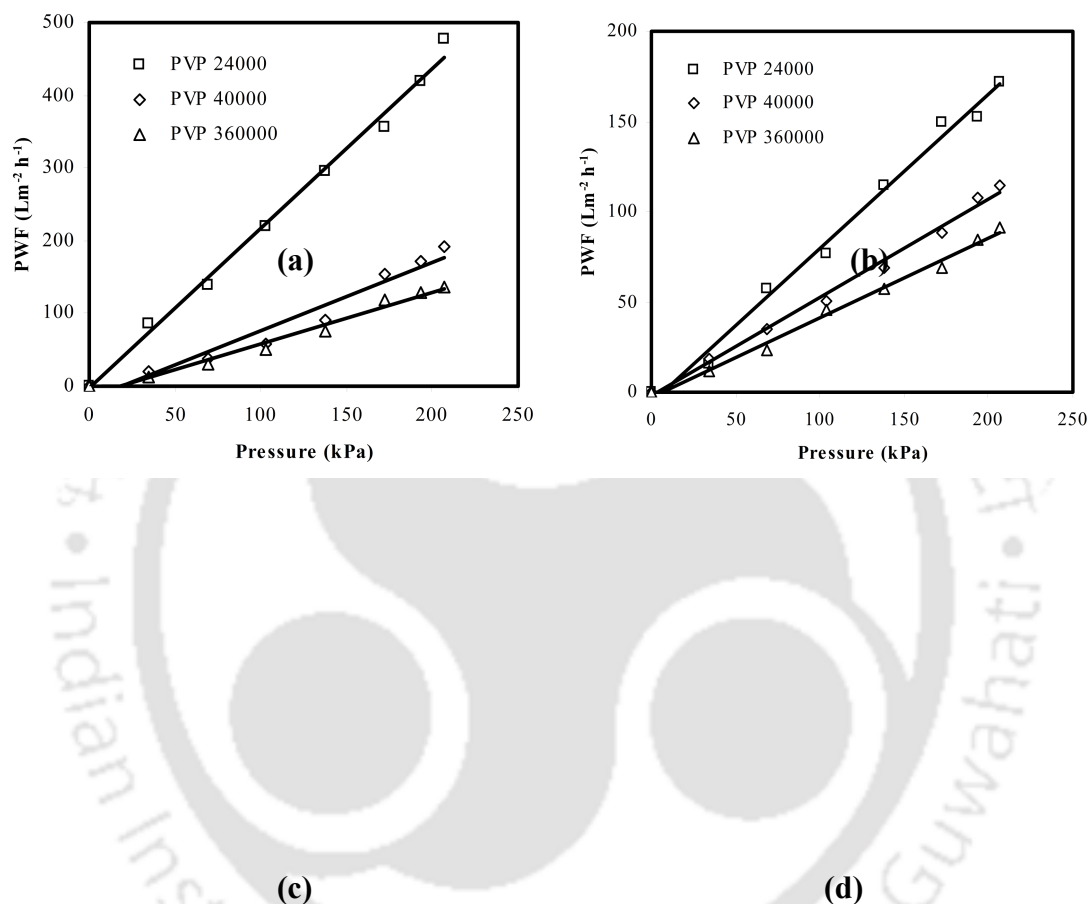


Fig. 3.10 Effect of transmembrane pressure on PWF for (a) PSf/NMP/PVP membranes; (b) PSf/DMAc/PVP membranes; (c) PSf/NMP/PEG membranes and (d) PSf/DMAc/PEG membranes.

Fig. 3.10 and is reported in Table 3.4. It is observed that increases with increase in the molecular weight of PVP while with increase in molecular weight of PEG, it shows

an opposite trend. for PSf/NMP/PVP membranes rises from 0.46 to 1.58 ($\text{m}^2\text{hkPaL}^{-1}$) and for PSf/DMAc/PVP membranes, it increases from 1.2 to 2.3 ($\text{m}^2\text{hkPaL}^{-1}$) when molecular weight of PVP increases from 24,000 Da to 3,60,000 Da. On the other hand, for PSf/NMP/PEG membranes decreases from 10.6 to 0.06 ($\text{m}^2\text{hkPaL}^{-1}$) and for PSf/DMAc/PEG membranes, it decreases from 7.1 to 0.27 ($\text{m}^2\text{hkPaL}^{-1}$) when molecular weight of PEG increases from 400 Da to 20,000 Da. The result clearly indicates that addition of both PVP and PEG with different molecular weights influence the formation of pores in the membranes, which affect the permeability as the latter is conceptually related to its pores for UF membranes [21, 22]. The decline in flux and the increase in with increase in molecular weight of PVP is attributed to the considerable reduction in pore size (compared to PSf/PEG membranes) with higher molecular weight PVP. According to the literature [4, 23], though most of the additives are washed away during coagulation and washing periods, removal of additives completely from the membrane matrix becomes more and more difficult as the molecular weight of additives such as PEG and PVP goes on increasing. Therefore, the residual additives, which are hydrophilic in nature, are likely to be entrapped inside the membrane matrix permanently, thus making the membrane more hydrophilic [4, 5, 23, 24]. It is reported by Chou et al. [25] in their study with PEG and cellulose acetate that PEG is entangled with the membrane matrix leading to its stable existence in the matrix. In the present study, it is possible that swelling of those trace amount of PVP

predominantly takes place due to its hydrophilic and hygroscopic nature. This in turn blocks the pores resulting in reduction of flux. With increase in molecular weight of PVP, the swelling rate also increases resulting in pore blocking to a great extent. Thus, though porosity (N_f) increases with increase in molecular weight of PVP (Table 3.3), the PWF is lowered and consequently θ is increased for higher molecular weight PVP. The suppressed sub layers of the membranes especially with PVP 360000 also likely to offer more resistance to water permeation resulting in lower flux [10].

Again, the increase in PWF and decrease in θ with increase in molecular weight of PEG is attributed to the fact that the presence of trace amount of PEG in the membrane matrix can change the hydrophobic behaviour of PSf membrane to hydrophilic behaviour. This combined with increased porosity (Table 3.3) may allow more water molecule to pass leading to an increase in PWF [11].

3.2.3. Effect on equilibrium water content (EWC)

Equilibrium water content (EWC) is an important parameter for membrane characterization as it is closely related to PWF and membrane porosity. Table 3.4 reports the effect of molecular weight of PVP and PEG, the pore formers, on EWC of different membranes which is calculated using Eq. (2.25). It may be found from the table that increase of molecular weight of PVP and PEG increases the EWC of all membranes [10, 11]. From the table, it is observed that for PSf/NMP/PVP membranes, the EWC for PVP

24000 is 46.8%, for PVP 40000 is 58.2% and for PVP 360000 is 73.4%. Similar trend is seen for PSf/DMAc/PVP membranes, where for PVP 24000 it is 56.5%, for PVP 40000 it is 67.2% and for PVP 360000 it is 70.0%. Similarly, for PSf/NMP/PEG membranes, it is observed that the EWC for PEG 400 is 56.8%, for PEG 6000 is 68.2% and for PEG 20000 is 78.8%; while with PSf/DMAc/PEG membranes, for PEG 400 it is 58.6%, for PEG 6000 it is 69.1% and for PEG 20000 it is 76.4%. This increasing trend confirms the presence of increasing number of pores in the membrane with the increase of molecular weight of the additives (as discussed in section 3.1). The pores on the surface as well as the cavities in the sub-layer are responsible for accommodating water molecules in the membranes [10, 11, 26].

Table 3.4 Parameters related to membrane performance [10, 11]

Membranes	EWC (%)	PWF ($\text{Lm}^{-2} \text{h}^{-1}$) at 103.4 kPa	R_m ($\text{m}^2 \text{h kPaL}^{-1}$)	CF
M ₁	46.8	219.7	0.46	1.76
M ₂	58.2	91.7	1.2	3.0
M ₃	73.4	49.7	1.58	6.67
M ₄	56.5	76.4	1.2	1.55
M ₅	67.2	66.9	1.3	1.31
M ₆	70.0	45.8	2.3	1.12
M ₇	56.8	9.5	10.6	6.67
M ₈	68.2	248.4	0.39	1.5
M ₉	78.8	1605.1	0.06	1.27
M ₉	58.6	12.2	7.1	8.75

M ₁₀	69.1	234.7	0.4	6.0
M ₁₁	76.4	308.7	0.27	3.8
M ₁₂				

3.2.4. Summary of the observations [10, 11]

The permeation performance of the prepared membranes with varying molecular weight of PVP and PEG was evaluated in terms of CF, EWC, PWF and θ . The overall observations can be summarized as follows:

- Except for PSf/NMP/PVP system, the CF decreases with increase in molecular weight of PVP or PEG in the other three systems i.e. PSf/DMAc/PVP, PSf/NMP/PEG and PSf/DMAc/PEG which is due to the presence of less number of macrovoids in membrane sub-layer. For PSf/NMP system, a highly porous substructure has possibly resulted with the presence of higher number of macrovoids due to addition of PVP of higher molecular weight.
- The PWF decreases while θ increases with increase in molecular weight of PVP possibly due to comparatively more compact structure of the resulting membranes and swelling of hydrophilic PVP which remains entrapped in the membrane matrix. Contradictorily, the PWF and θ are seen to enhance and reduce respectively with increase in molecular weight of PEG.

- The EWC increases which may be interpreted as an indication of increase in hydrophilicity as well as increase in number of pores of the membranes with increase in molecular weight of both the additives irrespective of the solvents used.

Abbreviations

CF	Compaction factor
Da	Dalton
DMAc	Dimethyl acetamide
DMSO	Dimethylsulfoxide
EWC	Equilibrium water content
NMP	N- methyl pyrrolidone
PAN	Polyacrylonitrile
PEG	Poly(ethylene glycol)
PSf	Polysulfone
PVP	Polyvinylpyrrolidone
PWF	Pure water flux ($\text{Lm}^{-2} \text{h}^{-1}$)
SEM	Scanning electron microscopy
TMP	Transmembrane pressure
UF	Ultrafiltration

Notations

Total pore area of membrane (cm^2)

PWF ($\text{Lm}^{-2}\text{h}^{-1}$)

Total hydraulic permeability coefficient ($\text{ms}^{-1}\text{MPa}^{-1}$)

Pore density () (from SEM)

Total number of pores per unit area of membrane (cm^{-2}) (from liquid displacement test)

Mean pressure (kPa) of the upstream and downstream of the membrane

Hydraulic resistance ($\text{m}^2 \text{ h kPa L}^{-1}$)

Mean pore radius (obtained from SEM) ()

Mean pore radius (obtained from gas permeation test) ()

Mean pore radius (obtained from liquid displacement test) (nm)

The pressure normalized gas flux $^{-1}$)
(ms

Greek symbols

Absolute porosity

Effective porosity (m^{-1})

Surface porosity

References

1. H. Strathmann, K. Kock, P. Amar and R.W. Baker, The formation mechanism of asymmetric membranes, *Desalination*, 16 (1975), 179 - 203.
2. P. S. T. Machado, A. C. Habert and C. P. Borges, Membrane formation mechanism based on precipitation kinetics and membrane morphology: flat and hollow fiber polysulfone membranes, *J. Membr. Sci.*, 155 (1999), 171 – 183.
3. R. M. Boom, I. M. Wienk, Th. Van den Boomgaard and C. A. Smolders, Microstructures in phase inversion membranes. Part 2. The role of a polymeric additive, *J. Membr. Sci.*, 73 (1992), 277 - 292.
4. I. M. Wienk, R. M. Boom, M. A. M. Beerlage, A. M. W. Bulte and C. A. Smolders, Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, *J. Membr. Sci.*, 113 (1996), 361 - 371.
5. B. Jung, J. K. Yoon, B. Kim and H. W. Rhee, Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite

- treatment of asymmetric polyacrylonitrile membranes, *J. Membr. Sci.*, 243 (2004), 45 - 57.
6. E. Reverchon and S. Cardea, Formation of cellulose acetate membranes using a supercritical fluid assisted process, *J. Membr. Sci.*, 240 (2004), 187 - 195.
 7. A. Idris, N. M. Zain and M.Y. Noordin, Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives, *Desalination*, 207 (2007), 324 – 339.
 8. A. J. Reuvers and C A Smolders, Formation of membranes by means of immersion precipitation. Part II, The mechanism of formation of membranes prepared from the system cellulose acetate-acetone-water, *J. Membr. Sci.*, 34 (1987), 67 – 86.
 9. K. Kimmerle and H. Strathmann, Analysis of the structure-determining process of phase inversion membranes, *Desalination*, 79 (1990), 283 – 302.
 10. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, Effect of molecular weight of PEG on membrane morphology and transport properties, *J. Membr. Sci.*, 309 (1-2) (2008), 209 - 221.
 11. B. Chakrabarty, A. K. Ghoshal, and M. K. Purkait, Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive, *J. Membr. Sci.*, 315 (1-2) (2008), 36 - 47.
 12. L. Palacio, P. Pradanos, J. I. Calvo and A. Hernandez, Porosity measurements by a gas penetration method and other techniques applied to membrane

- characterization, *Thin Solid Films*, 348 (1999), 22 - 29.
13. K. J. Kim and A.G. Fane, Low voltage scanning electron microscopy in membrane research *J. Membr. Sci.*, 88 (1994), 103 - 114.
14. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "SEM analysis and gas permeability test to characterize polysulfone membrane prepared with polyethylene glycol as additive", *J. Colloid Interf. Sci.*, 320 (2008), 245 – 253.
15. M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, 1991.
16. P. C. Carmen, *Flow of Gases through Porous Media*, Butterworths, London, 1956.
17. S. Munari, A. Bottino, G. Capannelli and P. Moretti, Membrane Morphology and Transport Properties, *Desalination*, 53 (1985), 11 – 23.
18. W. Y. Chuang, T. H. Young, W. Y. Chiu and C. Y. Lin, The effect of polymeric additives on the structure and permeability of poly(vinyl alcohol) asymmetric membranes, *Polymer*, 41 (2002), 5633 – 5641.
19. A. Idris and L. K. Yet, The effect of different molecular weight PEG additives on cellulose acetate asymmetric dialysis membrane performance, *J. Membr. Sci.*, 280 (2006), 920 – 927.
20. T. H. Young and L. W. Chen, A diffusion-controlled model for wet casting membrane formation, *J. Membr. Sci.*, 59 (1991), 169 – 181.
21. D. B. Mosqueda-Jimenez, R. M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier and J. P. Santerre, Influence of processing conditions on the properties of ultrafiltration membranes, *J. Membr. Sci.*, 231 (2004), 209 - 224.

22. A. G. Fane, C. J. D. Fell and A. G. Waters, The relationship between membrane surface pore characteristics and flux for ultrafiltration membranes, *J. Membr. Sci.*, 9 (1981), 245 - 262.
23. C. Feng, R. Wang, B. Shi, G. Li and Y. Wu, Factors affecting pore structure and performance of poly(vinylidene fluoride-co-hexafluoro propylene) asymmetric porous membrane, *J. Membr. Sci.*, 277 (1–2) (2006), 55 – 64.
24. J. Marchese, M. Ponce, N.A. Ochoa, P. Pradanos, L. Palacio and A. Hernandez, Fouling behaviour of polyethersulfone UF membranes made with different PVP, *J. Membr. Sci.*, 211 (2003), 1 – 11.
25. W.L. Chou, D.G. Yu, M.C. Yang and C.H. Jou, Effect of molecular weight and concentration of PEG additives on morphology and permeation performance of cellulose acetate hollow fibers, *Sep. Purif. Technol.*, 57 (2007), 207 – 217.
26. M. Sivakumar, R. Malaisamy, C. J. Sajitha, D. Mohan, V. Mohan and R. Rangarajan, Ultrafiltration application of cellulose acetate–polyurethane blend membranes, *Eur. Polym. J.*, 35 (1999), 1647 – 1651.

Chapter 4

Ultrafiltration (UF) of Oily Water: Experimental

This chapter focuses on the experimental studies carried out with the synthesized PSf membranes of four different compositions for oily wastewater separation. The series of experiments which were carried out with bovine serum albumin (BSA) solution to see the ultrafiltration (UF) applicability of the synthesized membranes are also reported here. In this study, parameters like pH of the BSA solution besides the type of membrane compositions were considered as the major factors to understand their effects on membrane performance. Later, this chapter focuses on the details of the preparation and characterization of the synthetic oil-in-water (o/w) emulsion which was used in the UF application. It also gives an insight into the details of the two modes of the UF experiments i.e. dead-end and cross-flow that were carried out with oily water (both synthetic and industrial) in this study.

4.1. Ultrafiltration experiments with BSA solution

The separation or purification of proteins is a crucial process specially in biotechnological fields due to its wide range of applications in biomedical and food industries. All the four types of membranes (PSf/NMP/PVP, PSf/NMP/PEG, PSf/DMAc/PVP and PSf/DMAc/PEG) which have been fabricated and characterized accordingly (described in Chapters 2 and Chapter 3), were used to separate bovine serum albumin (BSA) from its aqueous solution using the batch experimental set-up (Fig. 2.6) described in Chapter 2.

The performance was measured in terms of BSA rejection. The study was carried out as a preliminary effort to see the applicability of the synthesized membranes in ultrafiltration.

4.1.1. Procedure

The protein, BSA (molecular weight 68000 Da), was obtained from CDH Ltd., India. It was dissolved in deionized water and the concentration was kept constant at 1000 mgL^{-1} for all the experiments. UF experiments for BSA solutions were conducted in the dead-end mode mentioned previously (Fig. 2.6) under a transmembrane pressure (TMP) of 103.4 kPa at room temperature ($\approx 25^\circ\text{C}$). The pH of protein solution plays an important role in protein-membrane interaction [1, 2]. The BSA solution was adjusted to two different pH values with the help of buffer solutions: one at isoelectric point (IEP), which is 4.8 and the other at above IEP, which is 9.5. Duration of each experiment was one hour. The permeate was collected in a measuring cylinder over a constant time interval. The flux was calculated using an equation similar to that for calculating PWF (Eq. (2.25)), which is:

(4.1)

where, J is permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$), V is volume of the permeate (L).

Percentage rejection of BSA was calculated using Eq. (1.3), where, C_p and C_f are the concentrations of BSA in the permeate and in the feed in mgL^{-1} , respectively. The BSA

concentration in the permeate was determined using a UV-vis spectrophotometer (Perkin-Elmer Lambda-35) at a wave length of 280 nm. After cleaning the used membrane thoroughly several times by distilled water, the membrane permeability was re-evaluated with pure water. It was observed that the membrane permeability remained nearly constant between successive runs.

The results of the UF experiments are analyzed and the influence of increasing molecular weight of PVP and PEG on BSA separation and flux is highlighted in chapter 5.

4.2. Ultrafiltration experiments with oily water

Ultrafiltration (UF) experiments were initially carried out with synthetic oily water that was prepared in the laboratory. The membrane performance was measured in terms of permeate flux (PF) with o/w emulsion as feed, percent oil rejection (% R) and percent flux decline (% FD). At first, dead-end i.e. batch mode of operation was considered to study the effect of membrane properties and operating conditions on membrane performance; because it is well established that the dead-end mode of experiments are the most suitable option for better understanding of the fundamentals associated with any separation operations. In this phase of study, effects of operating conditions such as TMP and feed properties such as oil concentration in feed and feed pH were investigated and the TMP was optimized. Four suitable membranes from the four membrane compositions were selected based on their producing reasonable flux and rejection of oil within the chosen operating pressure range. Then a comprehensive study had been carried out with the four selected membranes to see further the effect of feed concentration and pH on

their performance at optimum TMP. Once the batch experiments were over, the next step was to carry out experiments in cross-flow mode with the selected membranes to see the impact of different cross-flow rates on membrane performance.

Later on, the selected membranes were tested for measuring their performances with 'real' oily water which was collected from Oil India Ltd. (OIL), Assam, India in both batch and cross-flow mode of operation.

4.2.1. Synthetic oily water

An emulsion is a mixture of two immiscible substances, where one substance is dispersed in the other, the continuous phase. In the petroleum industry, emulsions are not always desirable, as they can result in high costs and extensive damage to the environment [3]. In o/w emulsions, oil is dispersed as liquid droplets through the water which is the continuous phase. These oil droplets generally have a tendency to coalesce to form bigger drops. The smaller the droplets, the greater is the surface tension which means greater the force will be needed to merge among themselves; so such emulsion is said to be stable in comparison to an emulsion containing larger oil droplets. When surfactant is added to an emulsion, it coats the surface of each droplet and prevents the droplets from coalescing, making the emulsion more stable. As this study was associated with the UF of stable o/w emulsion, so it was attempted to prepare samples of oily water containing smaller sized oil droplets ($< 10 \mu\text{m}$). Addition of any surfactant to the oil-water mixture was avoided as the post treatment phase requires additional steps to remove the surfactant from the oil-free water. Common

emulsifying agents present in crude oil emulsions such as asphaltenes, resins, organic acids, and finely divided minerals usually exist as a film on the surface of dispersed droplets [4]. Finely divided solids in contact with oil and water can also form solid - stabilized emulsions. They act as a barrier to prevent coalescence of oil droplets and thus stabilized the emulsion sufficiently to carry out the experiments for many days.

4.2.1.1. Preparation and characterization of o/w emulsion

Crude oil (Sp. gravity: 0.871) supplied by Guwahati Refinery, Indian Oil Corporation Limited (IOCL), India was used without any treatment to prepare the emulsion. The model oily wastewater was prepared in the laboratory taking crude oil as the oil phase in Millipore water and the oil concentration in water was kept at the required value. The o/w emulsion was prepared by keeping the oil-water mixture in a sonicator tank (Model: S30H Elmasonic) for about 5 - 15 hrs depending upon the oil concentration at a temperature of 30⁰ C. The resulting o/w emulsion showed a uniform yellowish colour. The emulsion was stable with respect to coalescence and homogeneous nature of the solution (i.e. absence of oil layer on the top of the solution) for at least two weeks. During this period of two weeks, the droplet size distribution, absorbance and pH of the feed with regular time interval were found to be almost the same. But sometimes after two weeks, a thin film of oil was seen to come out of the solution gradually and form a ring at the top of the solution which may be due to the effects of buoyancy [5] and may be considered as an indication of beginning of coalescence of oil droplets. Similar kind of study was

carried out by Huotari et al. [6]. So, fresh feed was prepared after an interval of two weeks to keep the consistency of feed properties.

The prepared o/w emulsion was characterized in terms of average emulsion droplet size, pH, density and viscosity. The size distribution of the emulsion droplets in the feed was determined using a laser particle size analyzer (Malvern Mastersizer 2000, Model APA 5005) from which the average droplet size was calculated. The pH of the feed was determined using a digital portable water/soil analysis kit (Model: VSI – 06D1) and viscosity was measured by means of an Oswald Viscometer. The density was measured using a pycnometer of known volume. The pycnometer was filled with the feed and the mass of the feed was found out at the room temperature (25°C). From the values of the mass and volume of the feed contained in the pycnometer, the density was calculated. The method was repeated three times and the average value was considered.

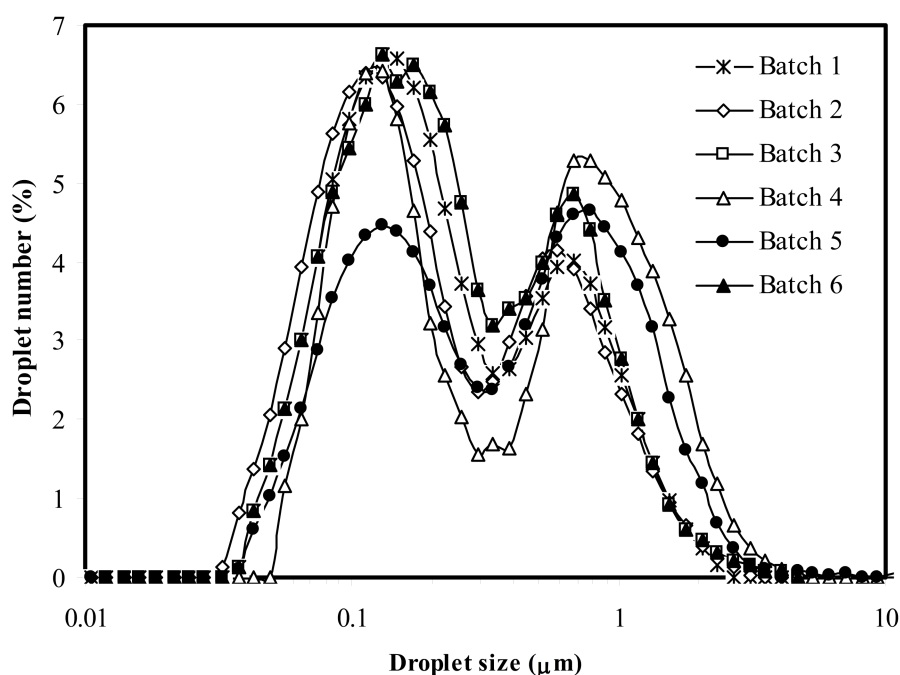


Fig. 4.1 Size distributions of oil droplets in feed prepared in different batches
Oil concentration: 100mgL⁻¹

Fig. 4.1 shows the size distributions of oil droplets in the feed prepared in some batches before conduction of the UF experiments. From the figure, it is observed that the distributions were almost similar with minor variations. It is also seen that the size range of the emulsion droplets in the feed is within 0.03 – 5 with an average size of 0.39 . The properties of the feed with 100 mgL⁻¹ oil content in normal conditions are shown in Table 4.1.

Table 4.1 Characteristics of o/w emulsion (feed)

Parameters	Values
pH	6.12
Density (kgm ⁻³)	995
Viscosity (kgm ⁻¹ s ⁻¹)	1.16 10 ⁻³
Emulsion droplet size distribution (µm)	0.03 – 5.0
Average droplet size (µm)	0.39

4.2.1.2. Ultrafiltration experiment in dead-end (batch) mode

Procedure

Ultrafiltration (UF) experiments of the synthetic oily water were carried out using the batch operation mode (Fig. 2.6) at a constant concentration of oil (100 mgL⁻¹) and at four

TMPs of 10, 15, 20 and 25 Psig i.e. 68.9, 103.4, 137.9 and 172.4 kPa, respectively with all the membranes prepared to make out the effect of TMP on the permeate flux and percent oil rejection. As mentioned before, three parameters were considered to measure the membrane performance i.e. permeate flux (PF), rejection of oil (R) and flux declination (FD).

PF was measured gravimetrically with a digital electronic balance by weighing the permeate using Eq. (4.1). was evaluated using Eq. (4.2):

$$(4.2)$$

where, is the weight of permeate (kg), is the density of permeate (kgL^{-1}), is the effective membrane area (m^2) and is the sampling time (h).

R (%) was calculated using Eq. (1.3), where, is the concentration of oil in the permeate (mgL^{-1}), is the concentration of oil in the feed (mgL^{-1}).

FD (%) after a certain time, t, was calculated using the following equation:

$$(4.3)$$

where, is the initial permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$) and is the permeate flux at time, ($\text{Lm}^{-2}\text{h}^{-1}$).

Researchers have used several methods to measure oil content in feed as well as in permeate [5]. They are: atomic absorption spectrophotometer (AAS) [7, 8]; total organic carbon (TOC) [9, 10, 11]; ultraviolet spectrophotometer (UV) [6, 12, 13, 14]; turbidity meter [15, 16]; gas chromatography (GC) [17]; and standard methods involving solvent extraction [18]. Each of these methods has its own advantages and disadvantages. In this study, the oil concentrations in the permeate and in the feed were determined using a UV-vis spectrophotometer (Perkin-Elmer, Lambda-35). In this method, the concentration of oil in an oily water sample is found out by knowing its absorbance value at the maximum wavelength from the UV - vis spectrophotometer. We know that crude oil is a complex mixture containing many different hydrocarbon compounds. Compositions of crude oil vary from place to place and accordingly the wavelength giving maximum absorbance also varies. In this study, the maximum absorbance was obtained at a wavelength of around 235 nm for all concentrations of oil. The concentration of oil in the permeate was found out by using a calibration curve.

To generate the calibration curve, feed samples (o/w emulsion) of different oil concentrations were prepared by mixing known weights of crude oil (collected from Guwahati Refinery, Assam, India) and deionised water through ultrasonic emulsification and the corresponding absorbances were found out in the UV spectrophotometer at 235 nm. Then concentration values were plotted against corresponding values of absorbance. The relation between absorbance versus concentration was found to be a linear one with $R^2 = 0.9973$. This relation was used for measuring concentration of unknown sample i.e. the permeate. The calibration curve so formed is shown in Fig. 4.2.

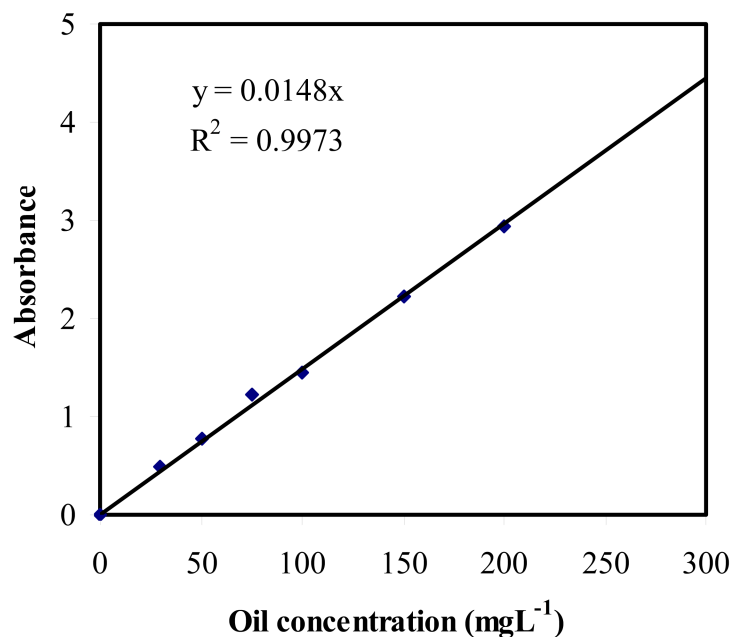


Fig. 4.2 Calibration curve for synthetic o/w emulsion

The declination of flux (FD) with time is an indication of membrane fouling. The membrane fouling is likely to be a combination of initial pore blocking by smaller oil droplets in the emulsion and deposition of oil particles on the surface which modifies the effective pore size distribution of membranes. Thus, after each UF experimental run, the membranes were cleaned with a laboratory detergent solution. To check the effect of membrane cleaning, the pure water permeability of each membrane was verified before and after cleaning the membrane. The membrane cleaning between each two runs was carried out using the following steps:

Step 1: Tap water washing for about 5 mins.

Step 2: Soaking the used membrane in detergent water solution (pH= 7.65) at a temperature of around 30 °C for about 60 mins.

Step 3: Tap water washing for 5 mins.

Step 4: Soaking the clean membrane in deionised water for 60 mins.

Step 5: Rinsing the membrane thoroughly with deionised water for 5 mins for removal of residual detergent from the membrane.

Optimizing TMP and types of membranes

From the findings of the sets of the batch experiments carried out at the various TMP range mentioned before, comparison of the flux and oil rejection was made with different kind of membranes. Based on that, the operating pressure was optimized in terms of reasonable permeate flux and high oil rejection with minimum membrane fouling. The most suitable membrane was selected from each category of the four membrane compositions (PSf/NMP/PVP, PSf/DMAc/PVP, PSf/NMP/PEG and PSf/DMAc/PEG) to carry out further experiments discussed subsequently.

Initial oil concentration and pH

Experiments were carried out with the selected four membranes at the optimum TMP to find out the effect of initial oil concentration and pH. Three initial concentrations of oil in the feed were considered viz. 75 mgL⁻¹, 100 mgL⁻¹ and 200 mgL⁻¹. The concentration range was so chosen in order to analyze the separation efficiency of the selected membranes in treating oily wastewater of relatively low oil concentration

domain (200 mgL^{-1}).

Experiments were also performed with oily water at different pH values i.e. 5 to 8 under the optimum TMP conditions with feed of oil concentration of 100 mgL^{-1} . The pH of the feed in normal condition is 6.12 and is adjusted to the desired values of 5 and 8 by using HCl or NaOH respectively. The pH range was so chosen in order to evaluate and compare the membrane performances with a feed which would be slightly more acidic or alkaline with respect to the feed under the normal pH condition. The summary of all the operating conditions is presented in Table 4.2.

Table 4.2 Summary of operating conditions for batch study

Membrane type	Oil concentration in feed (mgL^{-1})	TMP (kPa)	Feed pH
M ₁ , M ₂ , M ₃	100	68.9, 103.4, 137.9, 172.4	6.12
M ₄ , M ₅ , M ₆	100	68.9, 103.4, 137.9, 172.4	6.12
M ₇ , M ₈ , M ₉	100	68.9, 103.4, 137.9, 172.4	6.12
M ₁₁ , M ₁₂	100	68.9, 103.4, 137.9, 172.4	6.12
M ₁ , M ₆ , M ₉ , M ₁₂	75, 100, 200	103.4	6.12
M ₁ , M ₆ , M ₉ , M ₁₂	100	103.4	5.0, 6.12, 8.0

4.2.1.3. Ultrafiltration experiments in cross-flow mode

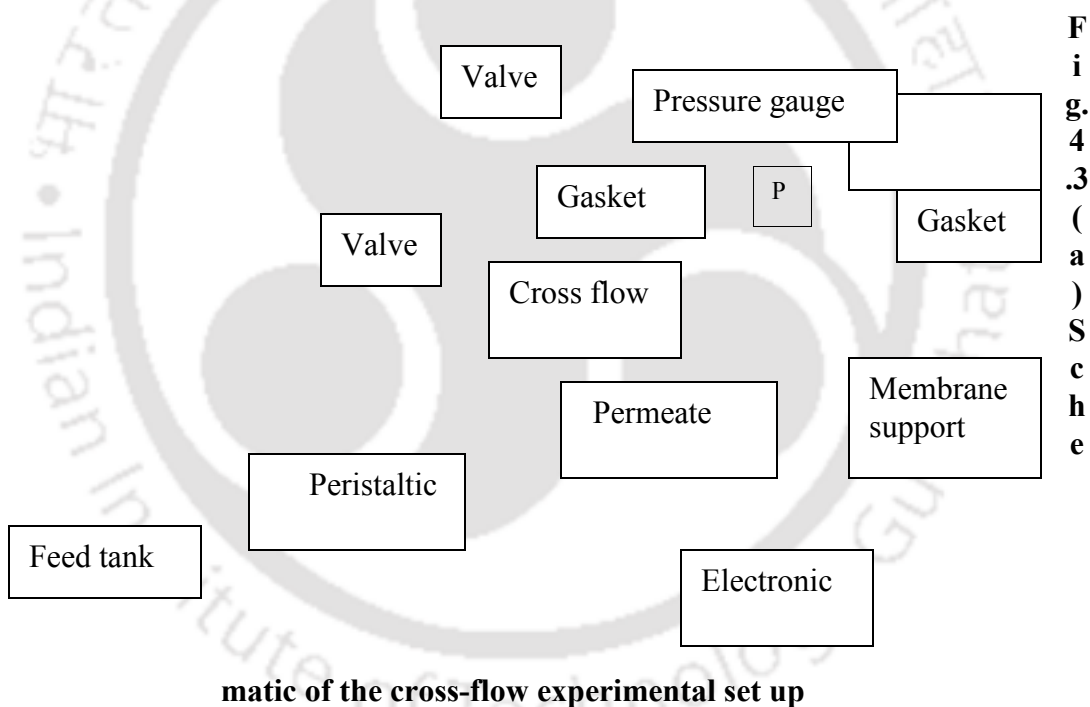
The dead-end mode is usually used mainly for laboratory experiments; while in contrast to that, cross-flow mode has been actually applied in continuous operations for the separation of solutes in industry. Cross-flow filtration differs from dead-end in that the retentate flows parallel to the membrane surface rather than normal to it. Hydrodynamic forces always drag particles toward the membrane surface in dead-end mode which results in enhancement of concentration polarization or build up of cake on the membrane surface. Although a cross-flow configuration limits the concentration polarization or cake deposit, the flux reduction is still significant due to fouling.

The schematic and the photograph of the cross flow experimental set up are shown in Figs. 4.3 (a) and (b) respectively. The setup consists of a feed tank, a peristaltic pump (Model PP20, Miclins India), a permeate tank and the cross-flow cell. The cell is a rectangular shaped stainless steel chamber with a cross-sectional area of $144 \times 10^{-4} \text{ m}^2$. The membrane sheet was placed inside the cell supported on a thin net type steel plate fitted with the help of a rubber gasket. The effective area of the membrane sheet was $6 \times 10^{-4} \text{ m}^2$. The cell is equipped with one pressure gauge at the middle which gives the TMP i.e. the pressure across the membrane. The feed solution was circulated by the peristaltic pump from the feed tank through the cell. The permeate side was open to the atmosphere and the TMP was controlled by adjusting the valve manually on the retentate side. The circulating flow rate was obtained from the reading displayed by the pump; the permeate was collected in a beaker on the electronic balance and the permeate flux was obtained by measuring the time to collect a certain weight of fluid. The retentate was

recycled continuously to the feed tank whilst the permeate sampled for analysis was returned to the feed tank for maintaining a consistent feed concentration.

Procedure

The cross-flow UF was carried out with the four selected membranes (based on the batch study) mainly to observe the effect of cross-flow rates (CFR) on the steady state flux and rejection at two different TMPs. The initial oil concentration in the feed was kept at 100



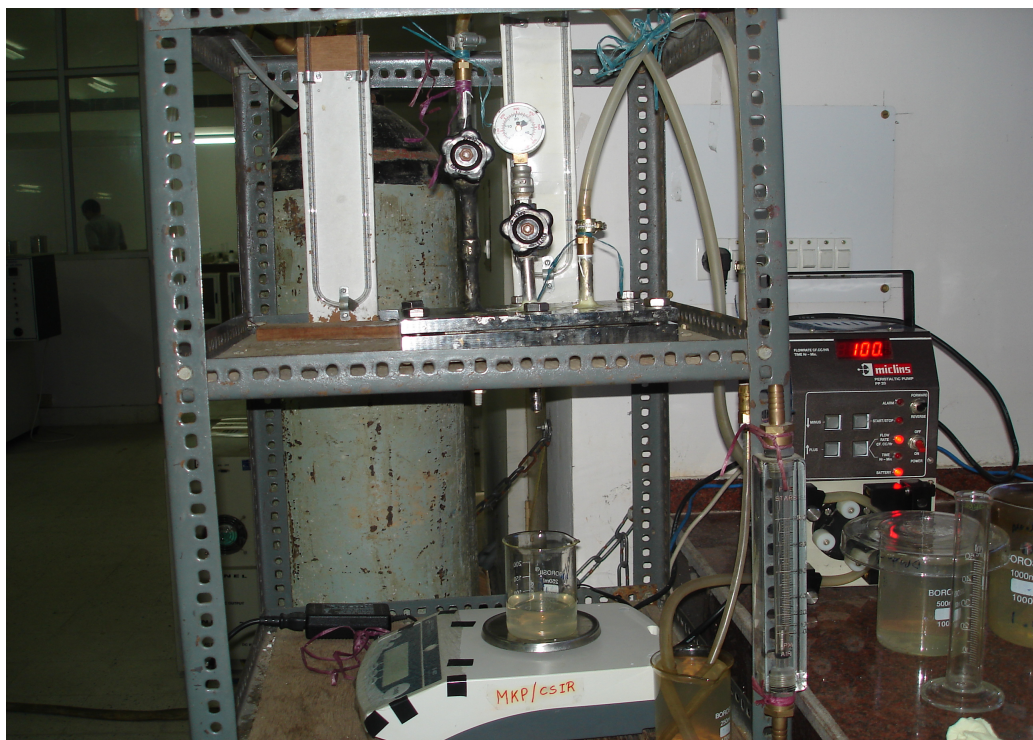


Fig. 4.3 (b) Photograph of the cross-flow experimental set up

mgL^{-1} and the pH was at its original value which was 6.12. The two TMP values were 103.4 kPa (15 Psig) and 172.4 kPa (25 Psig) and three CFR values i.e. $2.4 \times 10^{-6} \text{ m}^3\text{s}^{-1}$, $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ and $4.0 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ were considered to see the differences in membrane performance. The duration of each experiment was about one hour. Experiments were conducted at ambient laboratory conditions i.e. at a temperature of 25°C (approximately) with an initial feed volume of 500 mL. Since the permeate volume and its oil content were much smaller compared to the feed volume and its oil content, the feed concentration was assumed to be constant during each experiment.

The summary of all the operating conditions is presented in Table 4.3. After each run, the feed tank and the set up, including the membrane was washed thoroughly for 30 min. by

recirculation of distilled water. Further, membrane cleaning was accomplished by following the procedure as mentioned in section 4.2.2.1. All new experiments were performed with the cleaned membranes.

Table 4.3 Summary of operating conditions for cross-flow study

Membrane type	Oil concentration in feed (mgL ⁻¹)	TMP (kPa)	Feed pH	CFR (m ³ s ⁻¹)
M ₁ , M ₆ , M ₉ , M ₁₂	100	103.4, 172.4	6.12	2.4, 3.1, 4.0

Permeate fluxes were estimated as a function of time under the specified operating conditions using the same equation for batch flow i.e Eqs.(4.1) and (4.2).

The compositions of the retentate and permeate varied with filtration time, particularly at the early stage of the process; so the rejection of oil (R) was calculated after one hour when the flux reached almost the steady state, using the following equation:

(4.4)

where C_p and C_f are the concentrations of oil in permeate at steady state (after one hour) and in feed, respectively.

4.2.2. Industrial oily water

Industrial oily wastewater also known as ‘produced water’ was collected from Oil India Limited (OIL), Duliajan, Assam, India. It is a premier Indian national oil company and is mainly engaged in exploration and production of crude oil and natural gas. It is known that crude oil is found trapped in porous rocks beneath domes of impermeable rock. Since oil is lighter than water, it floats on water and becomes caught between the water below it and the impermeable surface above it. So when crude oil is extracted, it generally comes out of the well along with a significant amount of water and, often, small amount of natural gas. Conventional separation methods are employed to separate water and gas from the crude oil prior to sending to the refineries. This water which still contains considerable amount of small droplets of oil in the form of o/w emulsion is known as the ‘produced water’ or ‘formation water’.

Both batch and cross-flow UF experiments were carried out with this oily wastewater collected from the OIL using the four selected membranes to check their applicability.

4.2.2.1. Preliminary treatment and characterization

The ‘produced water’ so collected was not suitable for direct application to UF as it contained considerable amount of free floating oil on the top and solid particles at the bottom which are likely to clog the membrane pores as well as obstruct the flow through the pipings used in the experiment. So, preliminary treatments were carried out with the sample. At first, the solid particles were removed by gravity settling. Then the water was made free from the floating oil (formed by the coalescence of the bigger oil droplets) by skimming followed by normal filtering using a common porous filter paper. The resulting

oily water (i.e. the filtrate) which was almost free from solid particles and free oil, but still appeared turbid, was considered for carrying out further studies.

Before starting the UF experiments, the pretreated 'produced water' was characterized in terms of different parameters e.g. oil content, average size of the oil droplets, pH, density, total dissolved solids (TDS), specific conductivity (SC) and chemical oxygen demand (COD). The oil content in the water sample was found out by the spectrophotometric method as described in section 4.2.1.2. A new calibration curve was prepared with the crude oil collected from OIL, Duliagan, Assam which is shown in Fig. 4.4. The distribution of the size of the oil droplets and the remaining solid particles in the

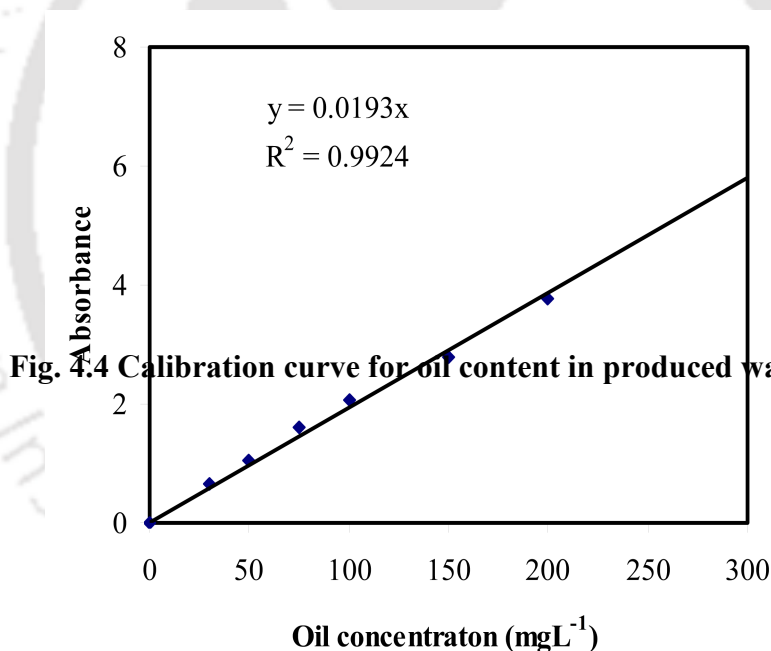


Fig. 4.4 Calibration curve for oil content in produced water

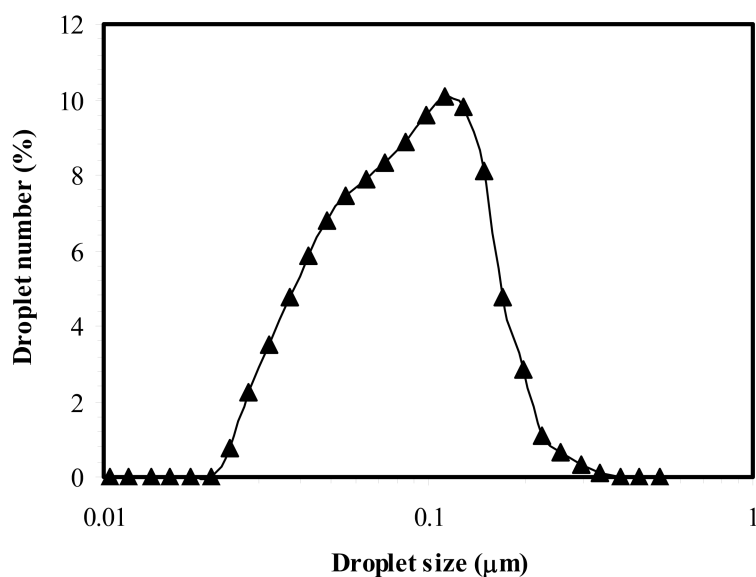


Fig. 4.5 Size distribution of oil droplets in produced water

‘produced water’ obtained by the laser particle size analyzer is shown in Fig. 4.5.

It is seen that the size ranges from about 0.02 – 0.2 with an average size of 0.1.

The pH, total dissolved solids (TDS) and specific conductivity (SC) of the water were obtained using the digital portable water/soil kit (Model: VSI – 06D1, VSI Electronic Pvt. Ltd. Chandigarh, India).

Chemical oxygen demand (COD) is often used as an important measurement of pollutants in wastewater. It is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. As both organic and inorganic components present in wastewater are subject to oxidation, COD signifies the presence of both types of components. Oil industries usually generate wastewater whose COD level is above the acceptable limit of $150 \text{ mg O}_2\text{L}^{-1}$ [USEPA]. Thus the 'produced water' was analyzed for COD content using the standard dichromate method known as Closed Reflux, Titrimetric method [19]. The principle behind this method is that most types of organic matter (specially volatile compounds) are more completely oxidized by a boiling mixture of chromic and sulfuric acids in a closed system. Here, the sample of water was refluxed in strongly acidic solution with a known excess of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) for 2 h. Then, the remaining unreduced $\text{K}_2\text{Cr}_2\text{O}_7$ was titrated with ferrous ammonium sulfate (FAS) to determine the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed and the oxidizable matter was calculated in terms of oxygen equivalent. The following equation was used to calculate COD:

$$\text{COD (mg O}_2\text{ L}^{-1}) = \quad (4.5)$$

where, V_b = mL FAS used for blank,

V_s = mL FAS used for sample,

= molarity of FAS, and

= milliequivalent weight of oxygen 1000 L^{-1} .

The results of the analysis of produced water are shown in Table 4.4.

Table 4.4 Analysis of produced water

Parameters	pH	Density (kg m^{-3})	TDS (mg L^{-1})	SC at 25°C (millimhos)	Oil content (after removing the free and unstable oil) (mgL^{-1})	COD (mgL^{-1})
Values	8.73	1001	4160	6.4	366	288

4.2.2.2. Batch (dead-end) ultrafiltration

At first, batch experiments were carried out with the four selected membranes using the batch experimental set up (Fig.2.6). The properties of feed (i.e. produced water) were maintained constant during the experiment to see the performance of the membranes under original conditions. Only the TMP was maintained at the optimum value obtained from the experiments with synthetic oily water. The PF was measured with respect to time while the oil rejection (% R) was obtained at the end of the experiment.

4.2.2.3. Cross-flow ultrafiltration

Experiments with produced water were also conducted in cross-flow mode at the optimum TMP (obtained from the batch study) and at a CFR of 3.1 (m³s⁻¹) using the cross-flow set up (Fig. 4.3). The PF and R (%) were found out as mentioned before. Finally, the batch results were compared with the cross-flow results.

Abbreviations

AAS	Atomic absorption spectrophotometer
BSA	Bovine serum albumin
CFR	Cross-flow rate
COD	Chemical oxygen demand
DMAc	Dimethyl acetamide
FAS	Ferrous ammonium sulfate
FD	Flux declination
GC	Gas chromatography
NMP	N- methyl pyrrolidone
PEG	Poly(ethylene glycol)
PF	Permeate flux
PSf	Polysulfone
PVP	Polyvinylpyrrolidone
SC	Specific conductivity
TDS	Total dissolved solids
TMP	Transmembrane pressure

TOC	Total organic carbon
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV	Ultraviolet spectrophotometer

Notations

mL of FAS used in blank (Eq. 4.5)

Effective membrane area (m^2)

mL of FAS used for sample (Eq. 4.5)

Concentration in the feed (mgL^{-1})

Concentration in the permeate (mgL^{-1})

Concentration in the permeate at steady state (mgL^{-1})

Permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$)

Initial permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$)

Permeate flux at time ($\text{Lm}^{-2}\text{h}^{-1}$)

Molarity of FAS (Eq. 4.5)

Volume of the permeate (L)

Rejection

Sampling time (h)

Weight of the permeate (kg)

Greek symbols

Density of the permeate (kgL^{-1})

References

1. D. A. Musale and S. S. Kulkarni, Relative rates of protein transmission through poly(acrylonitrile) based ultrafiltration membranes, J. Membr. Sci., 136 (1997), 13 - 23.
2. A. Higuchi, Y. Ishida and T. Nakagawa, Surface modified polysulfone membranes separation of mixed proteins and optical resolution of tryptophan, Desalination, 90 (1993), 127 - 136.
3. M. Elektorowicz, S. Habibi and R. Chifrina, Effect of electrical potential on the electro-demulsification of oily sludge, J. Colloid Interf. Sci., 295 (2006), 535 – 541.
4. M. F. Ali and M. H. Alqam, The role of asphaltenes, resins and other solids in the stabilization of water in oil emulsions and its effects on oil production in Saudi oil fields, Fuel, 79 (2000), 1309 – 1316.

5. A. Hong, A. G. Fane and R. Burford, Factors affecting membrane coalescence of stable oil-in-water emulsions, *J. Membr. Sci.*, 222 (2003), 19 - 39.
6. H. M. Huotari, I. H. Huisman and G. Tragardh, Electrically enhanced crossflow membrane filtration of oily waste water using the membrane as a cathode, *J. Membr. Sci.*, 156 (1999), 49 - 60.
7. I. W. Cumming, R.G. Holdich and I.D. Smith, The rejection of oil by microfiltration of a stabilised kerosene/water emulsion, *J. Membr. Sci.*, 169 (1) (2000), 147 – 155.
8. I. W. Cumming, R.G. Holdich and I.D. Smith, The rejection of oil using an asymmetric metal microfilter to separate an oil in water dispersion, *Water Res.*, 33 (17) (1999), 3587 – 3594.
9. P. Srijaroonrat, E. Julien and Y. Aurelle, Unstable secondary oil/water emulsion treatment using ultrafiltration: fouling control by backflushing, *J. Membr. Sci.*, 159 (1) (1999), 11 – 20.
10. F. F. Nazzari, and M. R. Wiesner, Microfiltration of oil-in-water emulsion, *Water Environ. Res.*, 68 (7) (1996), 1187 – 1191.
11. H. Ohya, J. J. Kim, A. Chinen, M. Aihara, S. I. Semenova, Y. Negishi, O. Mori and M. Yasuda, Effects of pore size on separation mechanism of microfiltration of oily water, using porous glass tubular membrane, *J. Membr. Sci.*, 145 (1998), 1 –14.

12. H. J. Li, Y. M. Cao, J. J. Qin, X. M. Jie, T. H. Wang, J. H. Liu and Q. Yuan, Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil-water separation, *J. Membr. Sci.*, 279 (2006), 328–335.
13. R. Pal, Techniques for measuring the composition (oil and water content) of emulsions — a state of the art review, *Colloid Surf. A: Physicochem. Eng. Aspects*, 84, (2-3) (1994), 141-193.
14. J. Zhong, X. Sun and C. Wang, Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration *Sep. Purif. Technol.*, 32, (1-3) (2003), 93 - 98.
15. B. Tansel, J. Regula and R. Shalewitz, Treatment of fuel oil and crude oil contaminated waters by ultrafiltration membranes, *Desalination*, 102 (1995), 301–311.
16. G. Rios, C. Pazos and J. Coca, Destabilization of cutting oil emulsions using inorganic salts as coagulants, *Colloid Surf. A: Physicochem. Eng. Aspects*, 138 (2–3) (1998), 383 – 389.
17. U. Daiminger, W. Nitsch, P. Plucinski and S. Hoffmann, Novel techniques for oil/water separation, *J. Membr. Sci.*, 99 (2) (1995), 197 – 203.
18. M. Hlavacek, Break-up of oil-in-water emulsions induced by permeation through a microfiltration membrane, *J. Membr. Sci.*, 102 (1995), 1 – 7.
19. L. S. Clesceri, A. E. Greenberg and A. D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association,

American Water Works Association, Water Environment Federation, 20th Edition, Washington (1998).



Chapter 5

Ultrafiltration (UF) of Oily Water: Results and Discussion

This chapter presents the results and discussions of the ultrafiltration (UF) experiments carried out in the present research work. At first, analyses of UF experiments for separation of BSA are reported where mainly role of membrane compositions as well as pH of the BSA solution is highlighted. Then an extensive study based on the findings of the UF of synthetic oily water in both batch and cross-flow mode is reported, where effects of various parameters such as transmembrane pressure (TMP), initial oil concentration, pH of oily water and membrane property are included. Fouling analysis is carried out based on the data obtained in the batch experiment to find out the relative contribution of different resistances towards membrane fouling. Finally, the separation efficiency of the selected membranes in industrial oily water has been discussed based on the results of the ultrafiltration of the 'produced water'.

5.1 Analysis of UF experiments with BSA solution

The rejection and flux characteristics of a membrane strongly depend on the structure of the membrane as well as the properties of the feed solution. So, the synthesized UF membranes were characterized by estimating rejection and flux during permeation experiment with protein (BSA) solution as feed.

5.1.1. Variation of permeate flux and BSA rejection

The main objective of the UF experiment was to investigate the rejection behaviour of BSA protein by different membranes prepared in the present work under identical conditions and thus confirming the applicability of the synthesized membranes in ultrafiltration application. The influence of increasing molecular weight of the two additives i.e. PVP and PEG on BSA separation and permeate flux is mainly focused in analyzing the results of this study. The flux and rejection of proteins by UF membranes can be explained under the concept of protein adsorption and consequent pore narrowing, as a result of both hydrophobic and electrostatic interactions between the membrane surface and the protein molecules [1, 2]. The morphological structure of the membrane (which includes both top-layer and sub layer) in protein transmission or rejection also play an important role.

5.1.1.1. Study with membranes prepared with PVP

The variation of permeate flux and rejection of BSA as a function of molecular weight of PVP are illustrated in Figs. 5.1 and 5.2 respectively for all the membranes when the feed solution is maintained at isoelectric point (IEP) i.e. at pH 4.8 and at above IEP (pH 9.3). From these figures, it is understood that the rejection and flux characteristics of a membrane strongly depend on the structure of the membrane as well as the properties of the feed solution. The variation in morphological structure of the membrane (which includes both top layer and sub layer) due to addition of PVP of different molecular weight and different solvents is an important factor in

protein transmission and rejection. Similarly, pH of BSA solution also seems to affect the rejection and flux characteristics to a great extent. This work has been published in the Journal of Membrane Science [3].

Effect of molecular weight of PVP

Fig. 5.1 shows the effect of molecular weight of PVP in the casting solution on the flux of protein i.e. BSA for all the membranes when the pH of the BSA solution is maintained at 4.8 and 9.3. It is observed that with increase in molecular weight of PVP from 24,000 Da to 3,60,000 Da, the flux decreases from 955 to 115 $\text{Lm}^{-2}\text{h}^{-1}$ (when pH of BSA is 4.8) and from 573 to 76 $\text{Lm}^{-2}\text{h}^{-1}$ (when pH of BSA is 9.3) for PSf/NMP membranes. Similarly, for PSf/DMAc membranes, the flux is seen to decrease from 38 to 23 $\text{Lm}^{-2}\text{h}^{-1}$ (when pH of BSA is 4.8) and from 54 to 26 $\text{Lm}^{-2}\text{h}^{-1}$ (when pH of BSA is 9.3).

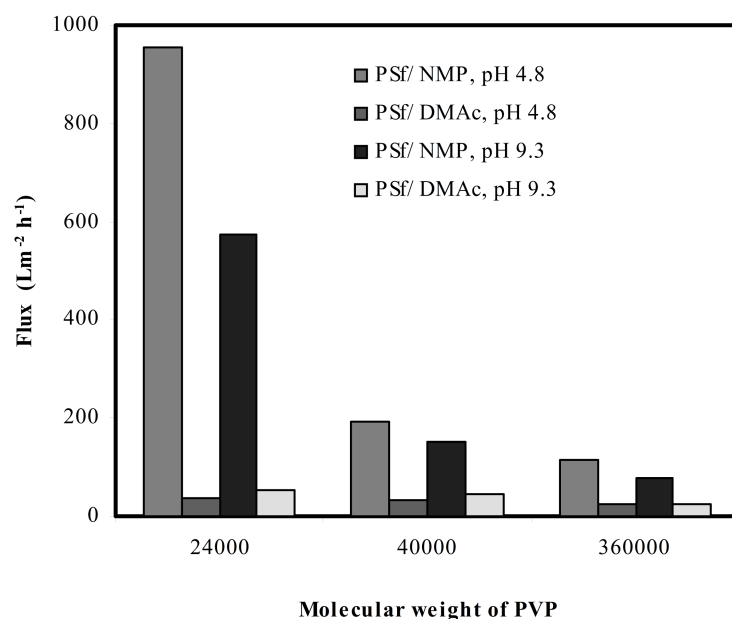


Fig. 5.1 Effect of molecular weight of PVP on BSA flux; membranes used:

PSf/NMP membranes and PSf/DMAc membranes; pressure: 103 kPa; duration of experiment: 1 h.

This decreasing trend of flux can be attributed to the formation of membranes with reduced average pore size on the top and suppressed sub layer due to addition of higher molecular weight PVP. The declination in BSA flux with increase in molecular weight of PVP could also be a consequence of increased susceptibility to pore plugging due to BSA adsorption. Initial flux declines are seen to be more pronounced and final fluxes are gradually lowered which is attributed to the loss of porosity by internal adsorption of protein leading to pore plugging. From Fig. 5.2, the increasing trend of rejection of BSA with increase in molecular weight of PVP can be observed irrespective of the solvents used and pH of BSA solution. When the pH is maintained at 4.8, the rejection increases from 2.4 to 33.2 % for PSf/NMP/PVP membranes and from 37 to 53 % for PSf/DMAc/PVP membranes; while with BSA at pH 9.3, the rejection increases from 2.2 to 63.3 % for PSf/NMP/PVP membranes and from 40.5 to 76.7 % for PSf/DMAc/PVP membranes.

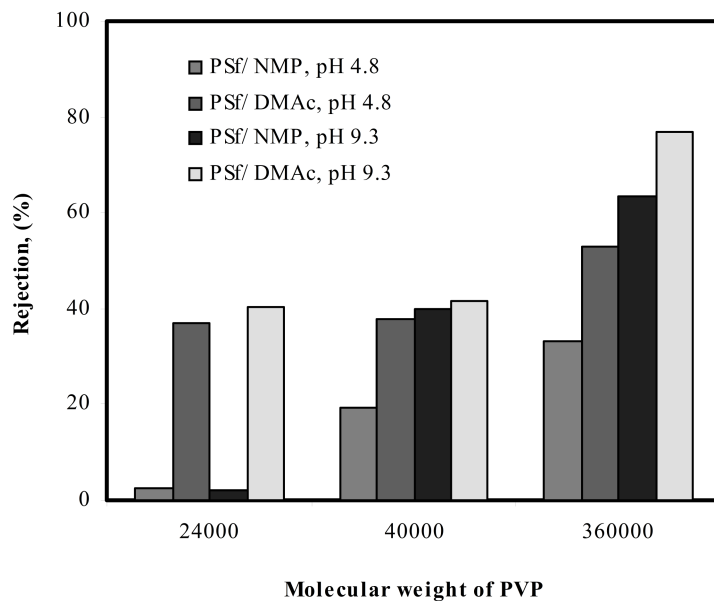


Fig. 5.2 Effect of molecular weight of PVP on BSA rejection; membranes used: PSf/NMP membranes and PSf/DMAc membranes; pressure: 103 kPa; duration of experiment: 1 h.

The characteristic rejection profiles can be explained by adsorption phenomena. The increase in BSA rejection with increase in molecular weight is believed to be a manifestation of significant protein adsorption within and upon the membranes. Pore blockage and closure due to protein adsorption makes the membranes with high molecular weight PVP more retentive. Surface deposition of protein provides an additional barrier to solute transport. The reason for PVP 24000 membranes having minimum rejection is because of the fact that adsorption of protein on pore wall has less

effect on pore narrowing due to their relatively high pore size compared to PVP 40000 and PVP 360000 [3].

The high rejection and comparatively low flux with PVP 360000 membranes for both the pH values can also be understood from the morphology of their cross section [as discussed in Chapter 3]. The comparatively thick asymmetric layer probably explains the improvement in the rejection rate while the sub layer with suppressed macrovoids offers resistance resulting in rather low flux and high rejection.

Effect of pH of BSA solution

The effect of pH on BSA flux and rejection can also be observed from Figs. 5.1 and 5.2. BSA molecules are of no charge at the IEP (i.e. at pH 4.8) and negatively charged above the IEP and thus strongly negative at pH 9.3. Generally, the membrane would reject like charged BSA molecules. From Fig. 5.2, it is seen that the rejection is higher for pH 9.3 compared to pH 4.8 irrespective of the molecular weight of PVP and type of solvents used. This can be attributed to the repulsive interaction between the membrane and protein molecules which leads to hindered protein transmission through the pore (lower flux) and consequent higher rejections. At IEP, in absence of electrostatic interaction the membranes allow more protein transmission without much adsorption and consequently result in less rejection [3].

The role of solvent

The role of solvent in the casting solution on flux and rejection of proteins can also be noted from Figs. 5.1 and 5.2. It is seen from the figures that for membranes

prepared with DMAc, the permeate flux is lower and consequently protein rejection is more at both the pH values compared to NMP. This is attributed to the combined effects of membrane structure and electrostatic interaction between the membrane and BSA. With PSf/DMAc membranes, protein adsorption seems to be more due to hydrophobic or electrostatic interaction which decreases the flux as adsorption of protein on pore wall causes pore narrowing [4, 5]. The thick morphological structure of PSf/DMAc/PVP membranes with PVP 360000 (Fig. 3.1 (b)) can be a major factor for the highest BSA rejection (76%) obtained in this study [3].

5.1.1.2. Study with membranes prepared with PEG

The variation of permeate flux and BSA rejection data with different molecular weight of PEG are shown in Figs. 5.3 and 5.4 for NMP and DMAc solvents, respectively at pH 4.8 (i.e. at IEP) and at pH 9.5 (i.e. above IEP) conditions. From these figures, it is understood that both molecular weight of PEG and pH of the protein solution are important factors in protein rejection and flux. In this case, the flux and rejection show somewhat different trends from those shown by PSf/PVP membranes. The findings of this study are explained subsequently on the basis of the two pH values. This work is published in the Journal of Membrane Science [6].

Observation and analysis at pH 4.8

When the pH of the BSA solution is maintained near the IEP (i.e. pH = 4.8), it is observed that the flux gradually increases with increase in molecular weight of PEG from

400 Da to 20,000 Da for all membranes, irrespective of the solvents; This effect can be seen in Fig. 5.3. As protein carries no charge at its IEP, this trend is due to the result of hydrophobic/hydrophilic interaction between the protein molecules and the membranes. In general, hydrophilic membranes tend to adsorb less protein at its IEP and thus have higher flux than hydrophobic membranes [7]. This is because of the fact that less adsorption does not narrow down the pores. In the present study, increase in porosity (due to increased number of pores) of the membranes and possible increase in hydrophilicity (from water content test) as discussed earlier with increase in molecular weight of PEG, leads to increase in flux [6].

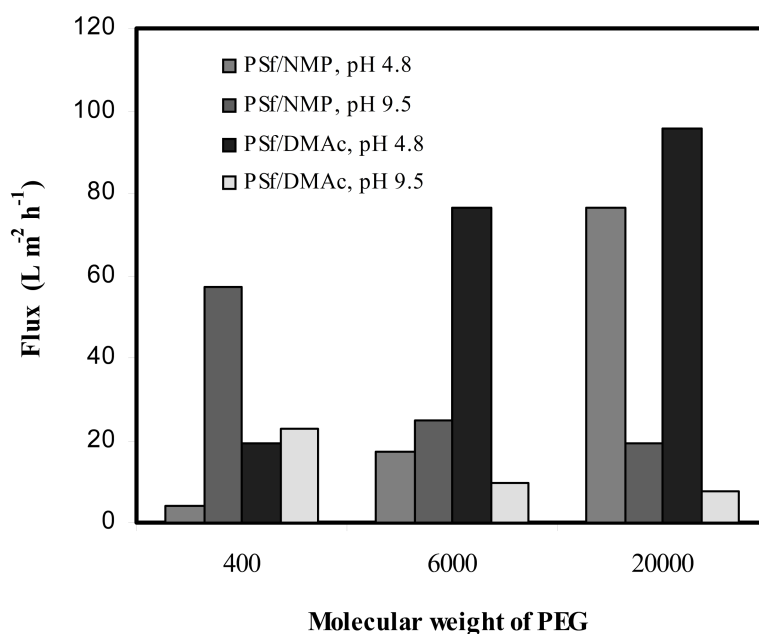


Fig. 5.3 Effect of molecular weight of PEG on BSA flux; membranes used: PSf/NMP membranes and PSf/DMAc membranes; pressure: 103 kPa; duration of experiment: 1 h.

On the other hand, from Fig. 5.4, it is seen that percent rejection of BSA increases with increase in molecular weight of PEG from 400 Da to 6000 Da. The increasing trend in percentage rejection with increase in molecular weight of PEG from 400 Da to 6000 Da is because of the resistance offered to the protein molecules by the dense and sponge-like structure of the membranes (Fig. 3.2) with PEG 6000. It is also found that rejection decreases beyond molecular weight of PEG 6000 Da. At pH = 4.8, in absence of electrostatic interaction, protein transmission should increase i.e. rejection should decrease with increase in molecular weight of PEG. The increase in membrane porosity (Table 3.3) as well as presence of finger-like cavities in the sub layer (Fig. 3.2) and possible increase in hydrophilicity with PEG 20000 allow more protein transmission without much adsorption and consequently may result in less rejection [6].

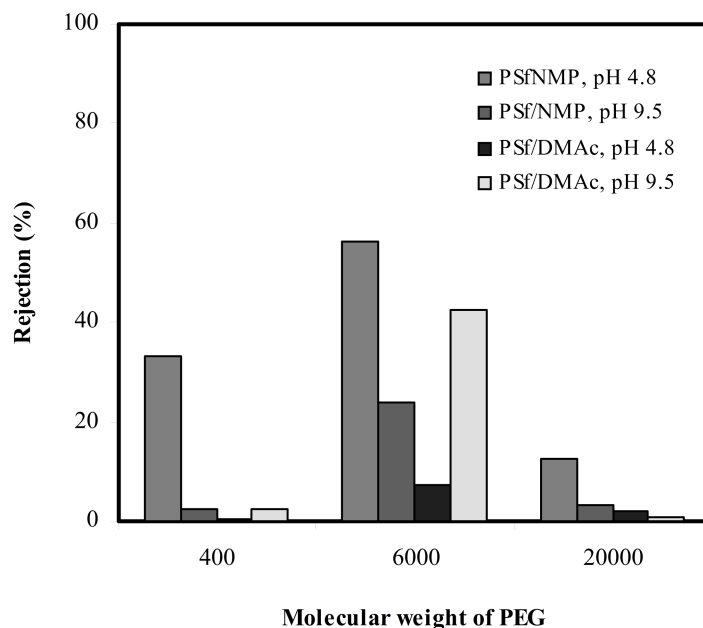


Fig. 5.4 Effect of molecular weight of PEG on BSA rejection; membranes used: PSf/NMP membranes and PSf/DMAc membranes; pressure: 103 kPa; duration of experiment: 1 h.

Observation and analysis at pH 9.5

When the pH of the solution is kept at 9.5, the flux gradually decreases with increase in molecular weight of PEG. In this case, adsorptive effects through electrostatic interactions between protein and membrane surfaces may become more pronounced. It is known that the charge on the protein and the difference in charge between the membrane and the protein determines the degree of adsorption of protein on the membrane surface [5]. Above IEP (i.e. pH = 9.5), protein carries a net negative charge resulting in repulsive

interactions between protein molecules and membranes. This interaction increases for membranes with increase in molecular weight of PEG possibly due to the difference in charge between the protein and the membrane surface leading to different degree of protein adsorption. The trend of percent rejection is similar to that at pH = 4.8. Apparently, it appears that the rejection should increase with increase in adsorption of protein as molecular weight of PEG increases. But experimental result is seen to be just reverse for PEG 20000 membranes. The reason for PEG 20000 membranes having minimum rejection is possibly because of the fact that adsorption of protein on pore wall has less effect on pore narrowing due to their very high porosity compared to PEG 400 and PEG 6000. The high rejection and comparatively low flux with PEG 6000 membranes for both the pH values may also be understood from the morphology of their cross section [as discussed in Chapter 3]. The thin asymmetric layer probably explains for the improvement in the rejection rate while the thick sponge-like sub layer offers resistance resulting in rather low flux and high rejection [6].

The role of solvent

The role of solvent in the casting solution on rejection of proteins can also be noted from the figures. It is seen that for NMP, the percentage rejection is found to be maximum at pH value of 4.8 which is 56.4 percent for PEG 6000; while for DMAc, it is maximum for pH value of 9.5 which is 42.4% for PEG 6000. This is attributed to the fact that at pH value of 4.8, adsorption of protein, taking place due to hydrophobic/hydrophilic interaction between the protein molecules and the membranes, on NMP membrane is

possibly more than on DMAc membrane resulting in higher rejection (56.4%). On the other hand, at pH value of 9.5, adsorption of protein, taking place due to the electrostatic attraction between the protein molecule and the membrane surface, is possibly more in DMAc membranes leading to higher rejection (42.4%) compared to NMP membranes.

Thus from the above study, it may be concluded that the hydrophobic or electrostatic interaction between protein molecules and membrane surface depending on the range of pH of protein solution determines the extent of protein rejection by a membrane. The morphological parameters of a membrane (such as porosity) and structure of membrane (with finger-like or sponge-like sub layer) also play a key role in this regard. Finally, effect of molecular weight of additives (i.e. PEG) and type of solvents (i.e. NMP and DMAc) should also be considered as important factors as they finally decide the morphology and permeation property of a membrane.

5.1.1.3. Summary of BSA ultrafiltration [3, 6]

From the above investigation of BSA separation with all the membranes, it is understood that all the parameters, i.e. membrane composition (which includes molecular weight of additive and the type of solvent used in the membrane casting solution) and pH of BSA solution play important roles in flux and BSA rejection. The trend of results obtained in this study is quite interesting considering the differences in findings with the two additives i.e. PVP and PEG.

- With PEG as additive, a significant increase in BSA rejection was observed when

molecular weight of PEG was increased from 400 to 6000 Da, beyond which the rejection was seen to decrease when molecular weight was increased from 6000 to 20,000 Da. So irrespective of solvents and pH of BSA, membranes prepared with PEG 6000 are considered to be the best; while in the study with PVP, rejection is found to increase with increase in molecular weight of PVP within the chosen range of molecular weight i.e. from 24,000 to 3,60,000 Da. So irrespective of solvents and pH of BSA, membranes prepared with PVP 360000 are considered to be the best.

- The pH of the protein solution also plays an important role in this regard. In case of the membranes prepared with PVP, the protein solution at pH 9.3 is found to be more favorable compared to that at pH 4.8 with respect to protein rejection for both type of solvents; while for membranes prepared with PEG, the rejection is found to be solvent dependent. In this case, protein solution of pH 4.8 is found to give better result with NMP as solvent but with DMAc as solvent, the solution has to be maintained at pH of 9.5 to get maximum rejection.
- Considering the role of the two solvents, for PSf/PVP membranes, DMAc seems to be better compared to NMP in terms of rejection of BSA for both the pH values. For PSf/PEG membranes, NMP may be considered better compared to DMAc in terms of maximum rejection.
- Comparing the membranes prepared with both types of additives, i.e. PEG (molecular weights 400, 6000 and 20,000 Da) and PVP (molecular weights 24,000, 40,000 and 3,60,000 Da) in terms of BSA rejection, it can be concluded

that membranes prepared with PVP may be considered better (with $\%R_{\max} = 76\%$)

than those prepared with PEG (with $\%R_{\max} = 56.4\%$) irrespective of the two

solvents i.e. NMP and DMAc.

5.2. Analysis of UF experiments with synthetic oily water

Any UF application requires optimization of different parameters in order to get better permeate flux (PF) and rejection of solute ($\%R$). Again, both the PF and $\%R$ depend on the kind of membrane used, if other operating parameters such as the feed concentration, the transmembrane pressure (TMP) and the pH of the feed are kept constant. So, investigations were carried out on the synthetic oily water with all the twelve membranes prepared at TMP of 68.9 kPa, 103.4 kPa, 137.9 kPa and 172.4 kPa. The feed concentration was maintained at 100 mgL^{-1} with normal pH value (i.e. at 6.12). Details of the experimental part are given in Chapter 4.

5.2.1. UF experiment in batch (dead-end) mode

In this section, the effects of variations of TMP on membrane performance are discussed with respect to PF, $R (\%)$ and flux declination (FD). Based on this, the optimum TMP is selected. The selection of the most suitable membranes out of the four membrane compositions is made based on the results obtained under the optimum TMP. This work is published in the Journal of Membrane Science [8].

5.2.1.1. Effect of transmembrane pressure

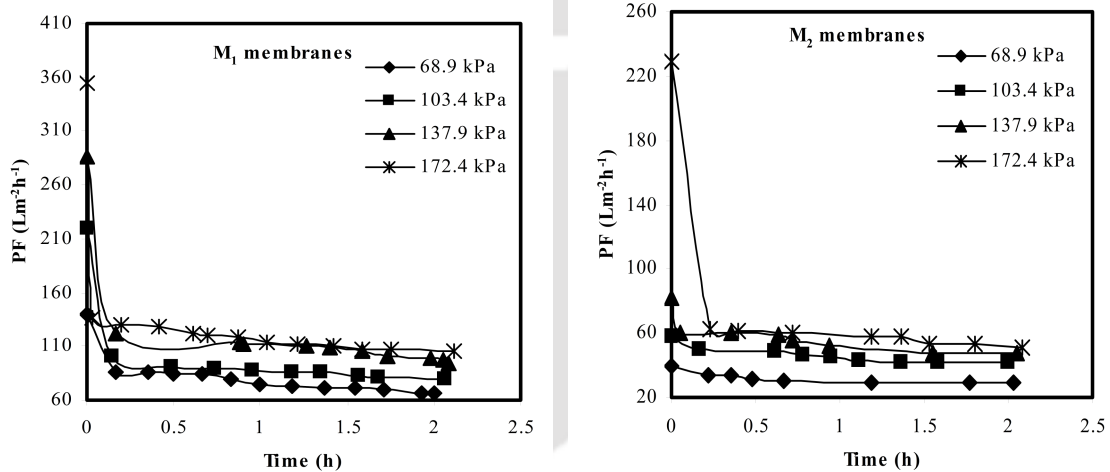
Permeate flux

Figure 5.5 and 5.6 show the permeate flux as a function of time at different pressures for the PSf/PVP and PSf/PEG membranes respectively. The trend of variations of flux with time at all the pressures is found to be almost the same irrespective of the types of membrane. The flux is initially found to decline rapidly with time and finally becomes almost constant with time. Possible reason for flux declination throughout the experiment is pore blocking due to the existence of size distribution of membrane pores and oil droplets and concentration polarization due to increase in retentate concentration. However, at the initial stage of the experiment, since the retentate concentration is not very high, the concentration polarization effect will be negligible [9, 10]. In that case, pore blocking by oil droplets could be the major factor for initial flux declination. This sharp initial flux declination is attributed to the membrane pore blocking by the smallest oil droplets. The effect of pressure on permeation flux for the different membranes can also be understood from Fig. 5.7 which shows permeate flux calculated after 1 hr as a function of TMP for all the membranes. The M₁₀ membrane has not been considered for further study as the permeation rate is found to be very small to carry out the experiment. From the figure, the flux is seen to increase with increase in pressure irrespective of the types of membrane used within the given pressure range. The increase in flux with pressure is due to increase in driving force across the membrane. However, the increase in flux with pressure is not seen to be exactly linear which indicates the existence of

additional resistance (i.e. resistance due to adsorption and concentration polarization) [8].

Flux decline (FD)

The pressure affects the rate of flux decline. Higher the pressure, greater is the rate of flux decline as seen from Fig. 5.5 and 5.6. The increase in flux declination with higher pressure may be connected with the build-up of the concentration polarization layer and with pore blocking mechanisms which was also observed by Koltuniewicz and Field



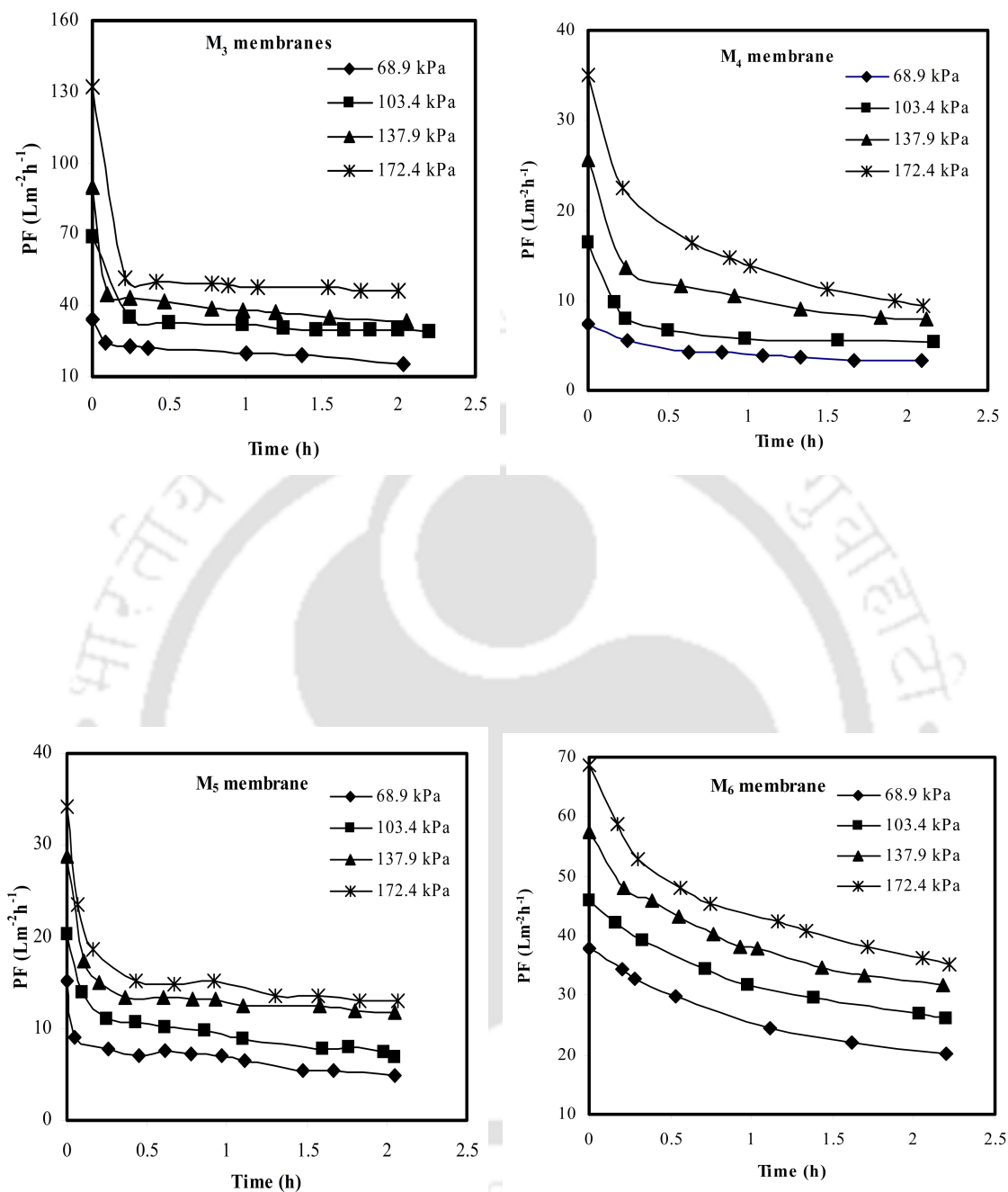
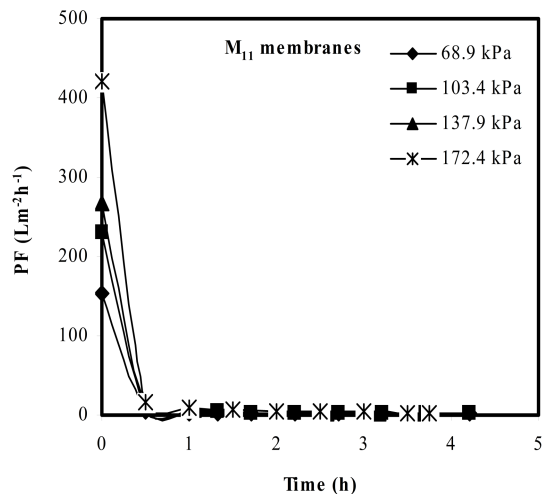
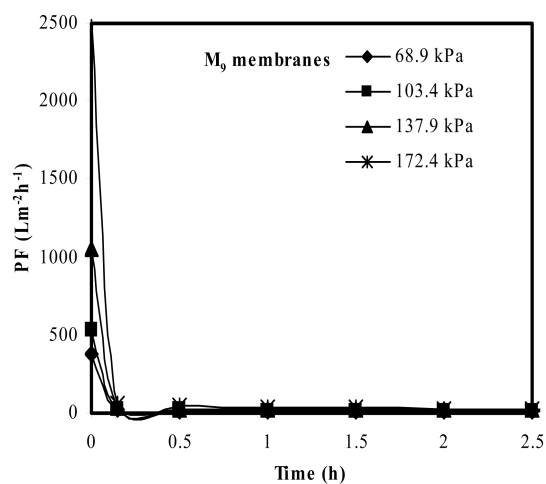
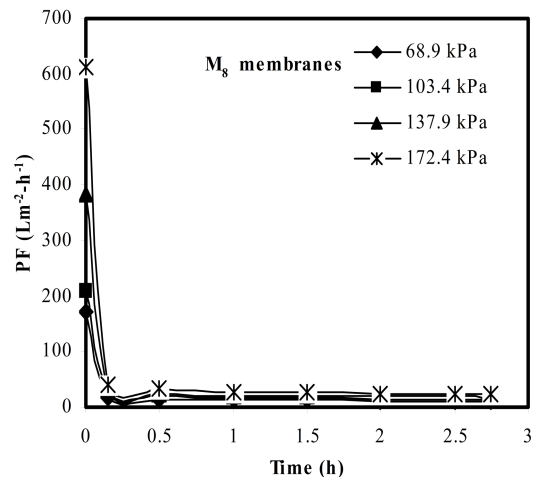
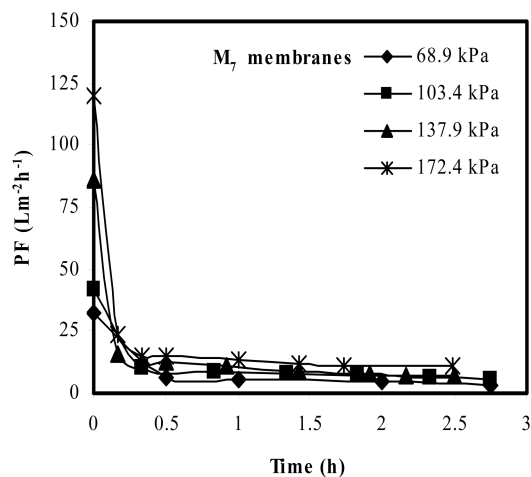


Fig. 5.5 Variation of permeate flux (PF) with time for PSf/PVP membranes; initial oil concentration: 100 mgL^{-1} ; pH : 6.12.



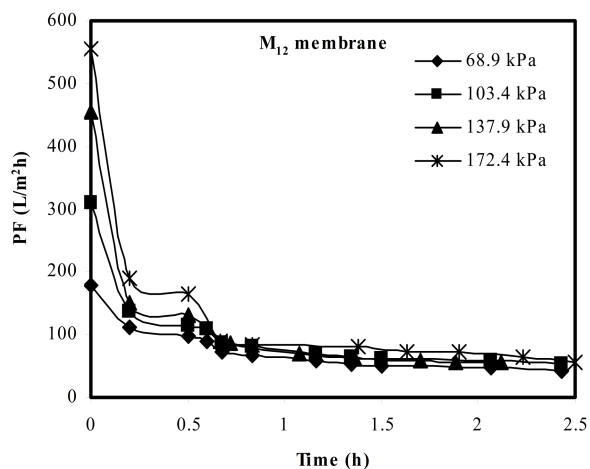


Fig. 5.6 Variation of permeate flux (PF) with time for PSf/PEG membranes; initial oil concentration: 100 mgL⁻¹; pH : 6.12.

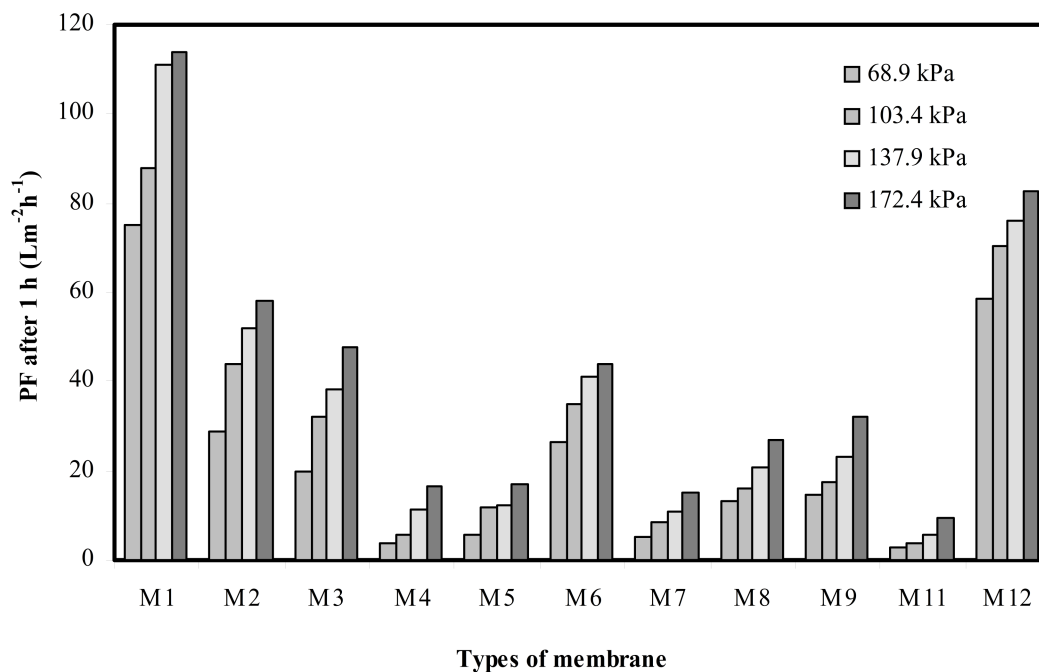


Fig. 5.7 Permeate flux (PF) of different membranes at different pressures [8]

[10]. Increase in pressure increases the number of collisions between the emulsion droplets, which in turn break the film between the oil and water causing the oil droplets to coalesce and form large droplets. As a result, a layer containing large oil droplets starts forming just above the membrane surface which may be compressed on the surface at higher pressure leading to membrane fouling at a higher rate. This declines the flux. However at each pressure, for all the membranes, the permeation flux is seen to reach almost a constant value after some time [8].

Fig. 5.8 represents the FD (%) of different membranes calculated at 0.5, 1, 1.5 and 2 hrs after the experiments were started at a TMP of 103.4 kPa. It is observed that the percent flux declination for each membrane in the first hour is higher than the second hour. As discussed earlier, total membrane resistance consists of two parts viz. resistance due to pore blocking and resistance due to concentration polarization. In the first hour, most of the oil droplets participate in the blocking phenomenon by pore sealing causing flux declination at a higher rate. As time passes, pore blocking process is gradually stopped and the oil layer, which is formed by settling of oil droplets on membrane surface (i.e. concentration polarization), begins to dominate the total membrane resistance. As pore blocking is a very fast process, flux declination also takes place at a faster rate. On the other hand, concentration polarization is a slow process, so corresponding flux declination rate is reduced at the later stage [8].

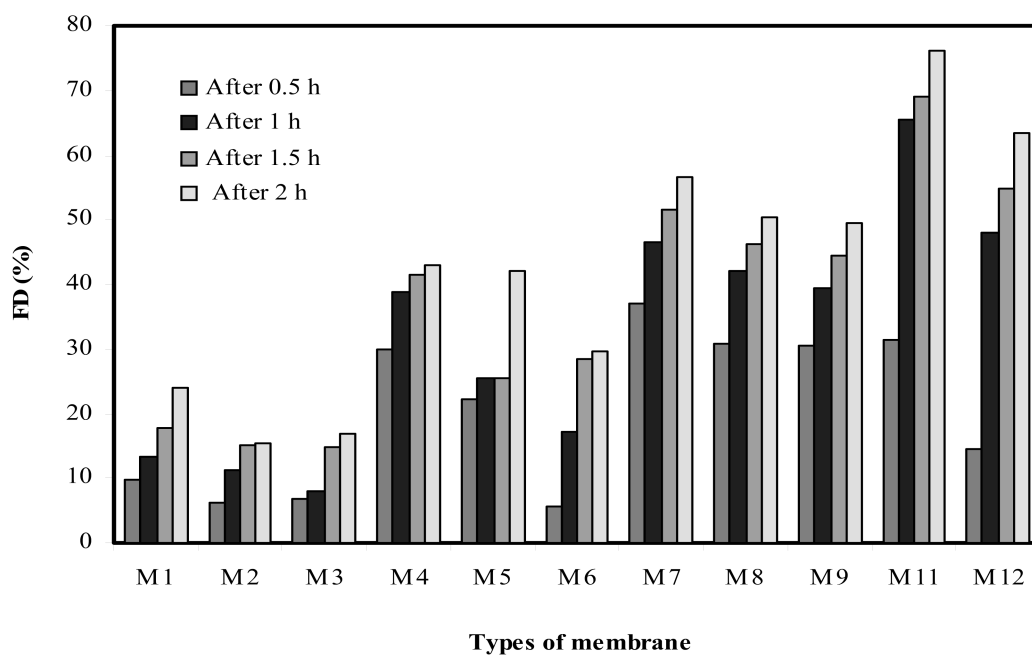
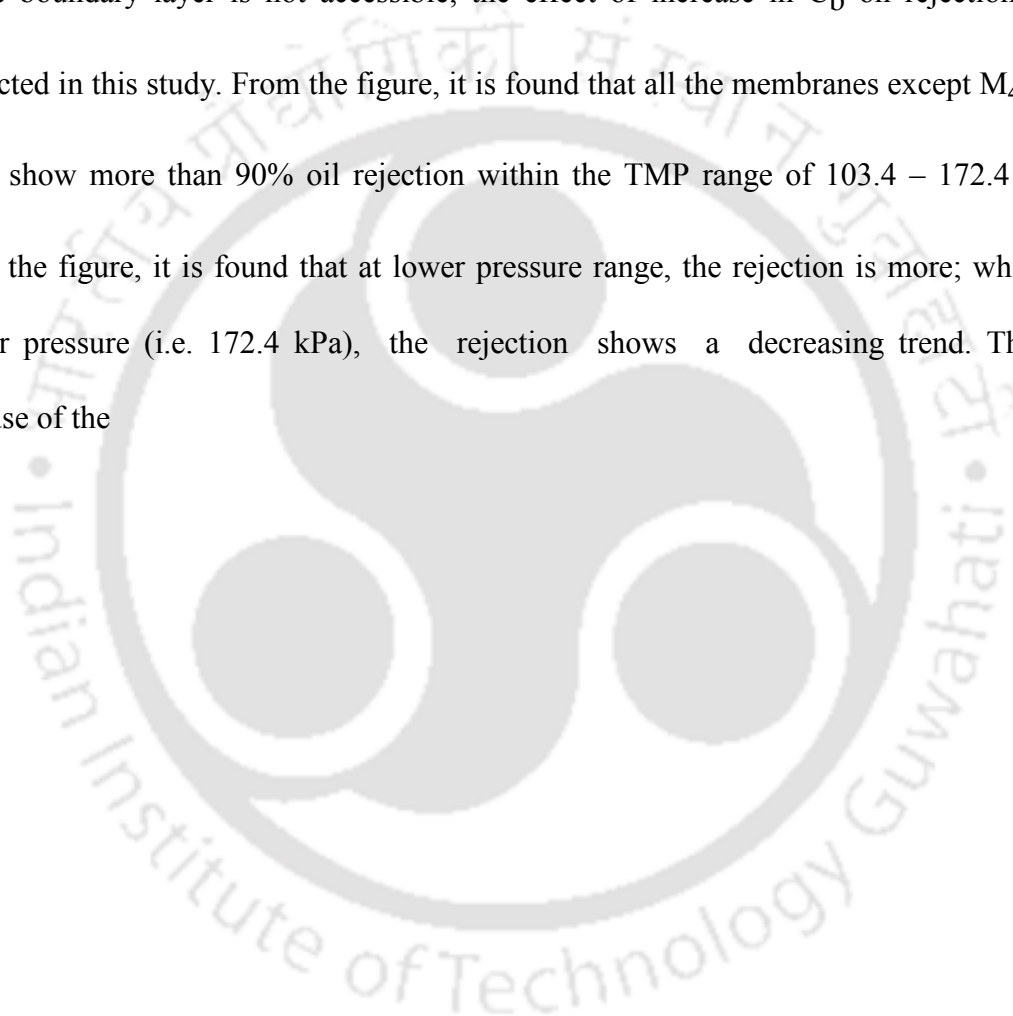


Fig. 5.8 Variation of FD (%) with time for different membranes at 103.4 kPa [8]

Rejection of oil

The rejection of oil from the synthesized oily water is calculated as % R using Eq. (1.3) and is reported in Fig. 5.9. The actual membrane rejection will be higher than the rejection calculated by Eq. (1.3) due to change in concentration in the boundary layer because C_b , the bulk concentration increases with time. However, since the concentration in the boundary layer is not accessible, the effect of increase in C_b on rejection was neglected in this study. From the figure, it is found that all the membranes except M₄ and M₁₁, show more than 90% oil rejection within the TMP range of 103.4 – 172.4 kPa. From the figure, it is found that at lower pressure range, the rejection is more; while at higher pressure (i.e. 172.4 kPa), the rejection shows a decreasing trend. This is because of the



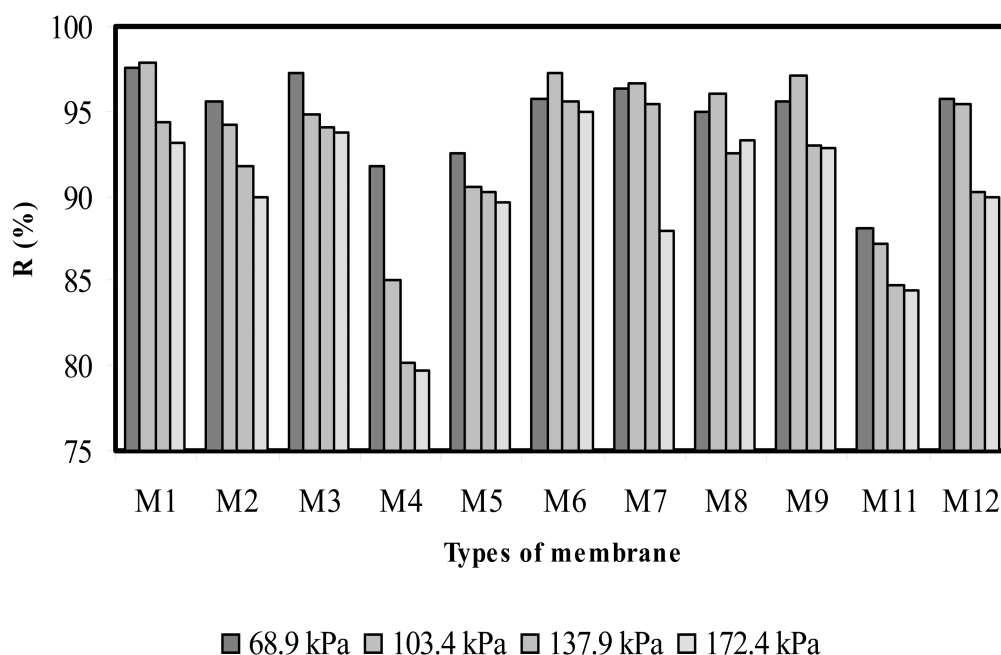


Fig. 5.9 Effect of TMP on oil rejection (% R) [8]

fact that higher pressure drop across the membrane would enhance wetting and coalescence of the oil droplets by increasing convection and this would impose some oil droplets to pass through the membrane pores along with the permeate. In other words, as the TMP increases, the applied pressure overcomes the capillary pressure that prevents the oil from entering the membrane pores.

From the above study which includes the trends of permeate flux, flux declination rate

and percent oil rejection at various TMP, 103.4 kPa (15 psig) may be considered as the most preferable TMP for achieving utmost membrane performance [8]. Further analysis as well as investigations were carried out at this pressure only.

5.2.1.2. Effect of membrane type

Permeation flux

Average pore size, pore size distribution, porosity and hydrophilicity are some important membrane properties which play a key role in determining the permeate flux. Here, though the average pore size for all the membranes is almost in the same range (Table 3.3), there is difference in the pore size distribution for all the membranes. Under such situation, the variation of permeation flux for different membranes can be due to (i) difference in porosity, (ii) difference in hydrophilicity and (iii) difference in thickness of the oil layer formed above the membrane surface. The effect of variation of the ratio of droplet size to membrane pore size which is usually considered to be an important factor [9] in evaluating membrane performance is assumed to be negligible considering the fact that the ratio remains almost the same for each type of membrane.

The effect of membrane types on permeate flux (PF) can also be studied from Fig. 5.7.

The clear difference in the values of PF of different membranes under similar operating conditions, can be observed from the figure as well as from Table 5.1 with M₁ and M₁₁ membranes exhibiting the highest flux (87.7 Lm⁻² h⁻¹) and the lowest flux (3.7 Lm⁻² h⁻¹), respectively. The figure reveals that M₁ and M₁₂ are membranes with higher PF (>60 Lm⁻² h⁻¹); M₂, M₃, M₅, M₆, M₈ and M₉ have moderate PF (10 - 60 Lm⁻² h⁻¹);

while the others i.e. M₄, M₇ and M₁₁ have lower PF (<10 Lm⁻² h⁻¹) at the TMP of 103.4 kPa. As a whole, PSf membranes prepared with PVP/NMP (i.e. M₁, M₂ and M₃) and PEG 20000/ DMAc (i.e. M₁₂) show reasonably good flux compared to the membranes prepared with PEG/NMP and PVP/DMAc combinations. The difference in PF for different membranes is attributed to the variation of their morphological structure due to the addition of different molecular weight additives viz. PVP and PEG in the individual membrane system. The membranes M₆, M₉ and M₁₂ are seen to exhibit comparatively higher flux as water molecule can easily pass through them due to higher porosity and possibly higher hydrophilicity [8]. However, the trend of higher flux for membranes prepared with higher molecular weight additive is not seen to be followed by the PSf/NMP/PVP membranes. In the case of M₁, M₂ and M₃ membranes, PF decreases with increase of molecular weight of PVP. This implies that along with porosity and hydrophilicity, the morphology of the membrane sub layer also plays an important role in determining the PF. This reasoning can be supported from the fact that the CF values (Table 3.3) decreases with increase in molecular weight of the additives (i.e. PVP and PEG) for all the membrane systems except PSf/NMP/PVP system where the trend is just reverse. As reported earlier [3, 6], compaction factor (CF) is related to the structure of the membrane specially membrane sub layer. Higher the CF, more likely the membrane compacts due to the presence of large number of macrovoids in the sub layer resulting in narrower passage for permeate flow. As M₁ membrane has the lowest CF value compared to M₂ and M₃ membranes, it exhibits the highest PF among M₂ and M₃ membranes. As

a whole, for each membrane system, the membrane having the lowest CF may be regarded as the best membrane among the other two membranes in terms of producing the highest flux. This explains the fact that M_1 , M_6 , M_9 and M_{12} are the membranes (with the lowest CF) having the maximum flux within their respective systems.

Table 5.1 Comparison of the performance of different membranes after 2 h at optimal TMP (103.4 kPa); initial feed oil concentration: 100 mgL⁻¹; pH: 6.12.

Membranes	PF (Lm ⁻² h ⁻¹)	R (%)	FD (%)	SP
M_1	79.8	97.8	24.1	323.8
M_2	42.2	94.2	15.5	256.5
M_3	29.2	94.8	16.9	163.8
M_4	5.3	85	42.8	10.5
M_5	9.0	90.5	42.1	19.3
M_6	26.8	97.2	29.7	87.7
M_7	6.6	96.6	56.7	11.2
M_8	15.0	96.1	50.4	28.6
M_9	16.5	97.1	49.3	32.5
M_{11}	3.1	87.2	76.1	3.6
M_{12}	57.3	95.5	63.3	86.4

Flux declination (FD)

Figure 5.8 illustrates the percent declination of flux data for different membranes with respect to time which have been calculated on the basis of initial permeate flux of o/w emulsion using Eq. (4.3). From the figure, it is seen that different membranes have experienced different degree of flux declination for a feed of constant oil concentration (i.e. 100 mgL^{-1}) and constant TMP (i.e. 103.4 kPa), which is attributed to the difference in pore size distribution between the membranes. As from the previous study, it was found that for each system with increase in molecular weight of additive, the pore size distribution becomes narrower and it is a well known fact that membranes with narrow pore size distribution experience less degree of flux declination. The possible role of the degree of hydrophilicity also can not be ruled out in this regard. Changes in membrane structure due to swelling of membrane can be another factor causing the initial rapid reduction of flux [11]. During the course of UF, large oil droplets settle on the membrane surface acting as a barrier to permeate flow; while the small droplets try to pass through the membrane pores causing pore blocking. The extent of fouling is seen to be higher with membranes prepared with lower molecular weight additives. This supports the fact that due to increase in hydrophilicity, initial fouling is comparatively less for M₃, M₆, M₉ and M₁₂ membranes considering all the combination of solvents and additives [8].

Rejection of oil

Figure 5.9 reports the percent rejection of oil for different membranes within the operating pressure range. From the figure, it is observed that for all the pressure range, the

different systems of membranes follow different trends. For example, for PSf/NMP/PVP membranes the rejection is the maximum for membrane with PVP 24000 (i.e. M₁); while for PSf/DMAc/PVP membranes, the rejection is the highest for membrane with PVP 360000 (i.e. M₆). On the other hand, for PSf/NMP/PEG and PSf/DMAc/PEG membranes, the rejection is found to be higher for membranes with PEG 20000 (i.e. M₉ and M₁₂). These results are evidently due to the different structure (both top surface and sub layer) of the membranes formed from different combination of solvent and additives. Generally, membrane with bigger pore size combined with a looser structure results in poor separation performance. However, for almost all the membranes the oil separation is found to be above 90%.

From Fig. 5.10, it is seen that except M₄ and M₁₁, all the other membranes have met the maximum allowable discharge limit (i.e. <10 mgL⁻¹). However, considering the fact that the new European standards demand not more than 5 mgL⁻¹ of oil in the refinery wastewater [12], membranes M₁, M₆, M₇, M₈, M₉ and M₁₂ can be recommended for UF of oil [8].

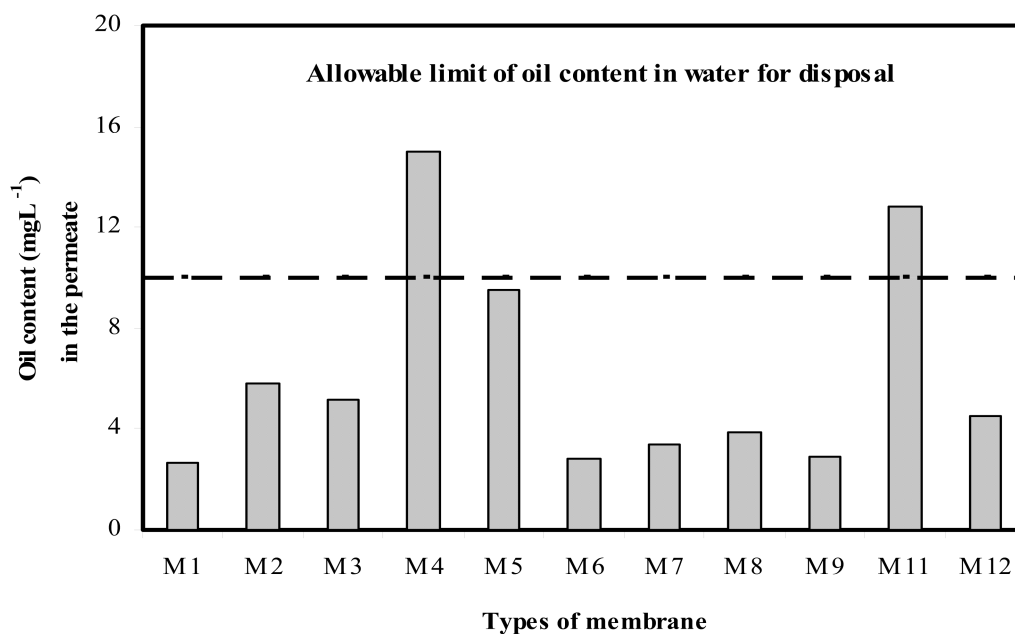


Fig. 5.10 Performance of different membranes in terms of permeate quality [8]

5.2.1.3. Identification of appropriate membranes

Based on the above analysis, comparison of the performances of all the membranes in terms of PF, R (%) and FD (%) was made, which is reported in Table 5.1. A parameter called 'selection parameter' (SP) in $\text{Lm}^{-2}\text{h}^{-1}$ is defined which relates all the criteria (i.e. PF, R and FD) for selection of membranes.

The relation is, (5.1)

So higher SP value for a membrane indicates higher flux or/and higher rejection with a lower range of fouling. The best membranes were selected from each of the four combinations i.e. PSf/NMP/PVP, PSf/DMAc/PVP, PSf/NMP/PEG and PSf/DMAc/PEG based on SP values (Table 5.1) and they are PSf/NMP/PVP-24000 (M_1), PSf/DMAc/PVP-360000 (M_6), PSf/NMP/PEG-20000 (M_9) and PSf/DMAc/PEG-20000 (M_{12}). All the subsequent experiments regarding the effect of oil concentration and pH on permeate flux and oil rejection were carried out under the optimal TMP condition (i.e. 103.4 kPa) and with the selected membranes (i.e. M_1 , M_6 , M_9 and M_{12}) which are discussed in the following sections.

5.2.1.4. Effect of initial oil concentration in feed

The effect of feed oil concentration on the permeate flux and oil rejection for the four selected membranes are shown in Fig. 5.11 and Table 5.2 respectively. The figure indicates that as oil concentration increases, permeate flux decreases; this is attributed to the increase in additional resistance to permeate flow by the rejected oil particles on the membrane surface with the increase in oil concentration in the feed. Again as the oil concentration increases, the percent oil rejection increases (Table 5.2); the maximum rejection is found to be 98.9% with M_6 membrane for 200 mgL⁻¹ feed concentration. Oil droplets retained by the membrane build up a boundary layer on the membrane surface

which accumulates the oil droplets and reduces the permeate flux [8]. Increase in oil concentration in the feed would increase the oil concentration in the boundary layer resulting in more reduction of flux and at the same time enhance in percent oil rejection.

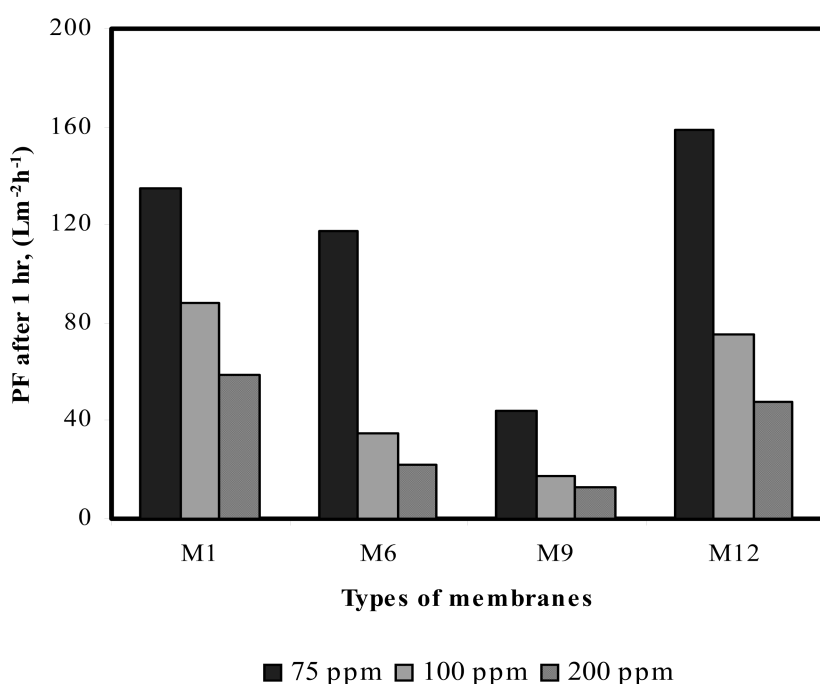


Fig. 5.11 Effect of initial feed oil concentration on permeate flux (PF) for M₁, M₆, M₉ and M₁₂ membranes; TMP: 103.4 kPa; initial oil concentration: 100 mgL⁻¹; pH: 6.12 [8].

Table 5.2 Effect of initial oil concentration in feed on oil rejection (% R); TMP:103.4 kPa; pH: 6.12.

Initial oil concentration in feed (mgL ⁻¹)	% Rejection for different membranes			
	M ₁	M ₆	M ₉	M ₁₂
75	88.8	85.4	88.6	84.4

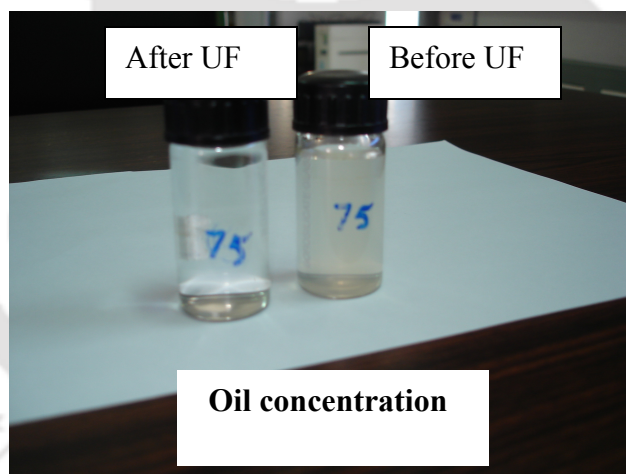
100	97.8	97.2	97.1	95.5
200	98.5	98.9	98.3	96.3

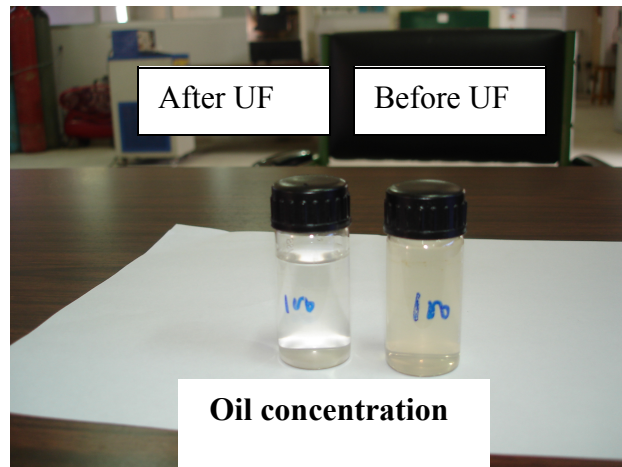
Table 5.3 reports the percent flux declination calculated after one hour of the experiment for different concentrations. It is observed that flux declination increases with feed oil concentration. The maximum declination is obtained with M₉ and M₁₂ membranes indicating that the fouling is higher in those membranes compared to the other two. The M₁₂ membrane exhibits the quickest fouling trend after the introduction of the oil emulsion into it. The lower flux declination with M₁ and M₆ membranes reveals that both the membranes are least prone to fouling by oil particles which may be considered as an evidence of good membrane performance [8].

Table 5.3 Effect of initial oil concentration in feed on flux declination (% FD); TMP:103.4 kPa; pH: 6.12.

Membranes	FD (%) after 1 h		
	75 mgL ⁻¹	100 mgL ⁻¹	200 mgL ⁻¹
M ₁	11.26	12.3	26.43
M ₆	10.59	17.04	22.07
M ₉	20.97	39.4	50.04
M ₁₂	46.9	48.1	61.14

Fig. 5.12 shows the photographs of oily water sample having three different oil concentrations i.e. 75, 100 and 200 mgL⁻¹ before and after batch UF using M₁ membrane.





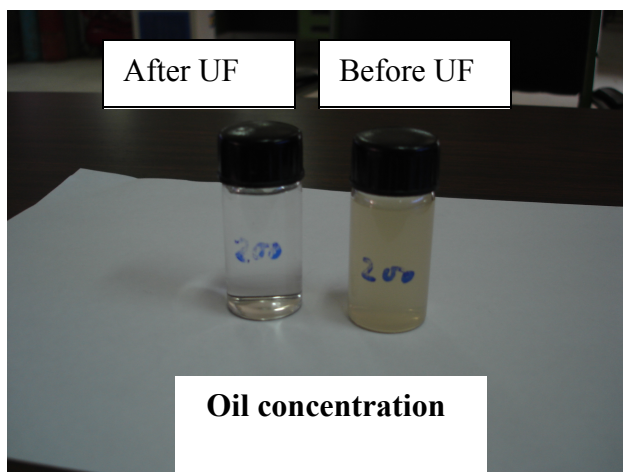


Fig. 5.12 Photographs of feed sample of different oil concentration before and after UF

5.2.1.5. Effect of pH

Figure 5.13 shows the time dependence of permeate flux for all the four selected membranes with varying pH of feed. i.e. 5.0, 6.12 and 8.0. The effect of pH on permeate flux is found to be complex as the trend of flux variation is different with different membranes. The emulsion stability is assumed to be not significantly affected by the decrease of the pH of the feed from its original value of 6.12 to 5 or increase of the pH to 8. From the figure, it is seen that the steady permeate flux (~flux after 2 hr) is highly

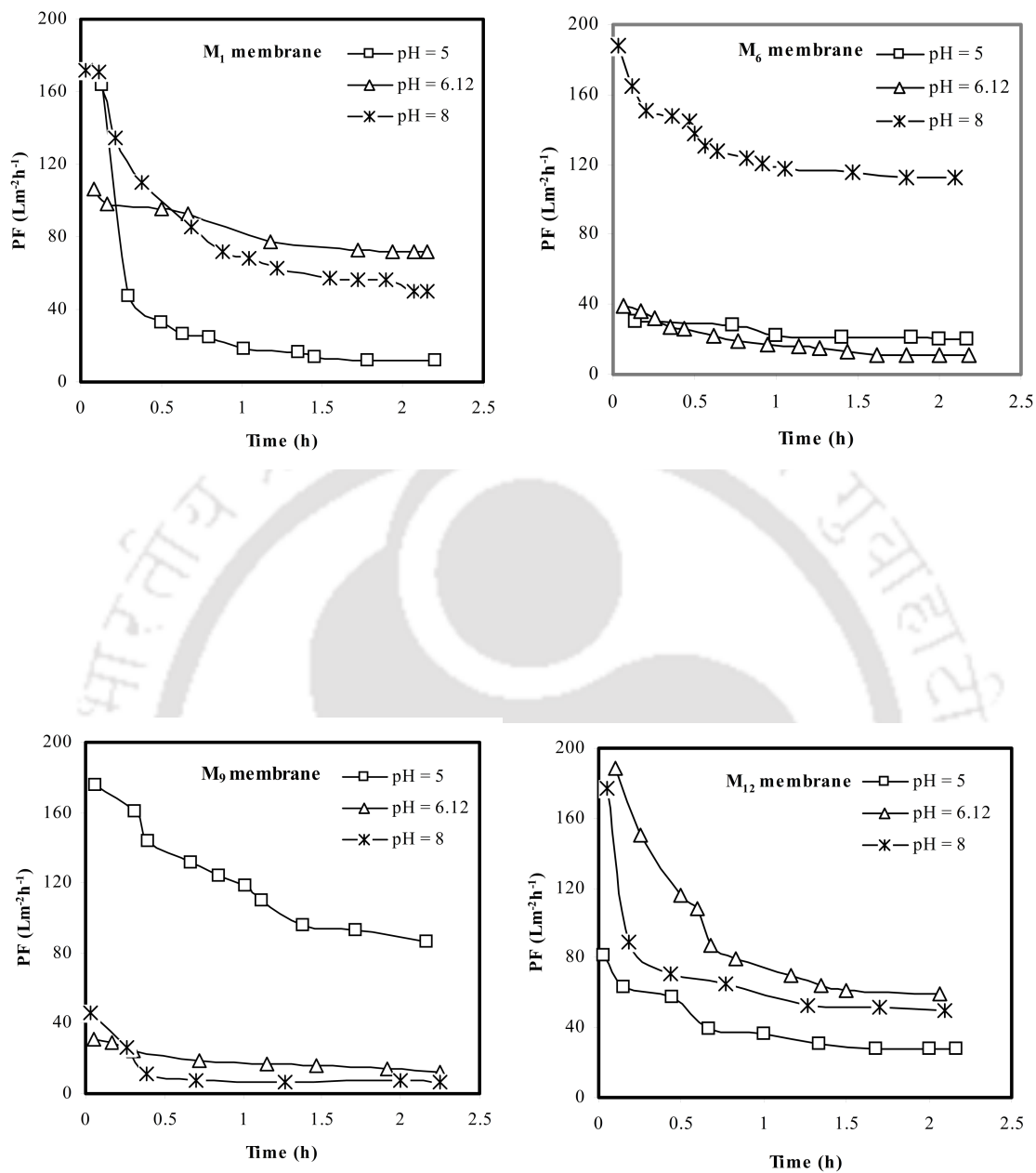


Fig. 5.13 Time dependence of permeate flux (PF) for different pH of feed [8]

dependent on the pH of the feed solution. For example, with M₁ and M₁₂ membranes the flux is higher at the original pH (i.e. 6.12) than the other two pH values. For M₆ membrane, the flux is much higher at pH 8 compared to the other two pH values, while M₉ membrane exhibits maximum flux with feed of pH 5. The permeate flux is highly dependent on the amount of oil particles adsorbed onto the membrane surface and into the pores of the membrane and the extent of adsorption depends on the type of interactions taking place between the emulsion droplets and the membrane material such as hydrophobic/hydrophilic interactions, hydrogen bonding, van der Waals interaction and electrostatic effects. Here with the variation of pH, the natural surfactants present in the crude oil possibly play an important role. It is reported that surfactants may either decrease or enhance permeate flux because of their adsorptive interactions with the membrane surface due to electrostatic forces or hydrophobic effects [13]. Because of the different composition of the membranes, the interaction between the membrane surface and the oil particles with surrounding surfactant film also varies with variation of pH; this probably has resulted in different trend of flux variation with different membranes for different values of pH. Again with all the membranes, the extent of fouling (obtained from % FD values) is mostly found to be higher with the pH values other than the normal pH i.e. 6.12 (Fig. 5.13); this could be due to the fact that the emulsion droplets deform slightly at the change of its original pH which may allow some amount of oil to pass through the membrane pores resulting in adsorption of oil on the pore wall [8]. This is also supported by the fact that lower rejection of oil has resulted at the pH values of 5 and 8 (Table 5.4) irrespective of all the four membranes. Based on this study, the performance

of the membranes may be compared at their respective optimal pH values as shown in Table 5.5. It is seen that the SP values for M₆ and M₉ membranes are improved significantly at their optimal pH i.e. pH 8 and pH 5 respectively, compared to those when the feed is at the original pH value (Table 5.1). It may also be noted that the M₁ membrane performs the best and has the highest SP (Table 5.5).

Table 5.4 Effect of pH on oil rejection (% R)

Membrane	R (%)		
	pH 5	pH 6.12	pH 8
M ₁	97.43	97.8	96.65
M ₆	93.9	97.2	93.0
M ₉	94.64	97.1	93.0
M ₁₂	94.9	95.5	93.25

Table 5.5 Comparison of performance of M₁, M₆, M₉ and M₁₂ membranes after 2 h under optimal pH condition; TMP: 103.4 kPa [8].

Membrane	Optimal pH	PF (Lm ⁻² h ⁻¹)	R (%)	FD (%)	SP
M ₁	6.12	79.8	97.8	24.1	323.8
M ₆	8	113	93.0	40	262.7
M ₉	5	85	94.6	51	157.7

M ₁₂	6.12	57.3	95.5	63.3	86.4
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5.2.1.6. An overview of the performance of the selected membranes

From the investigations described in the preceding sections, the performance of all the four membranes can be analyzed. The four membranes have significantly different PWF values (Table 3.4) and the final PF values after 2 h of ultrafiltration (Table 5.1) are seen to be much lower than the clean membrane fluxes. This indicates that the primary resistance to permeate flow is provided by the fouling layer formed on the membrane along with the membrane itself. The M₉ membrane has the highest original PWF (Table 3.4), due to its high permeability. But it demonstrates the quickest fouling after the oil emulsion was introduced resulting in a low flux at the optimal pressure condition. This fact can be more clearly understood from Fig. 5.14. The figure compares the fouling trends of M₁, M₆, M₉ and M₁₂ membranes based on their respective PWF data at

a

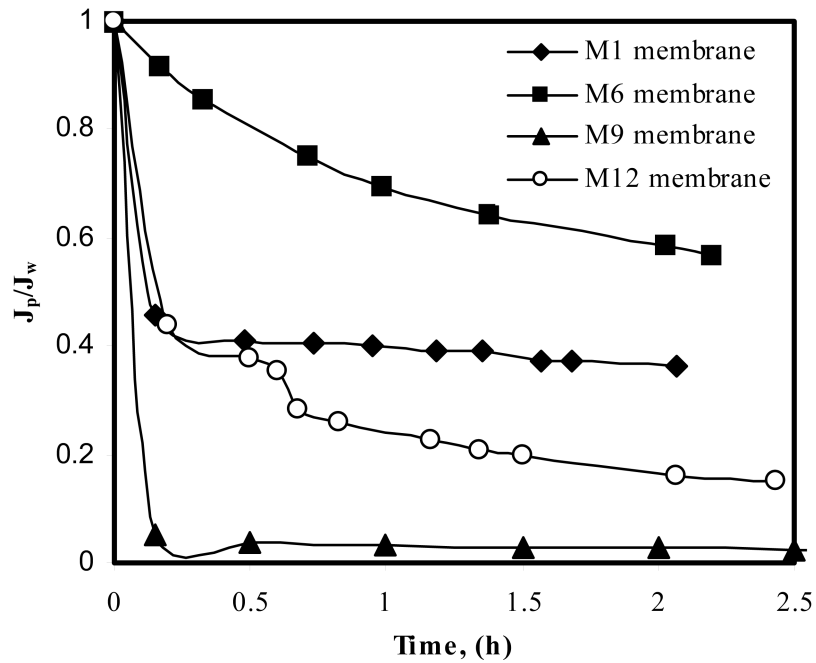


Fig. 5.14 J_p/J_w vs time plot for M₁, M₆, M₉ and M₁₂ membranes at 103.4 kPa; TMP: 103.4 kPa; feed pH: 6.12 [8].

TMP of 103.4 kPa. The figure shows that M₉ membrane has experienced the quickest fouling trend just after introduction of the o/w emulsion though the FD value calculated based on the initial flux of o/w emulsion shows the highest value (63.3%) for the M₁₂ membrane (Table 5.1). Again the lowest relative flux declination from PWF, which is observed with M₆ membrane, is attributable to less fouling. Considering the pH effect on

membrane performance at the optimal pressure value (Fig. 5.13 and Table 5.4), M₁ and M₁₂ membranes give the best performance with the feed at normal pH (i.e. 6.12) in terms of flux and rejection. M₆ and M₉ membranes though has performed well in terms of producing higher flux with feed of pH 8 and pH 5 respectively, but they give higher oil rejection only with feed of normal pH. The difference in performance of these membranes can be assigned to many factors like, the variation of membrane pore size distributions, the difference in the interaction between the membrane material and the feed and formation of any temporary or permanent fouling layer. Again considering the aspect of membrane cleaning, the washing was found to be perfect in restoring the PWF within of the original value for all the four membranes. This implies that the fouling was almost reversible in nature. But certain and definite decrease of the flux from its original value may be attributed to the existence of little amount of irreversible fouling due to pore blocking [8].

5.2.1.7. Summary of the dead end experiment [8]

The findings of this study are summarized as follows:

- With increase in pressure across the membrane, the flux increases and the relation between the flux and pressure is not exactly linear indicating the existence of an additional resistance besides the membrane resistance. For a constant pressure, the permeate flux is found to be more with more porous membranes though the extent of fouling for different membranes can also be a key factor for altering the final flux values. The flux declination is found to be

more while the oil rejection is in decreasing trend with increase in pressure. The TMP at which the flux and rejection are optimal is found to be 103.4 kPa for all the membranes.

- Porosity, pore size distribution and morphology of the membrane sub layer seem to play a major role in determining the permeate flux as well as flux declination. However, possible increase of hydrophilicity with high molecular weight PVP and PEG may also be another deciding factor.
- M₁, M₆, M₉ and M₁₂ membranes are found to be the most suitable membranes in terms of achieving reasonable flux and separation of oil in the optimal pressure condition.
- Feed characteristics such as concentration and pH affect the flux and rejection significantly. With increase in concentration, flux decreases and rejection increases due to formation of oil layer on membrane surface leading to increase in total resistance. The pH effects on the flux and rejection fluctuate with membrane composition. Higher flux with higher rejection are anticipated with M₁ and M₁₂ membranes at normal pH condition (i.e. 6.12) while M₆ and M₉ membranes are found to produce higher flux in slightly alkaline (pH 8) and slightly acidic (pH 5) condition respectively. However, increasing acidity or alkalinity of the feed solution has caused lower rejection for all the four selected membranes.
- The membrane fouling is found to be almost reversible in nature though the existence of little amount of irreversible fouling due to pore blocking can not be ignored.

5.2.2. Analysis of fouling mechanism

A detailed theoretical study was carried out based on the batch ultrafiltration results for M₁, M₆, M₉ and M₁₂ membranes. Two approaches were made to analyze the flux decline mechanism. Firstly, the permeate fluxes are fitted to the conventional RIS model. The contributions of different resistances to the permeate fluxes for each membrane are evaluated to ascertain the controlling resistance to permeate flow for different membranes. Secondly, the initial flux declination is analyzed with the four constant pressure filtration models based on the fact that flux declines due to membrane blocking or fouling. The consequences of various membrane compositions due to addition of different molecular weight additives have been discussed for both the approaches.

5.2.2.1. Theory

Resistance-in-series (RIS) model

Membrane fouling is a dynamic process starting with pore blocking followed by formation and growth of a cake layer on the membrane surface [14]. As UF of o/w emulsion continues, accumulation and deposition of oil droplets on the membrane surface begin because of sieving mechanism and an oil layer is formed. This layer resistance becomes dominant after the initial stage. So, the total resistance, during UF of oily emulsions is considered to be a combination of membrane intrinsic resistance, pore blocking resistance and resistance due to the deposited solute and oil layer on membrane surface which is also known as concentration polarization resistance. The RIS model

describes the relation between transport of solvent through the membrane (permeate flux) due to TMP based on Darcy's law as shown by Eq. (5.2):

(5.2)

where μ is the permeate viscosity, R_t is the total resistance, R_m is the membrane intrinsic (hydraulic) resistance, R_p is the resistance due to pore blocking and R_c is the resistance due to concentration polarization over the membrane surface.

Filtration model

Hermans and Bredee [15] proposed four different kinds of blocking models to describe the initial flux decline: complete blocking, intermediate blocking, standard blocking, and cake filtration. Hermia [16] derived a single equation (known as characteristic equation) to explain these models mathematically as

(5.3)

where, V is the filtrate volume; t is the filtration time; k_1 , k_2 , k_3 are the coefficients characterizing the different mechanisms of flux decline also known as resistance coefficient and blocking index respectively.

The membrane blocking phenomena can be described by these parameters, for example, $n = 2$ is for complete blocking, $n = 1.5$ is for standard blocking, $n = 1$ is for intermediate blocking, and $n = 0$ is for cake filtration. As the UF continues, the blocking models might change from one to another. For any membrane, the blocking models generally change to the cake filtration model after a certain period of time [17].

The complete blocking model (CBM) assumes that each particle reaching the membrane surface participates in the blocking phenomenon by pore sealing with no particle superimposition. The blocked surface area is proportional to the filtrate volume. The predicted volumetric flow rate of permeate ($\text{m}^3 \text{s}^{-1}$) with respect to time for this case is given by [18]:

(5.4)

where Q_0 = initial volumetric flow rate ($\text{m}^3 \text{s}^{-1}$); k is a constant (s^{-1}) and

(5.5)

where θ is the membrane surface blocked per unit of total permeate volume through the membrane (m^{-1}) and J_0 is the initial permeate flux ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$).

Thus the characteristic equation for the complete blocking phenomenon becomes

(5.6)

The standard blocking model (SBM) assumes that particles smaller than the membrane pore size deposit on to the pore walls reducing the pore size; thus the pore volume decreases proportionally to filtrate volume. In this case, the volume flow rate with respect to time for this case is predicted by:

(5.7)

where k is a constant (s^{-1}) and

(5.8)

where Δr is the decrease in the pore size due to adsorption on the pore walls per unit of total permeate volume (m^{-1}). The characteristic equation for this mechanism is:

(5.9)

In the intermediate blocking model (IBM), it is assumed that at any time a solid particle reaching an open pore seals it. It is less restrictive in such a way that not every particle

necessarily blocks the pores and here, superimposition of particle is allowed. Here, the volumetric flow rate versus time follows:

$$(5.10)$$

where, k is a constant (s^{-1}) and

$$(5.11)$$

where α is the membrane surface blocked per unit of total permeate volume through the membrane (m^{-1}).

The characteristic equation is given by:

$$(5.12)$$

The cake filtration model (CFM) is applicable when the particles are bigger than the pores; in such case, particles can not enter the pores and deposit onto the membrane surface and a filter cake is formed. It is also applicable at the latter period of the filtration experiment when most of the pores are already occupied and the newly arriving particles start depositing on the other particles arrived at first and a cake layer starts forming over the membrane surface. This model assumes that the cake thickness increases proportionally to filtrate volume. The time variation of the volumetric flow rate of

the permeate for this case is given by:

$$(5.13)$$

where, k_c is constant of cake filtration law (s^{-1}) which is given by

$$(5.14)$$

where, α is the ratio of cake resistance to the clean membrane resistance, A is the area of the cake per unit volume of permeate (m^{-1}). The characteristic equation of this blocking mechanism takes the following form:

$$(5.15)$$

All these models show a dependence of flux decline on the ratio of the particle size to the pore diameter. Here, the experimental data are attempted to fit the simple equations relating the filtrate flow rate () with filtration constants () corresponding to each model i.e. Eqs. (5.4), (5.7), (5.10) and (5.12) as shown in Table 5. 6.

Table 5.6 The four constant pressure filtration models in terms of [18]

Constant pressure filtration models	Expressions for
1. Complete blocking model (CBM)	(5.4)

2. Standard blocking model (SBM)	(5.7)
3. Intermediate blocking model (IBM)	(5.10)
4. Cake filtration model (CFM)	(5.13)

5.2.2.2. Determination of the individual resistances according to the RIS model

Independent determination of various resistances is essential in order to understand the nature and mechanism of membrane fouling by the oily water better. Initially, all the membranes were compacted at a pressure much higher than the pressure range in which experiments were conducted with o/w emulsion. So, it was assumed that the variation in flux declination during UF would not be due to discrepancy in membrane structure but only due to the difference in fouling behaviour of the membranes.

Membrane hydraulic resistance

After compaction, each membrane was subjected to UF at different TMP () (ranging 0-240 kPa), from which pure water flux (PWF) was calculated at different pressure using the following equation:

(5.16)

Where, J_w is pure water flux ($\text{Lm}^{-2}\text{h}^{-1}$), V is volume of water permeated (L), A is effective membrane area (m^2) and t is permeation time (h). The PWF was plotted

against the corresponding operating pressure which gave a straight line through the origin. The slope of this line gave the membrane permeability (). The membrane

hydraulic resistance () (m^{-1}) was calculated as

(5.17)

where is the viscosity of water ($\text{Pa}\cdot\text{s}$)

Pore blocking and concentration polarization resistances

The permeate flux of the UF experiments was calculated using the following equations:

(5.18)

where

Here, is the permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$), is the volume of permeate (L), is the

weight of the permeate (g) measured gravimetrically using a digital electronic balance,

is the density of permeate (gL^{-1}), is the effective membrane area (m^2) and is

the sampling time (h).

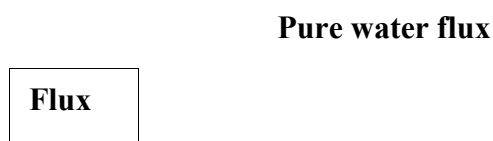
The total resistance () to permeate flow was calculated after 2 hr of UF operation using the following equation:

$$(5.19)$$

where, J is the permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$) after 2 hr.

Thus, (5.20)

The permeate flux was plotted against time for all the operating conditions and from the flux vs time curves different resistances were evaluated. It was seen that for all the membranes under different operating conditions, flux declines with time. This declination is related to different resistances. For calculation of different resistances, the flux vs time curve is divided into two sections – section I indicates a rapid drop in flux from initial PWF. Section II corresponds to a gradual decrease in flux with time approaching to nearly a steady state value (Fig. 5.15). The initial sudden drop of flux from the PWF value is attributed to the quick blocking of membrane pores [14]. The degree of pore

**Fig. 5.15**

A schematic representation of the two stages in flux decline:

(I) initial rapid drop from the flux of pure water filtration;

(II) long-term gradual flux decline.

blockage generally

depends on the shape and the relative size of the oil particles and the pores. On this basis, the pore blocking resistance () was evaluated as follows:

For a constant TMP,

(5.21)

(5.22)

where is the permeate flux ($Lm^{-2}h^{-1}$) at time ; is the time at which sharp drop

in flux transforms into a gradual decrease in flux as shown in Fig. 5.15.

The gradual and long term decrease in flux observed in section II is assumed to be due to the formation of a concentration polarization layer that acts as an additional layer of resistance. On this basis, the resistance due to concentration polarization () may be

correlated to the difference between *and sum of* and i.e.

(5.23)

5.2.2.3. Generation of characteristic curves according to the filtration models

In order to obtain the characteristic curves presented by Eq. (5.3), the experimental flux vs. time data were plotted for each membrane under the selected operating conditions. Each curve was smoothed to obtain a suitable polynomial function (). The initial flow rate () was obtained by putting into the polynomial function. Eq. (5.3) can be expressed in an alternative form as shown below [19]:

(5.24)

Thus,

(5.25)

The characteristic curves

for different membranes were generated from the

polynomial function () using Eqs (5.23) and (5.24). From the slope of these curves, the time at which transition from pore blocking mechanism to cake filtration occurs can be predicted [20, 21].

Again, the information obtained from the characteristic curves regarding the time upto which pore blocking mechanism prevails, was used to fit the experimental results into the simple equations for the different pore blocking mechanisms presented in Table 5.6. This helps in identifying the most appropriate model to explain the initial membrane fouling.

5.2.2.4. Observations and analysis

This section analyses the flux decline curve for various operating conditions. Using the concept of RIS model, the variations of different resistances with TMP and initial oil concentration in feed during UF operation are estimated for all the membranes. Also, the permeate data are used to test the four constant-pressure filtration models in order to find out the fouling mechanism.

(I) Resistance- in- series (RIS) model

The individual resistances were determined using the theory of RIS model in order to determine their contributions to the filtration of oily water. Also the effects of TMP and initial oil concentration on these resistances are discussed in this section.

Membrane hydraulic resistance ()

The of M^1 , M^6 , M^9 and M^{12} membranes are found to be 1.86 (m₋₁), 7.32 (m₋₁), 0.24 (m₋₁) and 1.09 (m₋₁) respectively (Table 5.7). As is an intrinsic property of the membrane, it is invariant with operating conditions i.e. TMP and oil concentration.

Calculation of , and

The contributions of different resistances (i.e. , and) for all the membranes under different conditions are calculated using Eqs. (5.18), (5.21) and (5.22) and their values calculated at TMP 103.4 kPa are reported in Table 5.7. Fig. 5.16 shows a typical versus time curves obtained from the flux decline data for all the membranes at a TMP of 103.4 kPa and with initial feed concentration of 100 mgL⁻¹. For all the membranes, the total resistance () is seen to increase with time within a 2 hr operation. This may be attributed to the increase in thickness of the accumulated oil layer (concentration polarization) with time above the membrane surface within the selected period of time.

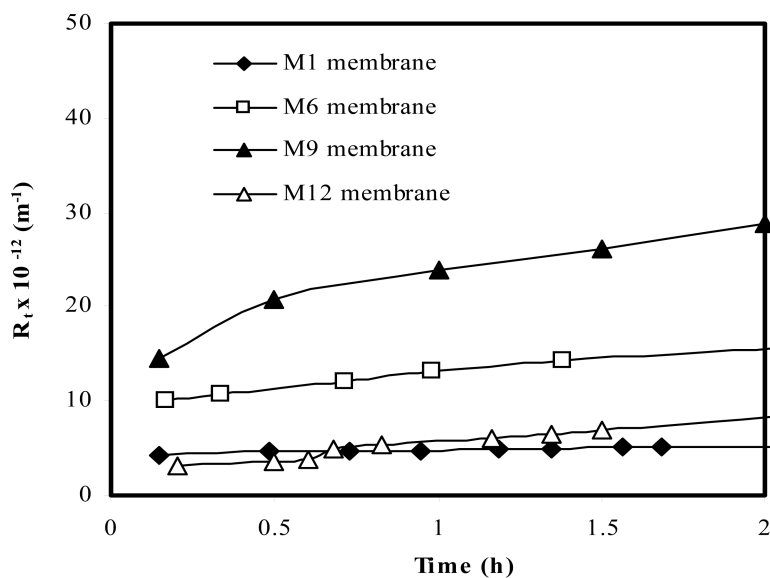


Fig. 5.16 Variation of total resistance () with time for M¹, M⁶, M⁹ and M₁₂ membranes; TMP: 103.4 kPa; initial oil concentration: 100 mgL⁻¹.

Effect of transmembrane pressure (TMP)

The main driving force of the UF process is the transmembrane pressure (TMP) which is

a difference in pressures at both sides of the membrane. The variation of R_t with TMP can be seen from Fig. 5.17 for all the membranes. The increasing trend of R_t with TMP for all the membranes may be explained by the fact that increase in pressure enhances the

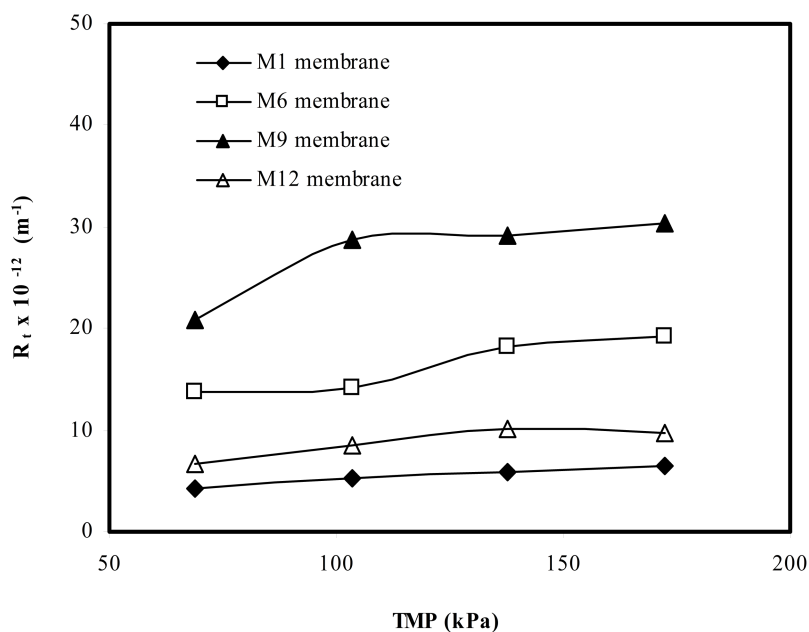


Fig. 5.17 Variation of total resistance () with TMP for M¹, M⁶, M⁹ and M₁₂ membranes; initial oil concentration: 100 mgL⁻¹; duration of experiment: 2h.

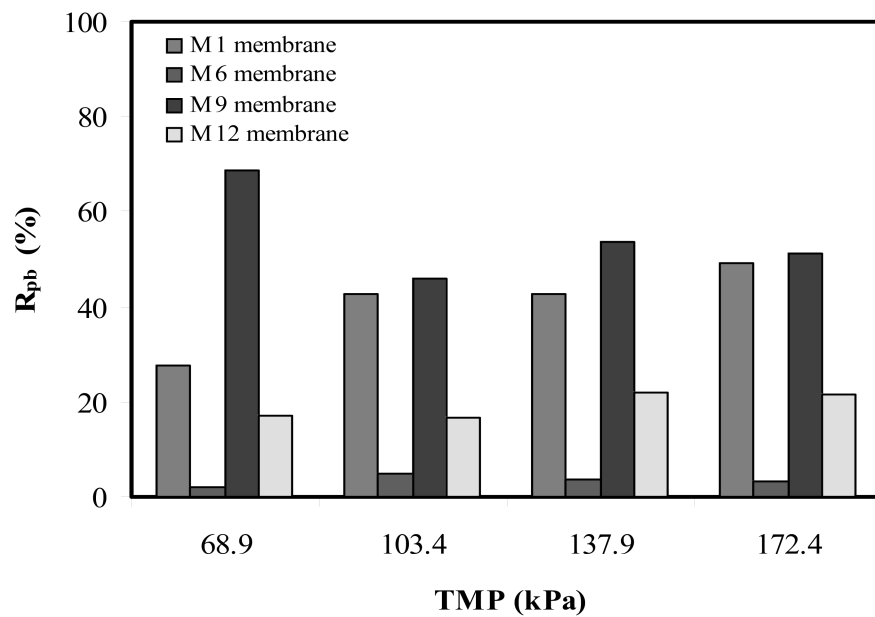
permeate flux and also forces more solute to the membrane surface causing membrane pore blocking as well as formation of oil layer on membrane surface at a faster rate. This also supports the fact that flux declination is higher at a higher TMP (Figs. 5.5 and 5.6) for all the membranes. Also from the figure, it is noted that the M₉ membrane in spite of having the lowest , exhibits the maximum while the for M¹ and M¹² are in the lower range. This fact can also be understood from Table 5.7 that reports the values of different resistances calculated for all the membranes at 103.4 kPa pressure. The higher permeability of M₉ membrane may initially allow penetration of more number of the small oil droplets into the pores which leads to sufficient constriction or plugging of pores for which, the resistance due to pore blocking and subsequently due to concentration polarization possibly becomes dominant over the hydraulic resistance.

Table 5.7 Different resistance values for M₁, M₆, M₉ and M₁₂ membranes at 103.4 kPa.

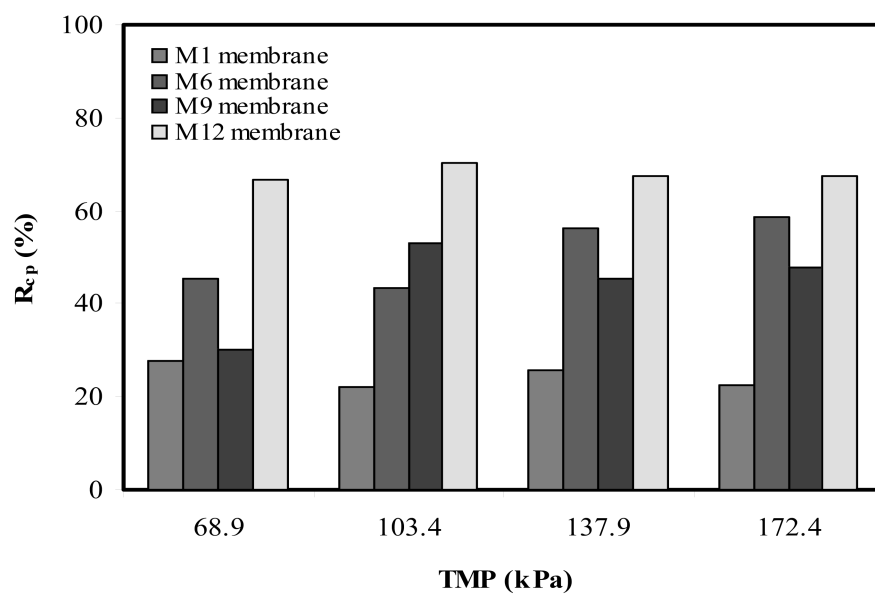
Membranes	(m ⁻¹)	(m ⁻¹)	(m ⁻¹)	(m ⁻¹)
M ₁	1.86	2.22	1.15	5.23
M ₆	7.32	0.66	6.16	14.14

M ₉	0.24	13.26	15.3	28.8
M ₁₂	1.09	1.39	5.93	8.41

On the other hand, M₆ membrane displays the highest R_{ms} , and so has a very low contribution from R_{ms} . Analyzing Table 5.7, it is understood that apart from the contribution of membrane hydraulic resistance, the contribution of R_{ms} is maximum for M₁ membrane while for the M₆ and M₁₂ membranes, R_{ms} plays the dominant role. In case of M₉ membrane, contributions of both R_{ms} and R_{mh} are higher and are almost of same magnitude. The effects of increase in TMP on R_{ms} and R_{mh} for different membranes are revealed in Figs. 5.18 (a) and 5.18 (b) which are the plots of R_{ms} and R_{mh} (expressed as % of R_{ms}) against TMP respectively. It may be noted from the figures that the trend of variations of both R_{ms} and R_{mh} are different for different membranes. It may possibly be due to the variation of morphology (both top surface and sub layer) of the membranes as



(a)



(b)

Fig. 5.18 Variation of (a) θ (%) and (b) ΔR (%) with TMP for M₁, M₆, M₉ and M₁₂ membranes; initial oil concentration: 100 mgL⁻¹; duration of experiment: 2h.

well as the membrane material. The variation of the pore size distribution along with porosity for the four types of membrane may result in different degree of fouling. The role of the degree of hydrophilicity of different membranes (due to addition of PVP or PEG of different molecular weight as additives during membrane preparation) can also play a key role in this regard; as it is a well known fact that hydrophilic membranes are least prone to fouling due to adsorption. These figures also confirm the fact that within the given TMP range, M₉ membrane exhibits the highest total resistance with maximum contribution from ΔR and θ . On the basis of the total resistance offered to the permeate flow, M₁ membrane may be considered the best membrane among the four membranes.

Effect of initial oil concentration

Fig. 5.19 shows the variation of the total resistance (ΔR) with initial oil concentration in feed. As expected, ΔR increases with increase in oil concentration. This is attributed to the formation of thicker oil layer on the membrane surface with feed of higher oil concentration. Oil droplets retained by the membrane build up a boundary layer on the membrane surface where the oil droplets accumulate and this increases the resistance. Increase in oil concentration in the feed would increase the oil concentration in the

boundary layer which adds more resistance to permeate flow resulting in more flux declination. M₉ membrane shows maximum $\text{at } 100 \text{ and } 200 \text{ mgL}^{-1}$ of feed oil concentration which is followed by M₆, M₁₂ and M₁ membranes. But for 75 mgL^{-1} concentration, M₉ and M₆ display almost similar while for M₁ and M₁₂ membranes are close to each other. Fig. 5.20 (a) and 5.20 (b) illustrate the individual contributions of and towards $\text{in } (\%)$ as a function of oil concentrations for all the membranes. It may be noted from these figures that the increase in total resistance

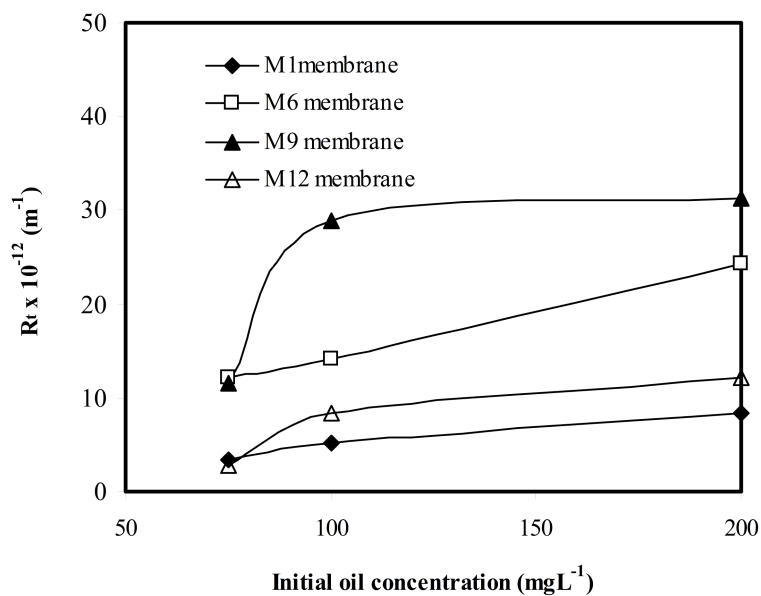


Fig. 5.19 Variation of total resistance () with initial feed concentration for M₁, M₆, M₉ and M₁₂ membranes; TMP: 103.4 kPa; duration of experiment: 2h.

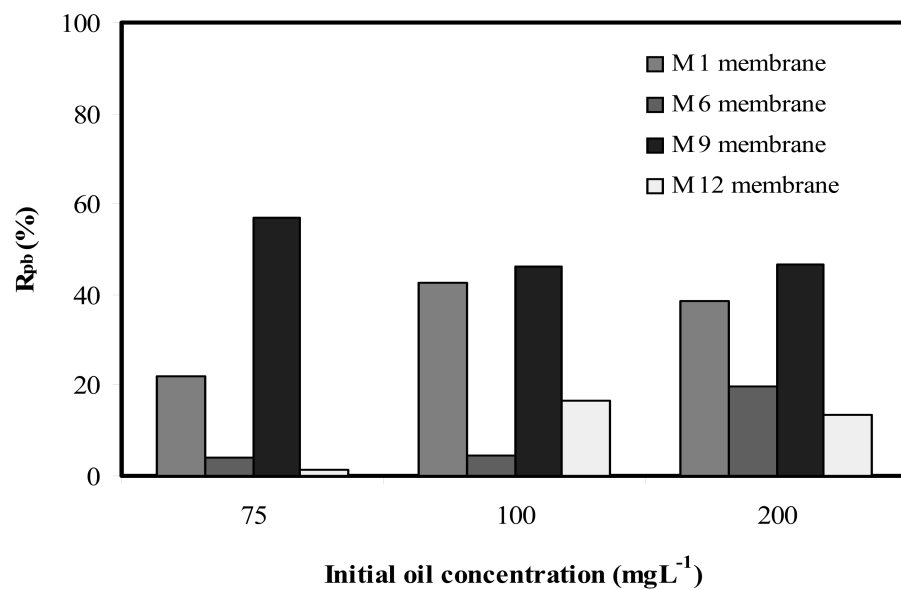
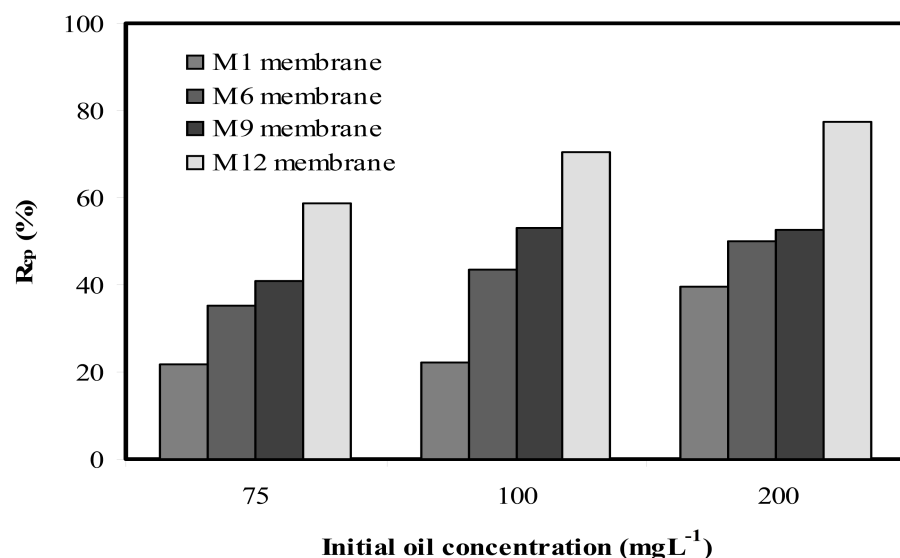


Fig. 5.20 (a) Variation of R_{ph} (%) with initial oil concentration for M¹, M₆, M₉ and M₁₂ membranes; TMP: 103.4 kPa; duration of experiment: 2h.



(b)

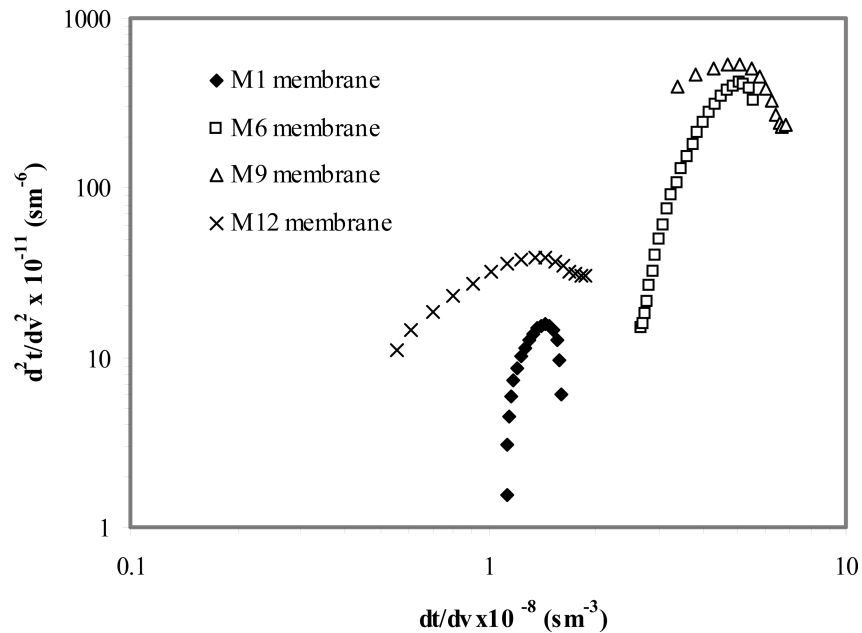
Fig. 5.20 (b) Variation of R_{sp} (%) with initial oil concentration for M₁, M₆, M₉ and M₁₂ membranes; TMP: 103.4 kPa; duration of experiment: 2h.

with oil concentration is mainly caused by the increasing trend of R_{sp} and at higher oil concentration, R_{sp} has become the dominant resistance. Thus at higher oil concentration, fouling occurs mainly by concentration polarization.

(II) Constant-pressure filtration models

The characteristic curves prepared by using Eq. (5.23) and (5.24) for all the four membranes i.e. M₁, M₆, M₉ and M₁₂ at TMP of 103.4 kPa and initial oil concentration of 100 mgL⁻¹ are shown in Fig. 5.21. The transition between pore blocking and cake filtration can be examined quantitatively from this figure. It is seen that each plot of

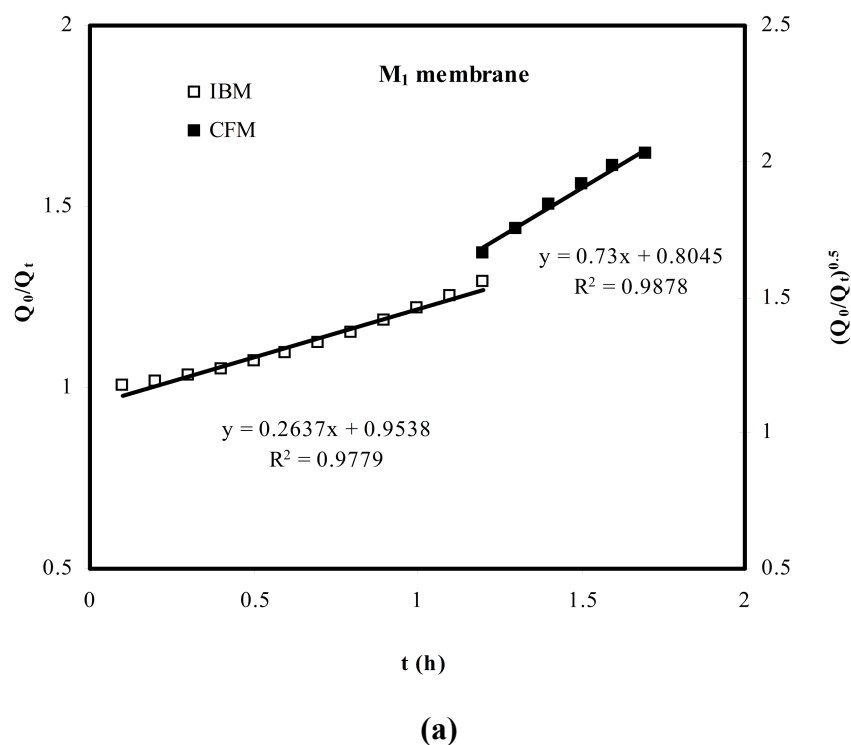
versus $\frac{d^2t}{dv^2} \times 10^{-11} \text{ (sm}^{-6}\text{)}$ attains a distinct maximum at a certain filtration time for each membrane which is followed by a drop in values of $\frac{d^2t}{dv^2} \times 10^{-11} \text{ (sm}^{-6}\text{)}$ resulting in a negative

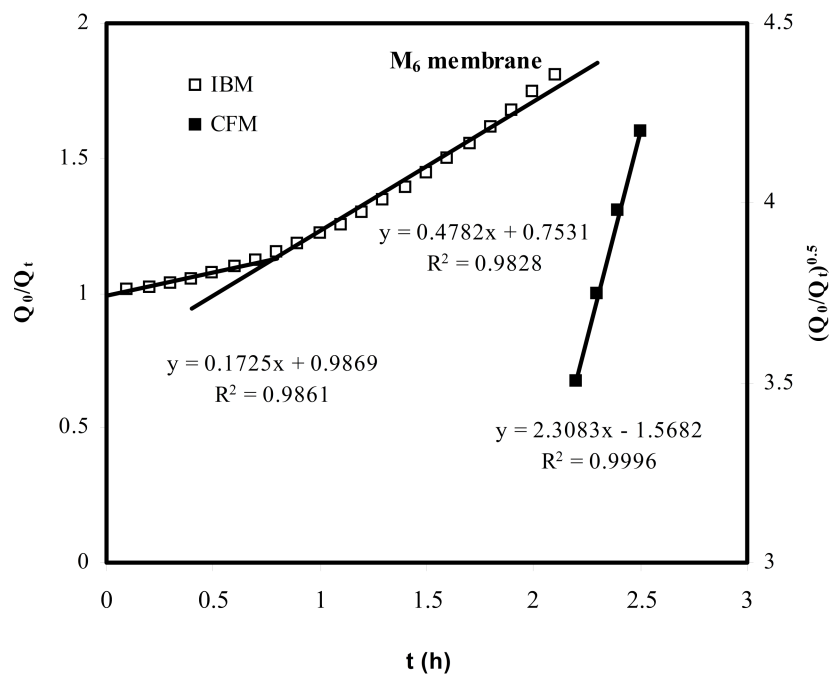


maximum. According to them, the decrease in $\frac{dJ}{dt}$ signifies the transition from pore blocking mechanism to cake filtration mechanism since a large reduction in the rate of flux decline ($\frac{dJ}{dt}$) occurs during this transition period. On the other hand, at lower values of $\frac{dJ}{dt}$ which correspond to the initial period of filtration, the results display a positive slope indicating the applicability of the Hermia's classical models. It is found that the slope value of each curve is not exactly equal to any of the values given by the Hermia's classical models (i.e. 0, 1 or 1.5). This may be due to the existence of more or less wide pore size distribution of the prepared membranes as well as the size distribution of the oil droplets in the feed. The characteristic nature of oil droplets such as deformation of its shape on application of pressure and interaction with the membrane surface also play important roles for not fitting into any of the classical models completely which were originally developed for solid particles. However, the most vital information that can be obtained from these plots (i.e. Fig. 5.21) is the time beyond which the fouling mechanism approaches a behaviour similar to cake filtration. This is due to formation of a gel-like layer on the membrane surface owing to the accumulation of oil particles on the membrane surface. Based on this information, efforts have been made to fit the experimental results during the initial period i.e. before transition to cake filtration (Fig. 5.21) into the first three equations of Table 5.6 corresponding to respective pore blocking mechanisms. It is found that the results give the best fit for the IBM, which is shown in Figs. 5.22 (a) – (d) for the four membranes; so IBM can be a good approximation for describing membrane fouling during the initial period of

filtration. This finding also supports the fact that as the average size of the oil droplets (340) is greater than that of the membrane average pore size (), so there is a least possibility that fouling occurs by pore constriction mechanism i.e. SBM. The results in the later period are seen to follow the CFM quite reasonably satisfying the equation corresponding to CFM (Table 5.6). From the linearity of the filtration data with the model equations, it can be said that fouling occurs first by intermediate pore blocking phenomenon and then by a trend close to cake formation mechanism. As in the present study, the TMP is not so high and the duration of operation is not too long, so the cake formation step may be approximated as the step of formation of gel layer or concentration polarization. Observation of the plots of Fig. 5.22 also reveals that the time up to which fouling is mainly dominated by pore blocking mechanism varies with membrane compositions i.e. membrane properties (Table 3.4). M₆ and M₉ membranes have comparable hydrophilicity as seen from their EWC values (Table 3.4). Again as the mean pore size (r_m) of these membranes is almost the same, the difference in time duration for pore blocking can be explained from the respective values of membrane resistance. M₆ membrane takes the longest time for pore blocking (2.2 h) while for M₉ membrane, it is the shortest (0.3 h). This indicates that M₆ membrane is less prone to fouling while M₉ membrane is inclined to quickest fouling. This may be attributed to the high and low hydraulic resistances () of the two membranes as

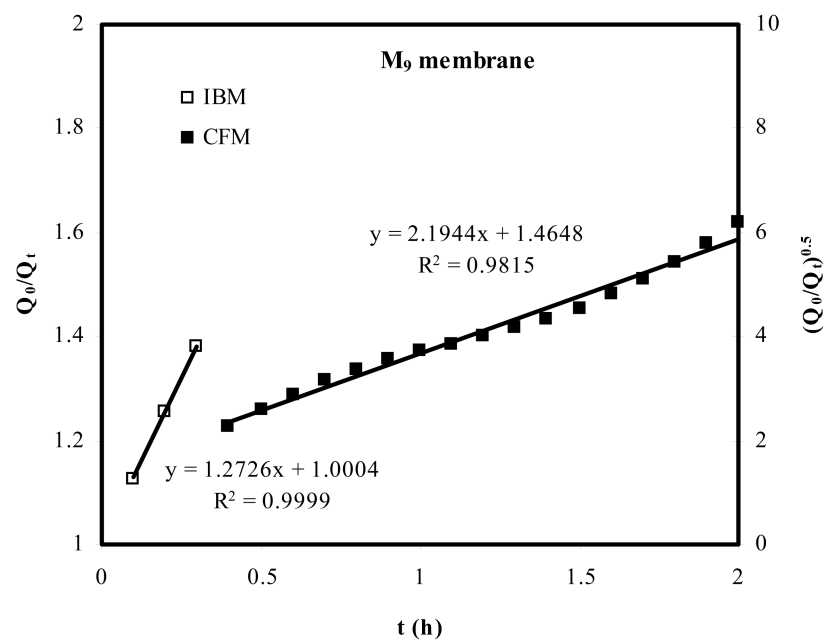
indicated in Table 5.7. M₉ membrane due its low resistance allows more permeation which leads to quick pore blocking. The change of slope within the initial period for M₆ membrane as shown in Fig. 5.22 (b) may be due to the superimposition of other blocking mechanisms with IBM. Again, for M₁ and M₁₂ membranes with similar average pore size, the difference in fouling trend may be explained in terms of hydrophilicity and . M¹² membrane has higher hydrophilicity (EWC) and lower in comparison to M¹ membrane, which allows more permeation and results in quick blocking. So, blocking of M₁₂ membrane is quicker than M₁ membrane.



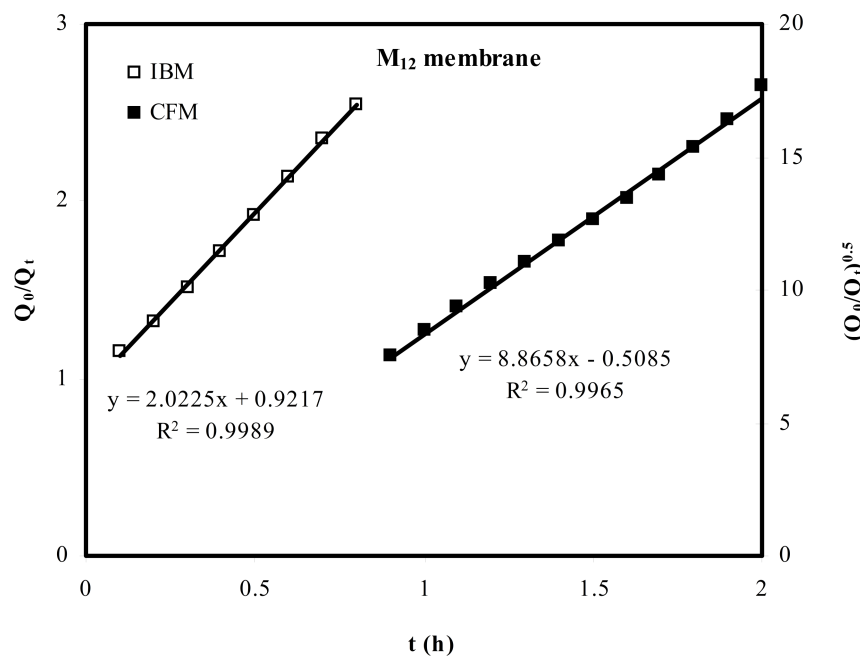


(b)

Fig. 5.22 Flux decline data for o/w emulsion plotted in accordance with IBM and CFM for (a) M_1 and (b) M_6 membranes



(c)



(d)

Fig. 5.22 Flux decline data for o/w emulsion plotted in accordance with IBM and CFM for (c) M₉ and (d) M₁₂ membranes

(III) Summary

The findings of the analysis of flux decline during UF of synthetic oil-in-water emulsions using PSf membranes based on the concepts of the RIS model and the filtration model are summarized as follows:

- The resistances R_{m1} , R_{m2} and R_{m3} quantified by the RIS model, are compared and their dependence on TMP and initial oil concentration are investigated. M₉ membrane with the lowest R_{m1} , is seen to exhibit the maximum total resistance ($28.8 \times 10^{12} \text{ m}^{-1}$) due to higher values of both R_{m2} and R_{m3} with M₁ membrane having the lowest value of R_{m1} ($5.23 \times 10^{12} \text{ m}^{-1}$) when the TMP is at 103.4 kPa and oil concentration is 100 mgL⁻¹. The contribution of R_{m1} is found to be maximum for M₁ membrane (42.5%) among the other two resistances compared to M₆, M₉ and M₁₂ membranes at TMP of 103.4 kPa; however for the M₆ and M₁₂ membranes, R_{m2} plays the dominant role in flux declination.
- The total resistance, R_{mT} increases with increase in both TMP and oil concentration in feed; but the variations of R_{m1} and R_{m2} greatly depend upon membrane properties.

- For a feed with higher oil concentration, is the dominant resistance irrespective of the membrane compositions and so, in such case concentration polarization may be regarded as the chief cause of membrane fouling.
- Application of the filtration model displays the fact that none of the models fit the data completely for the entire period for all the membranes. The IBM dominates the fouling mechanism up to a certain period for all the membranes beyond which a transition from pore blocking mechanism to cake filtration like mechanism takes place due to accumulation of oil particles on the membrane surface.
- The duration of pore blocking is found to depend upon membrane resistance; higher the resistance, longer is the period of pore blocking and the membrane is less prone to fouling.

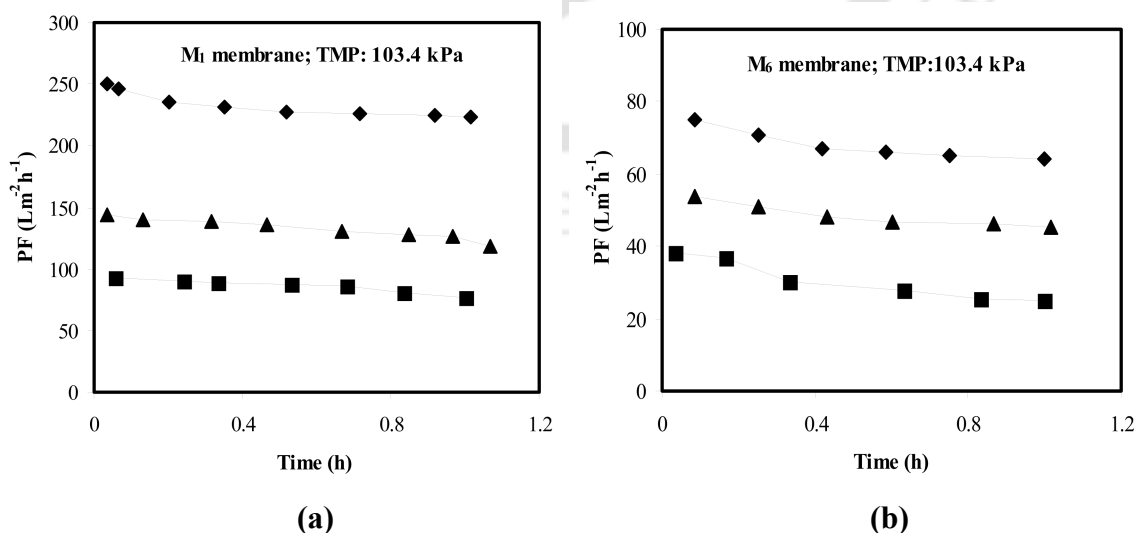
5.2.3. UF experiment in cross-flow mode

Feed properties like oil concentration and pH are some of the important factors that usually affect the membrane morphological properties and hence the performance. These effects are studied in the dead-end filtration study and have been elaborated in the previous sections. Similarly operating conditions such as transmembrane pressure (TMP) and cross flow rate (CFR) have significant effect on membrane performance. In this section, mainly the effects of different CFR on membrane performance are reported and discussed with respect to PF, R (%) and flux declination (FD) for two values of TMP. Details of the operating conditions as well as experimental set up are already discussed in

Chapter 4. The findings obtained for the four types of membranes (M_1 , M_6 , M_9 and M_{12}) under the same conditions are discussed highlighting the effect of CFR.

5.2.3.1. Effect of cross-flow rate (CFR)

Figs 5.23 and 5.24 show the variation of permeate flux with time for the four selected membranes at the two TMP values i.e. 103.4 kPa and 172.4 kPa respectively. From the figures, it is seen that the permeate flux decreases with time and approaches a steady state after a certain duration of time for all the membranes. The oil rejected by the membrane accumulates near the membrane surface and the concentration gradient causes the flux to decline. The flux declines at a higher rate in the initial period which is more obvious for higher TMP i.e. 172.4 kPa (Figs. 5.24) for all the membranes. However, M_9 and M_{12} membranes show significant flux declination even at TMP of 103.4 kPa indicating their higher fouling tendency compared to the other two (i.e. M_1 and M_6). The figures also depict the fact that the CFR has a significant impact on the flux values irrespective of the



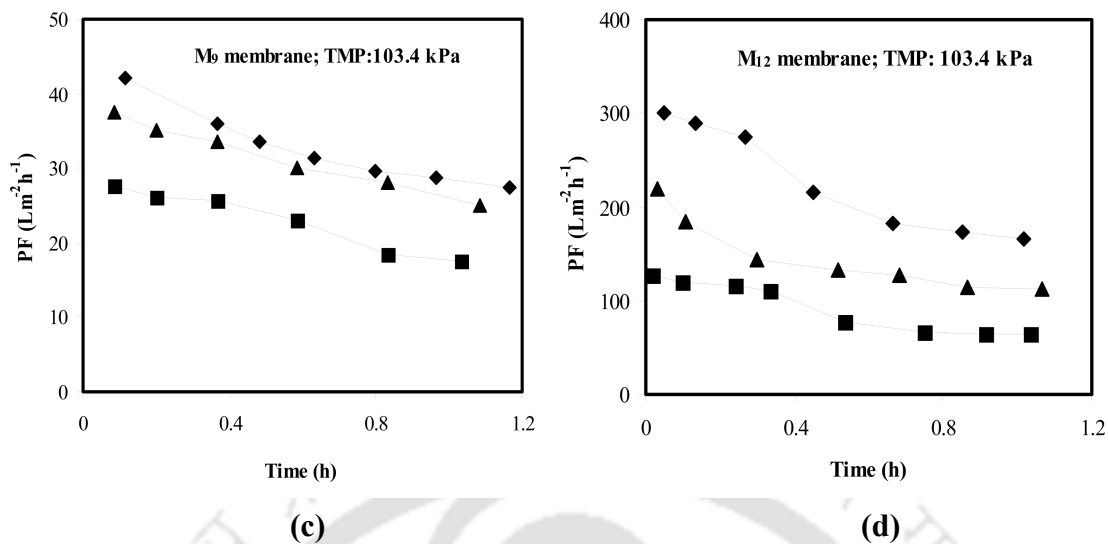
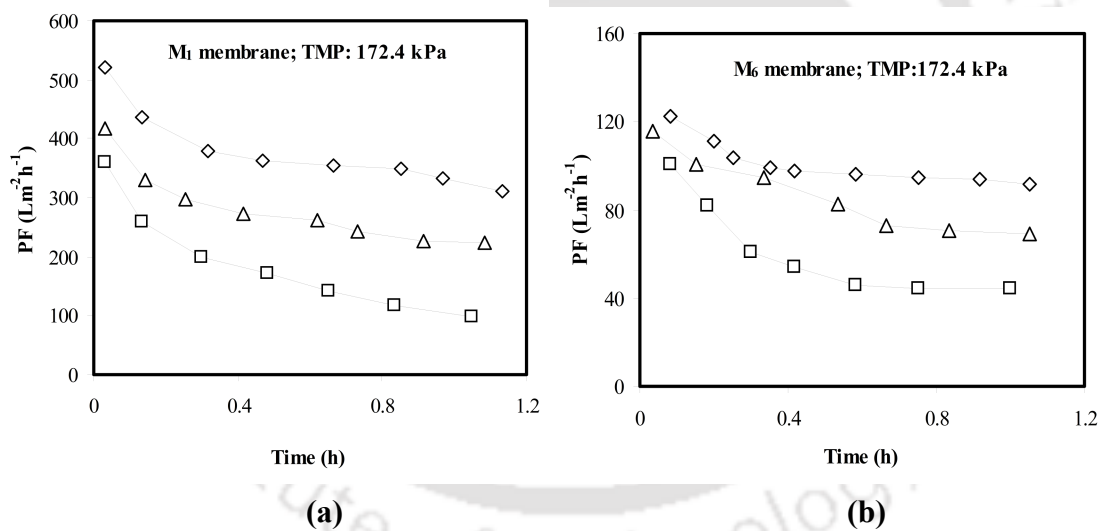


Fig. 5.23 Variation of permeate flux (PF) with time for M₁, M₆, M₉ and M₁₂ membranes at different CFR; TMP: 103.4 kPa; Oil concentration: 100 mgL⁻¹.



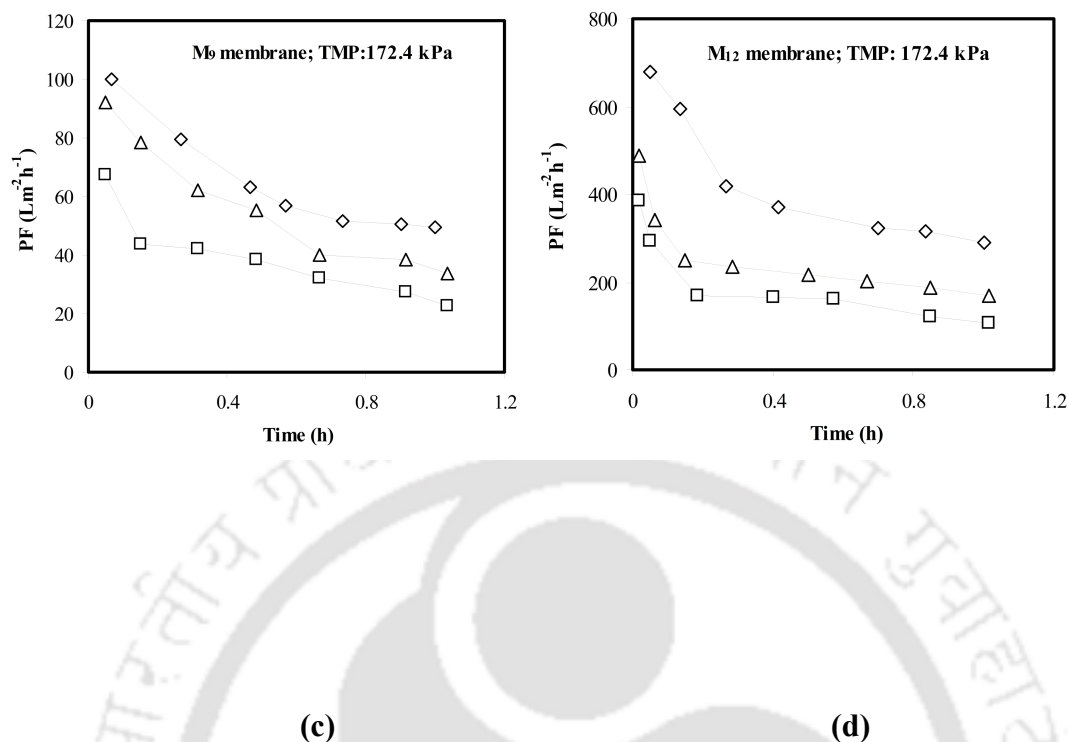


Fig. 5.24 Variation of permeate flux (PF) with time for M₁, M₆, M₉ and M₁₂ membranes at different CFR; TMP: 172.4 kPa; Oil concentration: 100 mgL⁻¹.

membrane types. For example, at TMP of 103.4 kPa, for M₁ membrane the flux increases from 77.0 to 223.0 Lm⁻²h⁻¹ when the CFR is raised from 2.4×10^{-6} to 4.0×10^{-6} m³s⁻¹; while at TMP of 172.4 kPa, the flux rises from 99.0 to 332.0 Lm⁻²h⁻¹. Similar observations are noted with all the membranes irrespective of the TMP. The accumulation of oil near the membrane surface gives rise to concentration polarization which can be mitigated at higher cross-flow velocities as turbulence increases near the membrane surface [22, 23].

The increase in flux with increase in CFR is due to the fact that at high CFR, the extent of accumulation of rejected oil on the membrane surface is decreased reducing the total

resistance. Therefore, higher flux is obtained at higher CFR for all the membranes. Table 5.8 reports the different values of PF calculated after 1 h at the two values of TMP considered in this study. It is seen that out of all the four membranes, the highest flux is obtained for M₁ membrane i.e. 332 Lm⁻² h⁻¹ for a CFR of 4.0 × 10⁻⁶ m³s⁻¹ and at a TMP of 172.4 kPa. The lowest flux is seen with M₉ membrane with a value of 17.6 Lm⁻² h⁻¹ at a CFR of 2.4 × 10⁻⁶ m³s⁻¹ and a TMP of 103.4 kPa. The effect of TMP can also be understood from Figs. 5.23 and 5.24 and Table 5.8 which reveal that higher PF is obtained at higher TMP irrespective of the cross-flow rates and the types of membranes

Table 5.8 PF values of M₁, M₆, M₉ and M₁₂ membranes at different conditions

Cross flow rates (CFR) × 10 ⁶ (m ³ s ⁻¹)	Permeate flux after 1 h (Lm ⁻² h ⁻¹)							
	103.4 kPa				172.4 kPa			
	M ₁	M ₆	M ₉	M ₁₂	M ₁	M ₆	M ₉	M ₁₂
2.4	77.0	24.8	17.6	64.0	99.0	44.0	22.8	108.0
3.1	126.1	45.3	25.0	112.2	226.0	69.4	49.6	170.0

4.0	223.0	64.0	28.7	165.0	332.0	91.0	33.5	291.0
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used. The same result was also obtained with the dead end mode of operation. Table 5.9 shows the FD values calculated after one hour of UF operation using Eq. (4.3) for the four membranes for all the three CFRs and the two TMPs. From the table, it is seen that high CFR reduces the % FD which supports the trend of increase of PF at higher value of CFR. For example, for M₁ membrane the FD value decreases from 16.6 % to 10.8 % at a TMP of 103.4 kPa and from 61.9 % to 36.2 % at 172.4 kPa when CFR is raised from 2.4 10^{-6} to 4.0 10^{-6} m³s⁻¹. These values of FD also reveal the effect of TMP on the extent of membrane fouling. The table also shows an increasing trend of % FD at higher TMP (172.4 kPa) compared to lower TMP (103.4 kPa) for all the membranes which is consistent with the batch UF study. The rejection of oil from the synthesized oily water is calculated as % R using Eq. (4.4) and is reported in Figs. 5.25 (a) and 5.25 (b).

Table 5.9 Values of FD (%) for different membranes at different operating conditions after 1 h of operation

Cross flow rate (CFR) 10^6 (m ³ s ⁻¹)	Flux declination (%)							
	103.4 kPa				172.4 kPa			
	M ₁	M ₆	M ₉	M ₁₂	M ₁	M ₆	M ₉	M ₁₂
2.4	16.6	18.4	36.2	50.0	61.9	56.2	66.1	72.1

3.1	12.5	16.1	33.1	49.0	45.7	39.9	63.6	65.1
4.0	10.8	14.6	31.7	45.1	36.2	25.6	49.0	57.2

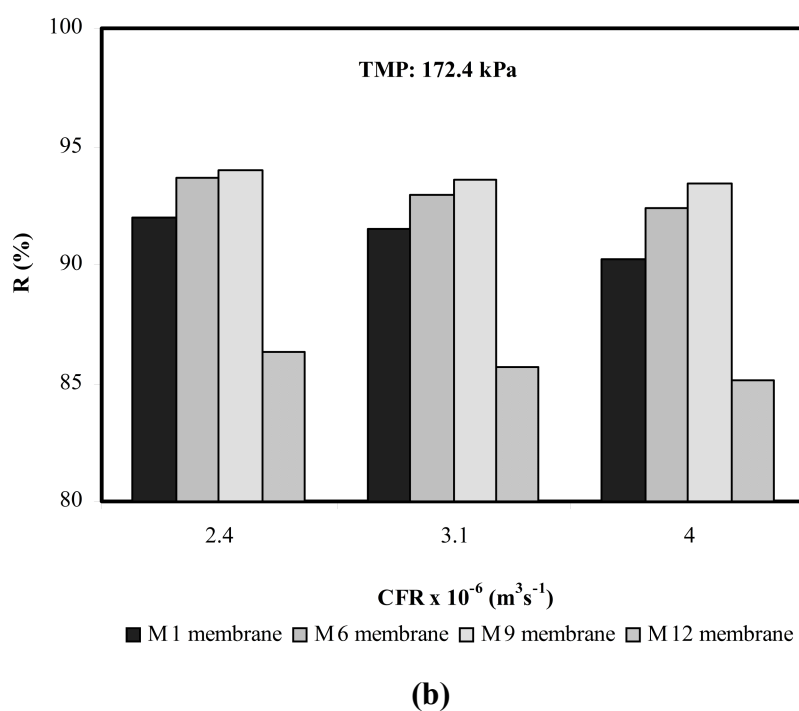
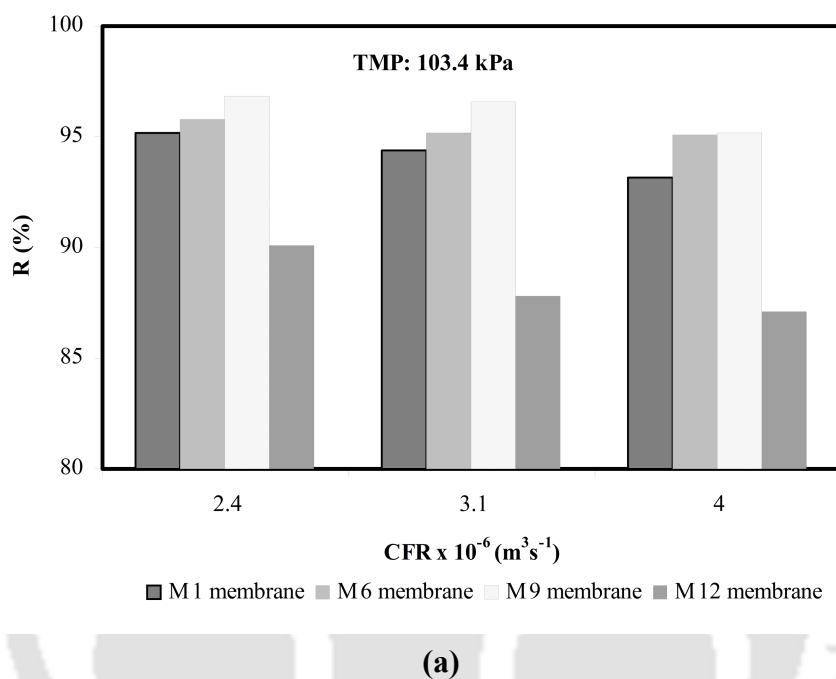


Fig. 5.25 Effect of CFR on rejection of oil (%R) at (a) 103.4 kPa and (b) 172.4 kPa

From the figures it is understood that the trends of R (%) with increase in TMP in cross-flow UF are similar to those obtained in the batch UF study; that is, R (%) decreases at higher values of TMP for all the CFR values considered. However, the increase in CFR has adverse effect on oil rejection as seen from Fig. 5.25. This is possibly due to the fact that high CFR leads to breaking of oil droplets into finer droplets which can cause penetration of some amount of oil through the pores resulting in less %R. Thus, despite getting a high PF value with high CFR, a very high CFR should not be recommended to avoid oil penetration through the membrane pores. The rejection is seen to be higher at 103.4 kPa for all the values of CFR compared to those at 172.4 kPa irrespective of the membrane types. Table 5.10 reports the % R values corresponding to all the four membranes obtained at the three CFRs and the two TMPs. It is seen that highest separation is obtained at a TMP of 103.4 kPa and a CFR of $2.4 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ for all the membranes.

Table 5.10 Values of % R for different membranes at different operating conditions after 1 h of operation

Cross flow rates (CFR) 10^6 (m^3s^{-1})	R (%)							
	103.4 kPa				172.4 kPa			
	M ₁	M ₆	M ₉	M ₁₂	M ₁	M ₆	M ₉	M ₁₂

2.4	95.2	95.8	96.8	90.1	92.0	93.7	94.0	86.3
3.1	94.4	95.2	96.6	87.8	91.5	93.0	93.6	85.7
4.0	93.2	95.1	95.2	87.1	90.2	92.4	93.4	85.1

5.2.3.2. Effect of membrane type

Analyzing Tables 5.8 and 5.9, the effect of membrane material and composition on PF and FD (%) can be understood. M₉ membrane shows the least PF while M₁ and M₁₂ membranes experience reasonably high flux for all the conditions. On the other hand, analyzing the FD (%) from Table 5.9, it is seen that M₁₂ membrane experiences the maximum FD indicating its highest tendency of fouling which is in agreement with that found in the batch study (Fig. 5.8). Considering the TMP value at 103.4 kPa and a CFR value of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$, the flux decline analysis up to 1 h of operation shows that M₁ membrane exhibits the least flux declination (i.e. 12.5%) which is followed by M₆ membrane while M₁₂ membrane is found to have the maximum FD (65.1%). Again, the % R is found to be above 90 % (i.e. oil content in the permeate is less than 10 mgL^{-1}) at both the values of TMP for all the membranes except M₁₂ membrane (Fig. 5.25, Table 5.10), the highest % R being obtained with M₉ membrane under all operating conditions.

This shows the applicability of the three membranes i.e. M₁, M₆ and M₉ for separation of oil. Table 5.11 demonstrates comparison of performances of all the four membranes in terms of SP calculated by using Eq. (5.1) at a TMP of 103.4 kPa and a CFR of

Table 5.11 Comparison of the performance of different membranes after 1 h at a TMP of 103.4 kPa and a CFR of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$

Membranes	$PF (\text{Lm}^{-2}\text{h}^{-1})$	$R (\%)$	$FD (\%)$	$SP (\text{Lm}^{-2}\text{h}^{-1})$
M ₁	126.1	94.4	12.5	952.3
M ₆	45.3	95.2	16.1	267.9
M ₉	25.0	96.6	33.1	72.9
M ₁₂	112.2	87.8	49.0	201.0

$3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$. From the values, it may be clearly seen that M₁ membrane performs the best which is followed by M₆ membrane. Thus, M₁ membrane may be recommended out of the four membranes for industrial application.

5.2.3.3. Summary of the cross-flow experiment

The findings of the cross flow ultrafiltration study may be summarized as follows:

1. At constant TMP, with increase in CFR, the permeate flux increases; this is due to the removal of the accumulated oil from the membrane surface reducing the total resistance to permeate flow. However, the percent oil

rejection (% R) shows a marginal decreasing trend because of fragmentation of the droplets at higher CFR leading to oil penetration along with the permeate.

2. At constant CFR, increase in TMP increases the permeate flux; this is due to the increase in driving force across the membrane. However, rejection of oil (% R) is found to decrease as high TMP is likely to force the small sized oil droplets to pass through the pores of the membrane.
3. Higher TMP makes the flux decline faster at all CFR by introducing greater number of oil droplets into the membrane pores causing pore plugging at a faster rate while higher CFR has just the reverse effect by reducing the effect of concentration polarization.
4. All the membranes except M₁₂ membrane are found to produce permeate of acceptable quality (i.e. oil content less than 10 mgL⁻¹).
5. M₁ membrane is found to give the highest value of SP (952.3 Lm⁻²h⁻¹) while M₉ membrane shows a minimum value of SP (72.9 Lm⁻²h⁻¹) at a TMP of 103.4 kPa and a CFR of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$. Thus, M₁ membrane may be recommended for treating oily water at normal condition.

5.2.4. Comparison between dead-end and cross-flow mode

Table 5.12 compares the performance of the four selected membranes (i. e. M₁, M₆, M₉ and M₁₂) in dead-end and cross-flow mode of UF carried out with synthetic oily water in terms of PF, FD and R at a TMP of 103.4 kPa for both the modes and a CFR of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ for the cross-flow mode. Comparing the results of both the mode of UF, it may be inferred that cross-flow mode performance is better in terms of obtaining higher PF; the differences in the performances of the two modes may be attributed to the difference in fouling mechanism. However, dead-end mode is found to give better oil separation compared to cross-flow mode; this is due to the fact that in dead-end mode, the

Table 5.12 Performance of M₁, M₆, M₉ and M₁₂ membranes after 1 h in dead-end and cross-flow mode of UF; TMP: 103.4 kPa; Feed conc.:100 mgL⁻¹; CFR: $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$.

Membrane	Dead-end UF				Cross-flow UF			
	PF (Lm ⁻² h ⁻¹)	R (%)	FD (%)	SP (Lm ⁻² h ⁻¹)	PF (Lm ⁻² h ⁻¹)	R (%)	FD (%)	SP (Lm ⁻² h ⁻¹)
M ₁	87.7	97.8	13.3	644.9	126.1	94.4	12.5	952.3
M ₆	34.9	97.2	17.0	199.5	45.3	95.2	16.1	267.9
M ₉	17.5	97.1	39.4	43.1	25.0	96.6	33.1	72.9
M ₁₂	70.3	95.5	52.1	128.9	112.2	87.8	49.0	201.0

rejected oil droplets form a layer by coalescence with each other whose thickness grows with time by absorbing more and more oil droplets. On the other hand, in case of cross-flow mode due to constant flow of the feed, breakdown of some of the oil droplets

is likely to occur specially at higher value of CFR which results in a permeate accompanied by some number of smaller sized oil droplets as discussed before. However, the SP values are found to be higher for all the membranes in cross-flow UF compared to those found in dead-end flow which is mainly due to the higher values of PF.

5.3. Analysis of UF experiments with industrial oily water

Based on the study carried out with the synthetic oily water, the four membranes were tested to separate oil from the 'produced water' obtained from OIL, Assam. At first, the dead-end UF experiments were carried out with all the membranes under the optimum TMP condition i.e. 103.4 kPa (section 5.2.1.1). The feed after the pre-treatment steps (discussed in section 4.2.2.1 of Chapter 4) was subjected to UF operation without modifying its any of the properties shown in Table 4.4. The permeate obtained from each experiment was analyzed in terms of oil content and COD content. Finally, the cross-flow UF was carried out at a TMP of 103.4 kPa and a CFR of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ with the produced water. The cross-flow study with synthetic oily water shows that the performance of M_1 membrane was the best which was followed by the M_6 membrane; so these two membranes were considered for the cross-flow study with industrial oily water to see their applicability.

5.3.1. Analysis of dead-end mode

The produced water was subjected to ultrafiltration operation in dead-end mode using the four membranes at the optimum TMP i.e. 103.4 kPa. Fig. 5.26 illustrates the variation of permeate flux with time for the four membranes. Table 5.13 shows the performance of the four membranes with the produced water.

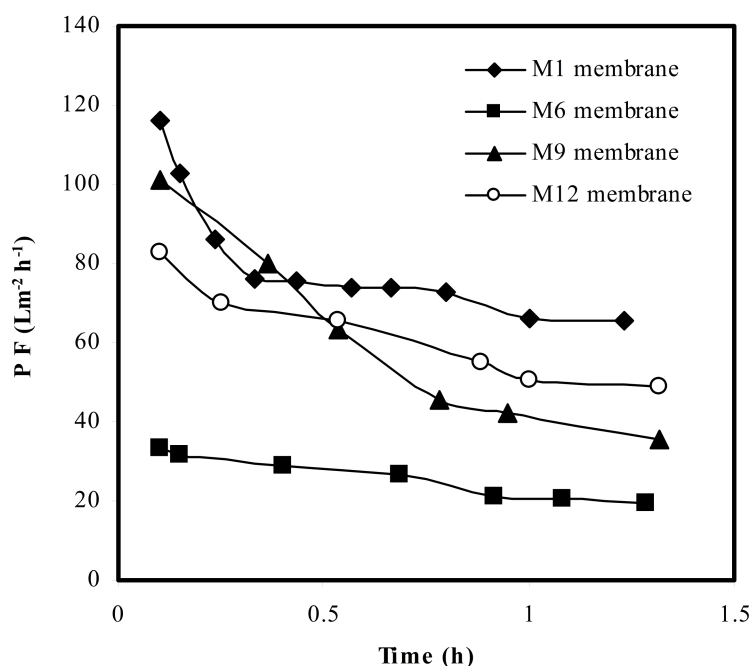


Fig. 5.26 Variation of permeation flux with time for M₁, M₆, M₉ and M₁₂ membranes with produced water as the feed (dead-end mode)

Table 5.13 Comparison of the performance of different membranes in dead-end UF of produced water after 1 h at a TMP of 103.4 kPa .

Membranes	PF ($Lm^{-2}h^{-1}$)	R (%)	FD (%)	SP ($Lm^{-2}h^{-1}$)
M ₁	66.0	86.7	43.3	132.2
M ₆	21.7	87.3	35.0	54.1

M ₉	40.1	88.4	60.3	58.8
M ₁₂	50.3	85.9	39.4	109.7

Observations

1. It is seen that M₁ membrane exhibits the highest flux after 1 h of operation which is 66.0 Lm⁻²h⁻¹ while the lowest flux is obtained with M₆ membranes which is 21.7 Lm⁻²h⁻¹. The M₉ and M₁₂ membranes show a flux of 40.1 Lm⁻²h⁻¹ and 50.3 Lm⁻²h⁻¹ respectively.
2. The oil separation capacity for all the membranes is found to be less with produced water compared to the synthetic oily water. The maximum R (%) is found to be 88.4 % with M₉ membrane (Table 5.13). The lower values of R (%) compared to those achieved in the experiments with synthetic oily water is attributed to the presence of comparatively smaller sized o/w emulsion droplets in produced water (Fig. 4.5) which results in penetration of some of the oil through the membrane pores.
3. The FD values are seen to be higher for all the membranes except M₁₂ membrane. This is attributed to the higher oil concentration in the feed (366 mgL⁻¹); because with increase in oil content, the amount of oil accumulated increases which increases the extent of fouling. Again the

lower trend of FD with M₁₂ membrane can be attributed to the effect of feed pH. However, maximum FD is seen to experience by M₉ membrane (60.3 %).

4. The M₁ membrane is found to be the most suitable membrane having the highest

SP value of 132.2 which is followed by the M₁₂ membrane with SP equal to 109.7. The M₆ and M₉ membranes demonstrate poor performance with SP values of 54.1 and 58.8 respectively.

5. Table 5.14 shows the quality of feed and permeate in terms of oil content and COD before and after filtration respectively. The COD content in the permeate is found to be within acceptable limit i.e. below 150 mgL⁻¹; while oil content is found to be higher than the acceptable limit of 10 mgL⁻¹.

Table 5.14 Analysis of produced water before and after UF at 103.4 kPa for different membranes; duration of experiment: 1h.

Membranes	Feed (before UF)		Permeate (after UF)	
	Oil content (mgL ⁻¹)	COD (mgL ⁻¹)	Oil content (mgL ⁻¹)	COD (mgL ⁻¹)
M ₁	366	288	48.5	115.0
M ₆			46.6	114.7
M ₉			42.4	114.2
M ₁₂			51.7	115.4

5.3.2. Analysis of cross-flow mode

Based on the results of the cross-flow ultrafiltration with synthetic oily water, the produced water was subjected to cross-flow operation under the TMP of 103.4 kPa and a CFR of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ with M_1 and M_6 membranes. Fig. 5.27 shows the behaviour of permeate flux with time at the selected operating conditions. M_1 membrane is seen to exhibit the highest flux ($128 \text{ Lm}^{-2}\text{h}^{-1}$), with a greater degree of flux declination (43.1 %) while for M_6 membrane, the flux is $70 \text{ Lm}^{-2}\text{h}^{-1}$ with flux declination of (31.6 %). However, the rejection of oil is found to be quite less compared to that of batch UF which is 77.5 % with M_1 membrane and 78.8 % with M_6 membrane.

Fig. 5.27 Variation of permeation flux with time for M₁ and M₆ membranes with produced water as the feed (cross-flow mode)

Observations

1. The performances of the selected membranes are found to be better in cross-flow mode compared to the dead-end mode in terms of permeate flux while dead-end mode results in better oil separation.
2. The results of the applicability of the membranes in separating oil from “produced water” by cross-flow UF shows that the oil content in the permeate has not met the discharge standard of 10 mgL⁻¹. The same observation is obtained with the batch UF.

Table 5.15 illustrates a comparison between the performance of the membranes with synthetic and real oily water (produced water) in both the dead-end and cross-flow modes of UF. The difference in the performance for all the membranes with real water from those obtained with synthetic oily water (Table 5.12) is possibly due to the difference in properties between the two feeds which are mainly the difference in oil droplet size distribution and the pH values. However, it is observed that the M₁ membrane displays the maximum value of SP irrespective of the type of feed (i.e. synthetic or real oily water) and the type of operation mode (i.e. batch or cross-flow) of UF.

Table 5.15 Comparison of the performance of different membranes in dead-end and cross-flow mode of UF for synthetic and produced water

Membranes	Dead-end UF		Cross-flow UF	
	Synthetic water	Produced water	Synthetic water	Produced water
	SP (Lm ⁻² h ⁻¹)	SP (Lm ⁻² h ⁻¹)	SP (Lm ⁻² h ⁻¹)	SP (Lm ⁻² h ⁻¹)
M ₁	644.9	132.2	952.3	230.2
M ₆	199.5	54.1	267.9	174.6
M ₉	43.1	58.8	-	-
M ₁₂	128.9	109.7	-	-

The results obtained from both the batch and cross-flow UF of the produced water show that the prepared membranes are successful in bringing down the oil content in the permeate from 366 mgL⁻¹ to approximately 50 mgL⁻¹ which is still higher than the acceptable discharge limit of 10 mgL⁻¹. But with the synthetic oily water, the permeate quality was up to the mark. The reason for the membranes not being able to do so with produced water may be explained from the difference in size distribution of oil particle for the produced water (Fig. 4.5) and the synthetic oily water (Fig. 4.1). Fig. 4.5 shows that the oil particle size in produced water ranges from about 0.02 – 0.2 with an average size of 0.1 while Fig. 4.1 illustrates the size range of the emulsion droplets in the synthetic oily feed to be within 0.03 – 5 with an average size of 0.39.

The performance of both batch and cross-flow UF with produced water suggests that further study needs to be carried out with real oily water i.e. produced water. Produced water collected from different oil collecting stations (OCS) of OIL has different

properties in terms of oil droplet size distribution, concentration and pH due to the presence of different surfactants and CODs. These waters may also be tested with the synthesized membranes to see and confirm their degree of performance. More experiments should be carried out with oily waste water or produced water collected from different sources other than OIL such as IOCL, ONGC, etc. using the membranes of same compositions.

In order to improve oil separation, the membranes can be modified to improve their properties such as pore size and pore size distribution, hydrophilicity etc. through the application of different techniques such as changing the composition of membrane casting solution, membrane surface coating etc. In addition, to tackle the difficulty of lower oil separation due to penetration of the smaller oil droplets along with the permeate, cascading effect of different membrane units e.g. UF followed by NF or RO should be explored to get a realistic membrane separation unit.

Abbreviations

BSA	Bovine serum albumin
CBM	Complete blocking model
CF	Compaction factor
CFM	Cake filtration model
CFR	Cross-flow rate
COD	Chemical oxygen demand
DMAc	Dimethyl acetamide

EWC	Equilibrium water content
FD	Flux declination
IBM	Intermediate blocking model
IEP	Isoelectric point
NF	Nanofiltration
NMP	N- methyl pyrrolidone
PEG	Poly(ethylene glycol)
PF	Permeate flux
PSf	Polysulfone
PVP	Polyvinylpyrrolidone
RIS	Resistance-in-series
RO	Reverse osmosis
SBM	Standard blocking model
SC	Specific conductivity
SP	Separation parameter
TMP	Transmembrane pressure
UF	Ultrafiltration

Notations

Constants (s^{-1}) (Eqs. 5.4 - 5.15)

Effective membrane area (m^2)

Bulk concentration (mgL^{-1})

Concentration in the feed (mgL^{-1})

Concentration in the permeate (mgL^{-1})

Concentration in the permeate at steady state (mgL^{-1})

Initial permeate flux ($\text{m}^3\text{m}^{-2}\text{s}^{-1}$)

Permeate flux ($\text{Lm}^{-2}\text{h}^{-1}$)

Pure water flux ($\text{Lm}^{-2}\text{h}^{-1}$)

Membrane surface blocked per unit of total permeate volume through the membrane (m^{-1}) (Eq. 5.5)

Decrease in the pore size due to adsorption on the pore walls per unit of total permeate volume (m^{-1}) (Eq. 5.8)

Membrane surface blocked per unit of total permeate volume through the membrane (m^{-1}) (Eq. 5.11)

Area of the cake per unit volume of permeate (m^{-1}) (Eq. 5.14)

Coefficients (Eq. 5.3)

Membrane permeability ($\text{mPa}^{-1}\text{s}^{-1}$)

Initial volumetric flow rate (m^3s^{-1})

Volume of the permeate (L)

Volumetric flow rate of permeate ($\text{m}^3 \text{s}^{-1}$)

Volume of water permeated (L)

Rejection (%)

Ratio of cake resistance to the clean membrane resistance (Eq. 5.14)

Resistance due to concentration polarization over the membrane surface

(m^{-1})

Membrane hydraulic resistance (m^{-1})

Resistance due to pore blocking (m^{-1})

Total resistance (m^{-1})

Filtration time (s^{-1}) (Eq. 5.3)

Sampling time (h) (Eq. 5.18)

Filtrate volume (m^3) (Eq. 5.3)

Weight of the permeate (kg)

Greek symbols

permeate viscosity (Pa-s)

Density of permeate (gL^{-1})

References

1. D. A. Musale and S. S. Kulkarni, Relative rates of protein transmission through poly(acrylonitrile) based ultrafiltration membranes, J. Membr. Sci., 136 (1997), 13 - 23.
2. A. Higuchi, Y. Ishida and T. Nakagawa, Surface modified polysulfone membranes separation of mixed proteins and optical resolution of tryptophan, Desalination, 90 (1993), 127 - 136.
3. B. Chakrabarty, A. K. Ghoshal, and M. K. Purkait, Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive, J. Membr. Sci., 315 (1-2) (2008), 36 - 47.

4. H. Hanemaaijer, T. Robbertsen, Th. van den Boomgaard and J. W. Gunnink, Fouling of ultrafiltration membranes. The role of protein adsorption and salt precipitation, *J. Membr. Sci.*, 40 (1989), 199 - 217.
5. D. A. Mussale and S. S. Kulkarni, Fouling reduction in poly(acrylonitrile-co-acrylamide) ultrafiltration membranes, *J. Membr. Sci.*, 111 (1996), 49 - 56.
6. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, Effect of molecular weight of PEG on membrane morphology and transport properties, *J. Membr. Sci.*, 309 (1-2) (2008), 209 - 221.
7. E. Matthiasson, The role of macromolecular adsorption in fouling of ultrafiltration membranes, *J. Membr. Sci.*, 16 (1983), 23 - 36.
8. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane, *J. Membr. Sci.*, 325, (2008), 427 - 437.
9. H. Ohya, J. J. Kim, A. Chinen, M. Aihara, S. I. Semenova, Y. Negishi, O. Mori, and M. Yasuda, Effects of pore size on separation mechanisms of microfiltration of oily water using porous glass tubular membrane, *J. Membr. Sci.*, 145 (1998), 1 - 14.
10. A. B. Koltuniewicz and R. W. Field, Process factors during removal of oil-in-water emulsions with cross-flow microfiltration, *Desalination*, 105 (1996), 79 - 89.
11. A. B. Koltuniewicz, R. W. Field and T. C. Arnot, Cross-flow and dead-end

- microfiltration of oily-water emulsion. Part I: Experimental study and analysis of flux decline, *J. Membr. Sci.*, 102 (1995), 193 - 207.
12. R. V. Lopez, S. Elmaleh and N. Ghaffor, Crossflow ultrafiltration of hydrocarbon emulsions, *J. Membr. Sci.*, 102 (1995), 55 - 64.
13. A. Byhlin and A. S. Jonsson, Influence of adsorption and concentration polarisation on membrane performance during ultrafiltration of a non-ionic surfactant, *Desalination*, 151 (2002), 21 - 31.
14. L. Song, Flux decline in cross flow microfiltration and ultrafiltration: mechanisms and modeling of membrane fouling, *J. Membr. Sci.*, 139 (1998), 183 – 200.
15. P. H. Hermans and H. L. Bredee, Principles of the mathematical treatment of constant pressure filtration, *J. Soc. Chem. Ind.*, 55 (1936).
16. J. Hermia, Constant pressure blocking filtration laws application to power-law non newtonian fluids, *Trans. Inst. Chem.Eng.*, 60 (1982), 183 - 187.
17. K. J. Hwang ,C. Y. Liao and K. L. Tung , Analysis of particle fouling during microfiltration by use of blocking models, *J. Membr. Sci.*, 287 (2007), 287 – 293.
18. W. R. Bowen, J. I. Calvo and A. Hernandez, Steps of membrane blocking in flux decline during protein microfiltration, *J. Membr. Sci.*, 101 (1995), 153 – 165.

19. R. W. Field, D. Wu, J. A. Howell and B. B. Gupta, Critical flux concept for microfiltration fouling, *J. Membr. Sci.*, 100 (1995), 259 – 272.
20. C. Ho and A. L. Zydney, A Combined Pore Blockage and Cake Filtration Model for Protein Fouling during Microfiltration, *J. Colloid Interf. Sci.*, 232 (2000), 389 – 399.
21. W. Yuan, A. Kocic and A. L. Zydney, Analysis of humic acid fouling during microfiltration using a pore blockage–cake filtration model, *J. Membr. Sci.*, 198 (2002), 51 – 62.
22. J. C. S. Wu and E. H. Lee, Ultrafiltration of soybean oil/hexane extract by porous ceramic membranes, *J. Membr. Sci.*, 154 (1999), 251 – 259.
23. N. Nabi, P. Aimar and M. Meireles, Ultrafiltration of an olive oil emulsion stabilized by an anionic surfactant, *J. Membr. Sci.*, 166 (2000), 177 – 188.

Chapter 6

Conclusions and Scope of Future Works

This chapter summarizes the inferences drawn from the present research work and provides suggestions towards the future direction. The major conclusions are briefly presented below:

6.1. Conclusions

Membrane synthesis and characterization

- All the PSf membranes prepared with PVP (molecular weights 24,000, 40,000 and 3,60,000 Da) and PEG (molecular weights 400, 6000 and 20,000 Da) as the additives and NMP and DMAc as the solvents in the w/w ratio of 12:83:5 are found to be asymmetric in nature.
- The pore size distributions of the membranes calculated by means of different standard methods are found to be in the ultrafiltration (UF) range, though there is discrepancy in the values obtained from different methods.
- For UF application of membranes, which is closely associated with membrane pore statistics, liquid permeation test can be recommended to get the realistic

picture of membrane morphology as a whole. Based on this test, the average size of the pores for all the membranes are found to be within 3 - 4 nm.

- With increase in molecular weight of PEG and PVP, the pore number as well as pore area per unit surface area i.e. porosity of the prepared PSf membrane is found to increase. For example, for PSf/NMP/PVP membranes, the pore number increases from 2.6×10^9 to 9.8×10^9 when the molecular weight of PVP increases from 24,000 to 3,60,000 Da. However, the average pore size is found to decrease marginally with increase in molecular weight of the additives i.e. PEG and PVP. For example, for PSf/NMP/PVP membranes, the average pore size decreases from 3.62 to 3.0 nm.
- The PWF decreases while $\frac{Q}{A \Delta P}$ increases with increase in molecular weight of PVP possibly due to comparatively more compact structure of the resulting membranes and swelling of hydrophilic PVP which remains entrapped in the membrane matrix. Contradictorily, the PWF and $\frac{Q}{A \Delta P}$ are seen to enhance and reduce respectively with increase in molecular weight of PEG. For example, for PSf/DMAc/PVP membranes the PWF decreases from 76.4 to 45.8 $\text{Lm}^{-2}\text{h}^{-1}$ while for PSf/DMAc/PEG membranes it increases from 12.2 to 308.7 $\text{Lm}^{-2}\text{h}^{-1}$ when the molecular weight of PVP and PEG increases.
- The increase of EWC with increase in molecular weight of both the additives for all the membrane compositions can be interpreted as an indication of

increase in hydrophilicity as well as increase in number of pores of the membranes irrespective of the solvents used.

Ultrafiltration of BSA solution

The findings of the batch ultrafiltration of BSA solution are:

- With PEG as additive, a significant increase in BSA rejection is observed when molecular weight of PEG is increased from 400 to 6000 Da, beyond which the rejection is seen to decrease when molecular weight is increased from 6000 to 20000 Da. So irrespective of solvents and pH of BSA solution, membranes prepared with PEG 6000 are found to be the best; while in the study with PVP, rejection is found to increase with increase in molecular weight of PVP within the chosen range of molecular weight i.e. from 24,000 to 3,60,000 Da. So irrespective of solvents and pH of BSA solution, membranes prepared with PVP 360000 are evaluated as the best.
- The pH of the BSA solution is seen to be an important parameter in the UF studies. In case of the membranes prepared with PVP, the BSA solution at pH 9.3 is found to be more favorable compared to that at pH 4.8 with respect to BSA rejection for both type of solvents; while for membranes prepared with PEG, the rejection is found to be solvent dependent. In this case, BSA solution of pH 4.8 is found to give better result with NMP as solvent but with DMAc as solvent, the solution has to be maintained at pH of 9.5 to get maximum rejection.

- Considering the role of the two solvents, for PSf/PVP system, DMAc is seen to be better compared to NMP in terms of rejection of BSA for both the pH values within the range of molecular weights of PVP used. For PSf/PEG system, NMP is observed to be better compared to DMAc in terms of maximum rejection for the range of PEG molecular weights used.
- Comparing the membranes prepared with both types of additives, i.e. PEG (molecular weights 400, 6000 and 20,000 Da) and PVP (molecular weights 24,000, 40,000 and 3,60,000 Da) in terms of BSA rejection, membranes prepared with PVP are found better (with $\%R_{\max} = 76\%$) than those prepared with PEG (with $\%R_{\max} = 56.4\%$) irrespective of the two solvents, i.e. NMP and DMAc.

Ultrafiltration of oily water

The results of the UF study with oily water (both synthetic and industrial) carried out in dead-end (batch) and cross-flow modes individually are as given below:

Dead-end and cross-flow UF with synthetic oily water

- The effects of transmembrane pressure (TMP) and feed properties such as concentration of oil in feed and pH of feed on membrane performance are mainly investigated in the dead-end UF operation. It is observed that with increase in TMP across the membrane, the permeate flux (PF) increases and the relation between the flux and pressure is not exactly linear indicating the existence of additional resistances besides the membrane hydraulic resistance.

- TMP also affects the flux declination (FD) as well as the amount of oil rejection (R). It is observed that FD increases while R is in decreasing trend with increase in TMP for all the membranes. The TMP at which the PF, R and FD are optimal is found to be 103.4 kPa for all the membranes.
- Porosity, pore size distribution, morphology of the membrane sub layer and hydrophilicity due to the presence of entrapped high molecular weight PVP and PEG within the membrane matrix play a major role in determining the PF as well as FD.
- Almost all the membranes are capable of producing a permeate of acceptable quality having oil content less than 10 mgL⁻¹.
- A parameter called 'selection parameter (SP)' which includes all the three performance parameters i.e. PF, FD and R has been defined to measure and compare the membranes. Based on the SP values, four membranes are selected from each of the four membrane compositions i.e. PSf/NMP/PVP, PSf/DMAc/PVP, PSf/NMP/PEG and PSf/DMAc/PEG. Accordingly, M₁ (PSf/NMP/PVP 24000), M₆ (PSf/DMAc/PVP 360000), M₉ (PSf/NMP/PEG 20000) and M₁₂ (PSf/DMAc/PEG 20000) membranes are found to be the most suitable membranes from each of the four individual membrane compositions in terms of achieving reasonable PF, lower range of FD and higher values of R in the optimal TMP condition.

- The analysis of the flux decline mechanism during dead-end operation using RIS model shows that the total resistance, R_{total} , increases with increase in both TMP and oil concentration in feed. For a feed with higher oil concentration, concentration polarization is found to be the chief cause of membrane fouling irrespective of the membrane compositions.
- Again, application of the filtration model displays the fact that the intermediate blocking model (IBM) dominates the fouling mechanism up to a certain period for all the membranes beyond which a transition from pore blocking mechanism to cake filtration like mechanism takes place due to accumulation of oil particles on the membrane surface.
- Feed characteristics such as concentration and pH affect the flux and rejection significantly. With increase in oil concentration in feed, PF decreases and rejection (R) increases. The pH affects the flux and rejection to different extent depending on the membrane composition.
- The effect of cross-flow rate (CFR) on membrane performance has been highlighted mainly in the cross-flow UF operation and it is found that with increase in CFR, the flux increases significantly; but the (%)R shows a decreasing trend.
- Out of the four membranes (i.e. M₁, M₆, M₉ and M₁₂), the highest separation was obtained with M₉ membrane (96.6 %) and the lowest separation was

obtained with M₁₂ membrane (87.8%) at a TMP of 103.4 kPa and a CFR of 3.6 m³s⁻¹. However, considering the SP values in cross-flow operation, M₁ membrane can be recommended under a TMP of 103.4 kPa and a CFR of 3.6 m³s⁻¹ based on its having the highest value of SP i.e. 952.3 Lm⁻²h⁻¹. The second most suitable membrane is the M₆ membrane with a SP value of 267.9 Lm⁻²h⁻¹.

- Comparing the performance of the selected membranes in dead-end and cross-flow UF with synthetic oily water, it is found that dead-end mode gives better oil separation than the cross-flow mode; However, the SP values are found to be higher for all the membranes in cross-flow mode compared to those found in dead-end flow which is chiefly due to the higher values of PF.

Dead-end and cross-flow UF with industrial oily water (produced water)

- In the dead-end operation, which is carried out at the TMP of 103.4 kPa with all the four membranes, M₁ membrane shows the highest flux after 1 h of operation which is 66.0 Lm⁻²h⁻¹ while the maximum R is found to be 88.4 % with M₉ membrane; however, M₁ membrane is found to perform the best with maximum SP value of 132.2 Lm⁻²h⁻¹ at the optimum TMP condition.
- The cross-flow operation which is carried out at the TMP of 103.4 kPa and a

CFR of $3.1 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ with M_1 and M_6 membranes, demonstrates that M_1 membrane exhibits a PF of $128 \text{ Lm}^{-2}\text{h}^{-1}$ with a SP value of $230.2 \text{ Lm}^{-2}\text{h}^{-1}$ while M_6 membrane gives a PF of $70 \text{ Lm}^{-2}\text{h}^{-1}$ with a SP value of $174.6 \text{ Lm}^{-2}\text{h}^{-1}$.

- Performances of the selected membranes in cross-flow mode are found to be better compared to the dead-end mode in terms of higher values of SP.
- Both dead-end and cross-flow UF of produced water show that the selected membranes are successful in reducing the oil content in water from 366 mgL^{-1} to about 50 mgL^{-1} which suggests that further investigations such as cascading of different membrane units need to be carried out to bring down the oil content to the acceptable limit i.e. below 10 mgL^{-1} .
- The difference in the performance for all the membranes with real oily water from those obtained with synthetic oily water is due to the difference in feed properties such as the size distribution of oil droplets and the pH values.
- Comparing the performance of all the membranes, M_1 (PSf/NMP/PVP 24000)

membrane is found to be the most suitable membrane in treating o/w emulsion as its performance is found to be consistent with both synthetic and industrial oily water in dead-end as well as in cross-flow modes of UF. Thus,

M₁ membrane can be recommended for treating oily water at normal condition.

6.2. Recommendations on future scope

More basic studies are needed to be carried out before deciding and establishing a process for pilot and / or industrial scale operation. Thus, the following works are suggested as an extension of the present study:

- In this work, the effects of increasing molecular weight of PVP and PEG on morphology and performance of PSf membrane have been studied. There is a scope of extending this work considering the effect of different concentrations of PVP and PEG in membrane morphology. Similar type of work can also be conducted for polymers other than PSf such as polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), cellulose acetate (CA), etc with the same additives or other organic additives such as acetone, maleic acid, glycerol, etc. to prepare the membranes and accordingly to study their morphology as well as performance.
- Further study on BSA rejection using the synthesized membranes may be carried out considering the effect of other operating conditions such as temperature, pressure, concentration, cross-flow velocity, etc. to have a better understanding on the membrane performance.

- In the present study with oily water, temperature effects on membrane performance have not been considered. As temperature plays an important role in flux and rejection of oil, its effect may be included in the future study with oily water.
- Extension of this work can be done by carrying out more study with real oily water in order to obtain better performance which may include modification of the membrane properties, adjustment of the real water characteristics that would suit the membrane properties.
- For the removal of oil from oily water, other membrane based techniques such as micellar enhanced ultrafiltration (MEUF) technique may be adopted by choosing a suitable surfactant and a comparative study may be made on the efficiency of that technique with the simple UF technique considered in the present study.
- This study has been conducted entirely with flat sheet membrane. A similar type of study may be carried out in other existing membrane modules such as hollow fiber module and spiral wound module and thus the process design variables may be optimized.
- The study may be extended further by testing the synthesized membranes for their applicability in other separation operations involving fruit juice, dye, black liquor, etc.

- A pilot plant for separation of o/w emulsion can be developed using the synthesized membranes and a complete economic analysis may be carried out. Based on this, the overall performance could be compared with other existing techniques.



Appendix I

Properties of Polymers and Solvents

I.1. Polysulfone (PSf)

Polysulfone belongs to a family of thermoplastic polymers. These polymers are known for their toughness and stability at high temperatures. They contain the subunit aryl-SO₂-aryl, the defining feature of which is the sulfone group. Polysulfones were introduced in 1965 by Union Carbide. Due to the high cost of raw materials and processing, polysulfones are used in specialty applications and often are a superior replacement for polycarbonates.

Chemically, polysulfone consists of repeating units of C₂₇H₂₂O₄S of molecular weight of 442.52 gmol⁻¹. It is produced by step polymerization of bisphenol-A and bis(4-chlorophenyl)sulfone, forming a polyether by elimination of hydrogen chloride. The chemical structure can be written as [1, 2]:

n

Such step polymerizations require highly pure monomer to ensure high molecular weight products. These polymers are rigid, high-strength, and transparent, retaining its properties between $-100\text{ }^{\circ}\text{C}$ and $+150\text{ }^{\circ}\text{C}$. Its glass transition temperature is $185\text{ }^{\circ}\text{C}$. Polysulfone is highly resistant to mineral acids, alkalis, and electrolytes, in pH ranging from 2 to 13. It is resistant to oxidizing agents, therefore it can be cleaned by bleaching. It is also resistant to surfactants and hydrocarbon oils. However, it is not resistant to low-polar organic solvents (eg. ketones and chlorinated hydrocarbons), and aromatic hydrocarbons. Mechanically, polysulfone has fairly high compaction resistance, recommending its use under high pressures. It is also stable in aqueous acids and bases and many non-polar solvents; however it is soluble in dichloromethane and methylpyrrolidone.

Polysulfone allows easy manufacturing of membranes, with reproducible properties and controllable size of pores. Such membranes can be used in applications like hemodialysis, wastewater recovery, food and beverage processing, and gas separation. These polymers are also used in the automotive and electronic industries [2, 3].

(I.2) N-Methyl-2-Pyrrolidone ($\text{C}_5\text{H}_9\text{NO}$)

N-methyl-2 pyrrolidone (NMP) is a clear, colorless liquid which turns yellow on exposure to heat. Its specific gravity is 1.03; its boiling point being $202\text{ }^{\circ}\text{C}$. It is miscible with water and its pH range is 7.5 - 8.0. The structural formula of NMP (molecular wt. 99.13) is shown below:

Pyrrolidone is a keto-pyrrole, that is a 5-membered lactam structure compound (gamma-butyrolactam). Lactam structure compound including pyrrolidone has good solvency property, therefore it is useful in industrial application as a solvent. NMP is used as a solvent for surface treatment for textiles, metal coated plastics, polymers, and paint removing. Pyrrolidone and its derivatives are used as intermediates for the synthesis of agrochemicals, pharmaceuticals, textile auxiliaries, plasticizers, polymer solvent, stabilizers, specialty inks and as a nylon precursor. NMP is used as a solvent for paint stripping and resins; cleaner for polymeric residues; metal finishing; printed circuit board manufacturing; SBR latex production; pigment dispersant; extraction of acetylene and butadiene; dehydration of natural gas and lube oil processing [4, 5].

(I.3) Dimethylacetamide (C₄H₉NO)

Dimethylacetamide (DMAc) is a colorless liquid with faint ammonia odor. Its density is 0.94 gcm⁻¹; its boiling point being 164 - 166 °C. DMAc is miscible with most other solvents, although it is poorly soluble in aliphatic hydrocarbons. It is miscible with water

and this high boiling liquid is commonly used as a polar solvent in organic chemistry.

The structural formula of DMAc (molecular wt. 87.12) is shown below:

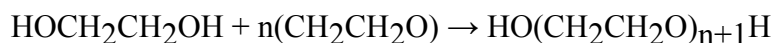
It is a useful as a medium for strong bases such as sodium hydroxide. Dimethylacetamide is commonly used as a solvent for fibers or in the adhesive industry. It is also employed in the production of pharmaceuticals and plasticizers as a reaction medium [4, 5].

(I.4) Poly(ethylene glycol) (PEG) ($C_{2n+2}H_{4n+6}O_{n+2}$)

Poly(ethylene glycol) (PEG) is also known as poly(ethylene oxide) (PEO) or polyoxyethylene (POE). It is a condensation polymer which is produced by the interaction of ethylene oxide with water, ethylene glycol or ethylene glycol oligomers. The reaction is catalyzed by acidic or basic catalysts. PEG has the following structure:

n

The numbers that are often included in the names of PEGs indicate their average molecular weights, e.g. a PEG with $n = 80$ would have an average molecular weight of approximately 3500 daltons and would be labeled PEG 3500. Most PEGs include molecules with a distribution of molecular weights, i.e. they are polydisperse. The size distribution can be characterized statistically by its weight average molecular weight (M_w) and its number average molecular weight (M_n), the ratio of which is called the polydispersity index (M_w/M_n). M_w and M_n can be measured by mass spectroscopy. PEGs are commercially available over a wide range of molecular weights from 300 gmol^{-1} to 10,000,000 gmol^{-1} . PEGs with different molecular weights have different physical properties (e.g. viscosity) due to chain length effects, but their chemical properties are nearly identical. Their melting points vary depending on the formula weight of the polymer. Polymer chain length depends on the ratio of reactants.



Depending on the catalyst type, the mechanism of polymerization can be cationic or anionic. The anionic mechanism is preferable because it allows one to obtain PEG with a low polydispersity. Polymerization of ethylene oxide is an exothermic process. Overheating or contaminating ethylene oxide with catalysts such as alkalis or metal oxides can lead to an explosion after few hours. PEG is compatible with most organic solvents e.g. methanol, benzene and dichloromethane and has excellent water-solubility. It has excellent hygroscopic property. It is insoluble in diethyl ether and hexane [2, 3, 6].

(I.5) Polyvinyl pyrrolidone (PVP) $(\text{C}_6\text{H}_9\text{NO})_n$

PVP, which was initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production, was invented by Prof. Walter Reppe and a patent was filed in 1939 for one of the most interesting derivatives of acetylene chemistry. It is a water-soluble polymer made from the monomer N-vinyl pyrrolidone as show below:

n

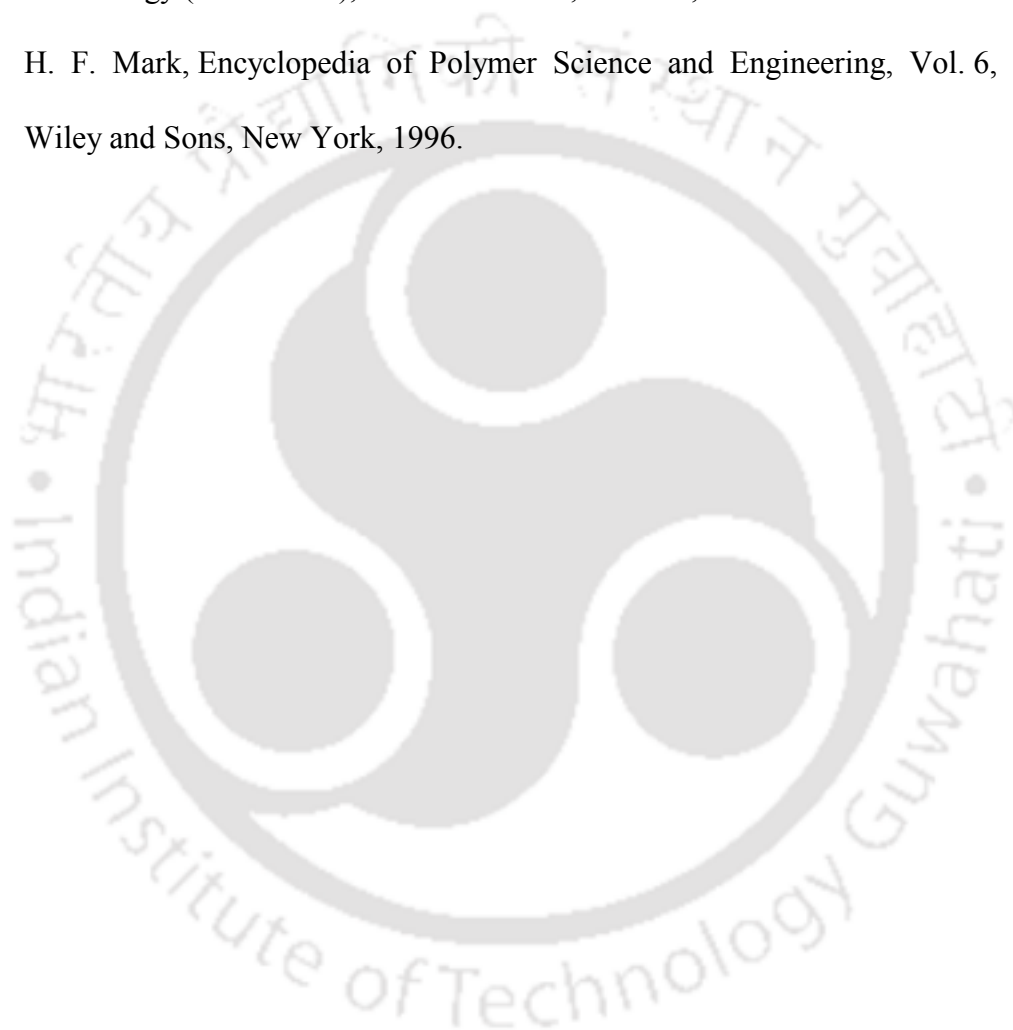
The monomer is carcinogenic and is extremely toxic to aquatic life. However the polymer PVP in its pure form is so safe that it is edible by humans. Polymerization can be carried out in bulk, in solution, or in suspension. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. A

special property of PVP is that it is soluble in many solvents e.g. water, alcohol (methanol, ethanol, propanol, butanol, glycol); ester alcohol (ethylene glycol monoethylether, diethylene glycol, polyethylene glycol, 1,4-butanediol); chlorinated hydrocarbon (dichloromethane, chloroform); amine (butylamine, ethylenediamine); acid (formic, acetic, propionic); dilute acid, base, low salt solutions. The reason for this phenomenon is that PVP has hydrophilic as well as hydrophobic functional groups, and therefore interactions with various solvents are possible. The nonsolvents are hydrocarbons (benzene, hexane, pentane, cyclohexane, toluene, xylene, mineral oil); ethers (dioxane, diethyl ether, ethyl vinyl ether); ketones (acetone, cyclohexanone); esters (ethyl acetate, methyl acetate); chlorinated hydrocarbons (carbon tetrachloride, chlorobenzene). In water it has the useful property of Newtonian viscosity. The pH of 5% PVP in water is 3 – 7 and has a density of 2.15 gcm^{-3} . It is highly hygroscopic in nature. When dry it is a light flaky powder, which readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. Both PEG and PVP are characterized by less toxicity, less skin irritation and completely safe to be handled with [2, 3, 6] .

References

1. Munir Cheryan, Ultrafiltration and Microfiltration Handbook, Technomic Publishing Co. Inc. Lancaster, Pennsylvania, U.S.A, 1998.
2. J. Brandrup and E. H. Immergut (Eds.), Polymer Handbook (3rd edition), John Wiley and Sons, New York, 1989.

3. J. E. Mark, (Ed.), Polymer data handbook, Oxford University Press, 1999.
4. J. I. Kroschwitz, (Ed.), Encyclopedia of Chemical Technology (4th edition), Vol. 4, John Wiley and Sons, New York, 1992.
5. R. L. Whistler, J. N. Bemiller, and E. F. Paschall (Eds.), Chemistry and Technology (2nd edition), Academic Press, Orlando, 1984.
6. H. F. Mark, Encyclopedia of Polymer Science and Engineering, Vol. 6, John Wiley and Sons, New York, 1996.



Appendix II

Sample Calculation

Determination of ‘ θ ’, by Liquid displacement method for M¹ membrane:

The pore radius () was calculated using the Eq.(2.14) i.e.

(2.14)

where, = Transmembrane pressure (TMP), Pa;

= Interfacial tension between the two liquids i.e. water-isobutanol-methanol

mixture and water = 0.35 Pa.m

The total hydraulic permeability coefficient was obtained by Eq. (2.15) i.e.

(2.15)

where, = , the contribution of the pores of radius between and , (ms⁻¹)

= pressure corresponding to the mean radius , (Pa)

(2.16)

, (m)

The pore density i.e. the number of pores having radii between r_1 and r_2 per unit area of the membrane surface, $N(r_1, r_2)$ was calculated using Eq. (2.17) i.e.

$$(2.17)$$

where, l = length of the pore which is equivalent to thickness of the skin layer

η = viscosity of the wetting liquid = 3.4 Pa.s

The mean pore radius $\bar{r}$ was calculated using Eq. (2.22) i.e.

$$(2.22)$$

Values calculated by using the above equations are shown in Table II.1.

Table II.1

(Pa)		(Pa)					
	(ms ⁻¹)	(m)	(ms ⁻¹)	(m)		(m ⁻²)	(m ⁻¹)
6894.76	4.25	101.52	-	-	-	-	-
20684.28	8.49	33.84	4.24	67.68	10342.14	1.6938	11.46
27579.04	10.6	25.38	2.11	29.61	23639.18	10.1135	29.95
34473.8	17.0	20.30	6.4	22.84	30643.38	66.09	150.97
48263.32	21.2	14.50	4.2	17.40	40219.43	99.619	173.38
55158.08	29.7	12.69	8.5	13.60	51480.87	417.833	568.14

75842.36	42.5	9.23	12.8	10.96	63867.25	1196.72	1311.63
89631.88	46.7	7.81	4.2	8.52	82162.56	849.219	723.57
103421.4	55.2	6.77	8.5	7.29	96034.16	2712.33	1977.03
124105.7	67.9	5.64	12.7	6.20	112823.3	6579.1	4093.18
137895.2	72.2	5.07	4.3	5.36	130637.6	3413.81	1829.23
151684.7	76.4	4.61	4.2	4.84	144461.6	4616.28	2236.85
172369.0	80.7	4.06	4.3	4.34	161366.7	6433.94	2791.01
186158.5	84.9	3.76	4.2	3.91	178998.6	8781.8	3434.25
206842.8	106.2	3.38	21.3	3.57	195956.3	57608.0	20578.9
220632.3	144.4	3.17	38.2	3.27	213515.1	134142.0	43977.7
227527.1	152.9	3.07	8.5	3.12	224026.7	34432.1	10758.8

(m⁻²);

= 94646.05 (m⁻¹);



Appendix III

Error Analysis

The errors in experimentally measured quantities and in parameters calculated from those measurements are important in that they determine the accuracy of calculation and predictions using those quantities. There are two types of errors viz. systematic error and random error. Systematic errors are the results of faulty assumptions or improper experimental measuring techniques. In this work, care was taken in eliminating systematic errors by appropriately designing the experiments and adopting qualified methods for analysis of the data. On the other hand, random errors result from variation in the precision of measuring parameters and the slight variations that occur in successive measurements made by the same observer under nearly identical conditions. Random errors cannot be eliminated. The focus of the error analysis presented in this section is on the random errors.

In most of the experiments performed in this work, the quantities that are measured directly are concentrations and permeate flow rates which are used to determine the rejection (%R) and permeate flux respectively.

III.1. Error in the measurement of oil concentration

Oil concentration in the aqueous phase was determined by measuring the absorbance value at a specific wavelength in the UV-Vis spectrophotometer. A calibration curve was prepared by taking the absorbance values against the corresponding known values of concentrations of oil as discussed in section 4.2.1.2. of Chapter 4. From Fig. 4.2, which

is the calibration curve between absorbance and concentration of oil, it is seen that the standard deviation of the predicted value from actual value of concentration is 0.9973. Thus, every measurement of oil concentration in synthetic oily water is associated with an error of 0.27 % whose effect on rejection values of oil can be ignored.

III.2. Error in the measurement of permeate flux

The errors in the values of permeate flux are related to the errors in the measurements used to calculate those values. In this section, statistical analysis is used for estimation of the uncertainty associated with the values of permeate flux. Determination of standard deviation is generally considered to be one of the best methods to estimate the uncertainty which is based on the following method:

If $x_1, x_2, \dots, x_n$ are the results of the measurements of a particular quantity, then the mean value of x (i.e. $\bar{x}$), is defined by

(III.1)

The uncertainty in the result is usually expressed as “root-mean-squared-deviation”, which is denoted as s_x , which is computed using the following Eq. (III.2):

(III.2)

Since in the present work, all the membranes were cleaned thoroughly after each experiment and before each experiment, the performance of all the membranes were checked through pure water flux (PWF) measurement, hence uncertainties involved in the PWF measurements are reported here.

The uncertainties involved in different experimental measurements for (PWF) for different membranes are estimated and shown in Table III.1.

Table III.1. Values of uncertainties estimated in PWF measurements for different membranes

Membranes	Run 1	Run 2	Run 3		Uncertainties (%)	
M ₁	221.6	220.7	216.9	219.7	2.53	1.15
M ₂	95.5	87.9	91.7	91.7	3.82	4.2
M ₃	53.5	47.8	47.8	49.7	3.3	6.6
M ₄	80.2	76.4	72.6	76.4	3.8	5.0
M ₅	68.9	65.0	66.9	66.9	1.9	2.8
M ₆	45.9	43.9	47.8	45.8	1.9	4.1
M ₇	9.9	9.2	9.5	9.5	0.38	4.0
M ₈	238.8	248.4	257.9	248.4	9.5	3.8
M ₉	1595.5	1614.6	1605.1	1605.1	11.7	0.7
M ₁₀	11.5	13.0	12.2	12.2	0.76	6.2
M ₁₁	232.2	246.5	225.5	234.7	10.7	4.5

M ₁₂	309.5	315.3	300.9	308.6	7.21	2.3
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List of Publications

International Publications:

1. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Structural and Transport Property Enhancement of Polysulfone Membrane due to PEG as Additive", International Journal of Chemical Sciences 5 (4) (2007) 1873 - 1881.
2. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Effect of Molecular weight of PEG on Membrane Morphology and Transport Properties", J. Membr. Sci. 309 (2008) 209 – 221.
3. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "SEM analysis and gas permeability test to characterize polysulfone membrane prepared with polyethylene glycol as additive", J. Colloid and Interface Science 320 (2008) 245 – 253.
4. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive", J. Membr. Sci. 315 (2008) 36 - 47.
5. B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, "Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane", J. Membr. Sci., 325 (2008) 427 – 437.

National Conference:

1. B. Chakrabarty, A. K. Ghoshal, M. K. Purkait, Preparation of Polysulfone membrane by phase inversion method, CHEMCON-2007.