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PREPARATION OF POLYSULFONE MEMBRANES

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ABSTRACT

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As it is known, a huge part of all commercially available membranes are prepared by immersion precipitation. This way is the primary way to get flat membranes. The advantages of immersion precipitation are: wide field of the polymers, which can be used (polymer must be soluble in a solvent or a solvent mixture) and ease of performing.

The literature part of this work deals with phase inversion membrane preparation methods and casting parameters affecting membrane performance. Also some membrane types and materials are discussed.

In the experimental part of this work 73 membrane samples were made with different casting parameters (polymer concentration in the casting solution and precipitation time) and tested for the retention and permeability. The results of these experiments are collected and combined into the figures and tables which are presented in this thesis.

This work showed and confirmed connection between membrane performance and casting parameters (concentration of polymer in the casting solution and precipitation time).

FOREWORD

This Master of Science Thesis has been done between the 1st of March and 31st of October 2009 for Lappeenranta University of Technology.

I would like to thank Laboratory of Membrane Technology and Technical polymer Chemistry for this possibility to do my thesis with this interesting subject. Also I would like to thank MSc. Liisa Puro for her interest and advices.

I would like to thank my examiners and supervisors Professor Mika Mänttari and Professor Andrzej Kraslawski for their advices and help during my work.

Also I would like to thank my parents and my brothers for supporting me during my thesis.

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1 INTRODUCTION

1.1 Membrane technology

Membrane is a selective barrier between two phases, regulating the transport of substances between two compartments.

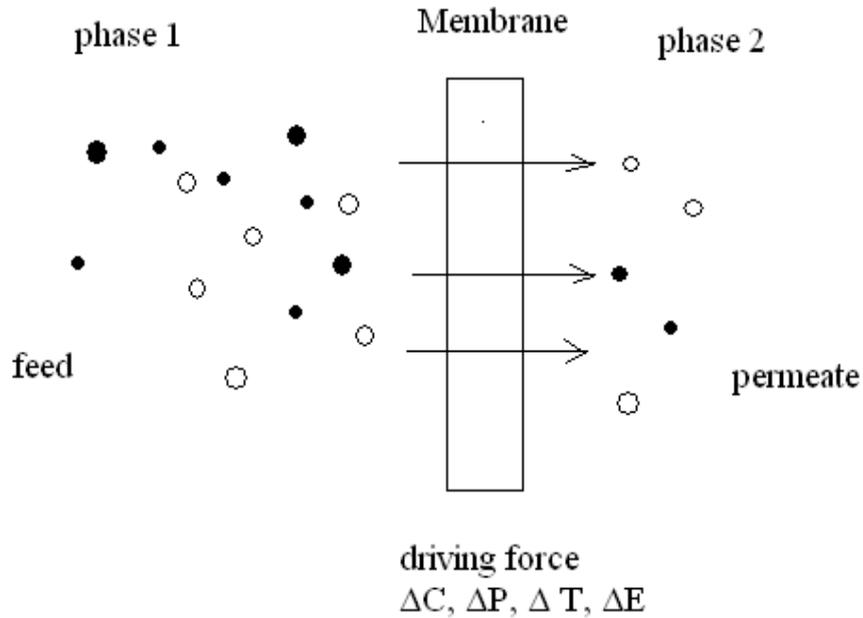


Figure 1.1. Schematic representation for membrane definition. [1]

Two phases, separated by the membrane, can be aqueous or gaseous. In this case, membrane is a permselective barrier [2] and if we want to have a mass transfer through it, we need a driving force.

Table 1.1 Classification of membrane processes according to their driving forces

Pressure difference, ΔP	Concentration difference, ΔC	Temperature difference, ΔT	Electrical potential difference, ΔE
Microfiltration	Pervaporation	Thermal-osmosis	Electrodialysis
Ultrafiltration	Gas separation	Membrane distillation	Membrane electrolysis
Nanofiltration	Dialysis		
Reverse osmosis	Liquid membrane		

In the Table 1.1 main driving forces of membrane process are shown: ΔC (concentration difference), ΔP (pressure difference), ΔT (temperature difference), ΔE (Electrical potential difference).

Today, membrane processes have ceased to be the subject of a narrow interest of small groups of scientists and experts in academic institutions and higher education establishments. Membrane methods of separation and purification are rapidly-growing scope of modern science. Medicine, biology, food industry, agriculture and many other industrial and scientific departments now seek for use the membranes. Membrane methods of separation of liquid and gaseous media today are well positioned in the arsenal of industrial processes. There are areas, where membrane technology in general has no competitors (hemodialysis). It is unexpendable in many processes of protecting the environment from pollution by industrial and municipal wastes.

Membrane technology has many advantages. For example, separation process do not need any additives, proceeds with low temperatures and uses a small amount of energy.[3] Membranes also represent the environmentally friendly branch of separation technology, because of its non-toxic composition.

The membrane technology spheres of usage:

1. Water treatment.

- obtaining of drinking water through desalination of sea water
- improvement of the quality of drinking water
- disinfection and sterilization of water

2. Food Industry.

- treated water for manufacturing processes
- concentrating of juices
- clarification of wine, beer
- processing of dairy products
- creating of the conditions for long-term storage of fruits and vegetables

3. Biotechnology.

- sterilization of technology media
- extraction of the components (enzymes, vitamins, etc.)

- concentration of products of biotechnological processes
- organization of continuous biotechnological processes

4. Wastewater treatment.

- wastewater treatment of pulp and paper, textile, electroplating and other industries
- treatment of domestic wastewater
- processing of liquid radioactive wastes

1.2 Aim and objectives

The aims of this thesis were:

- to study a manufacture of membrane (by phase inversion-immersion precipitation)
- to evaluate the effect of manufacturing parameters (concentration of the polymer in the casting solution, precipitation time) on the permeability and retention of the obtained membranes

About 73 membranes were made in this master thesis work (this was done to know the exact technology of producing membranes in laboratory scale and to get the repeatable results). A point of interest was also to study the influence of the polymer concentration (5, 8, 10, 12 15 and 17%) and time of precipitation on the membrane permeability.

2 LITERATURE PART

2.1 History of membrane technology

Main steps in the development of the Membrane technology were collected and combined into the Table 2.1.

Table 2.1. Membrane technology development. [1,4]

Time of invention, year Name of author (or company)	Short description
1748 Abbe Nolet	Abbe Nolet offered a new word “osmosis” to describe permeation of water through diaphragm
19th century	Membranes used as laboratory equipment
1887 Van’t Hoff	Van’t Hoff used membranes to prove his “limit law”
about 1887 Maxwell	Maxwell, in his work about kinetic theory of gases used semipermeable membranes
1907 Bechhold	Bechhold invent the technique for preparing nitrocellulose membranes
1930s	In 1930 microporous membranes started to be commercially available
1930-1950s	Scientists tried to prepare microporous membranes from different polymers
1945 Kolf	Membranes found first industrial application: testing of the drink water. First company for membrane preparation created in USA: “Millipore Corporation” W.J. Kolf demonstrated artificial kidney
1950-1960s	Membranes used in the laboratories and some industries, because of their costs and problems in operations

One of the main steps in the development of the membrane technology was the discovery of Loeb-Sourirajan process.

Table 2.2. Membrane technology development after 1960. [1, 4]

Time of invention, year Name of author (or company)	Short description
1960s Loeb, Sourirajan	Discovery of Loeb-Sourirajan process. Commercialization of reverse osmosis. Artificial kidneys are commercially available
1966 Alex Zaffaroni, Alza Company	Membranes in drug delivery
1960-1980s	Several companies started to produce high-performance membranes. Membranes got a different forms (flat, tubular)
1980 Monsanto Cynara and Separex GFT 980s	Prism® membranes became industrial tools for gas separation (hydrogen separation). Cynara and Separex offered membranes for separating carbon dioxide from natural gas. GFT commercialized first pervaporation system. MF, UF, RO and electro dialysis became industrial separations processes all over the world.

2.2 Membrane classification

Two main types of membrane classification exist. At first, membranes can be divided into biological and synthetic. The last group includes inorganic and organic membranes.

The second method of classification is based on the morphology or structure.

According to structure, all the membranes are divided into porous and non porous.

Membranes can be symmetric (microporous or non porous) and asymmetric. Non porous symmetric membranes are the homogeneous films. Microporous symmetric membranes

are very similar to conventional filter but have difference in the structure of the pores: dramatically small, stray, randomly placed pores.[4]

This master thesis is focused on the second type: asymmetric membranes. Asymmetric membrane consists of the sub-layer (mechanical support with pores and micropores), covered by thin skin layer (selective barrier).The presence of these two layers is the main asymmetric membrane characteristic. Both layers can be made from the same material and by the same operation or can be separately manufactured. If the layers have been made from different materials, membranes are called composite. In composite asymmetric membranes, top-layer can be performed by polymer and sub-layer by inorganic material.[5]

Skin layer must be defect-free and as thin, as it possible, to achieve high flux and selectivity. [2] Because of layers properties, asymmetric membranes find a wide range of applications both in gas and liquid separation.

2.3 Types of the membrane processes

Main types of the membrane processes were collected and presented on the Figure 2.1:

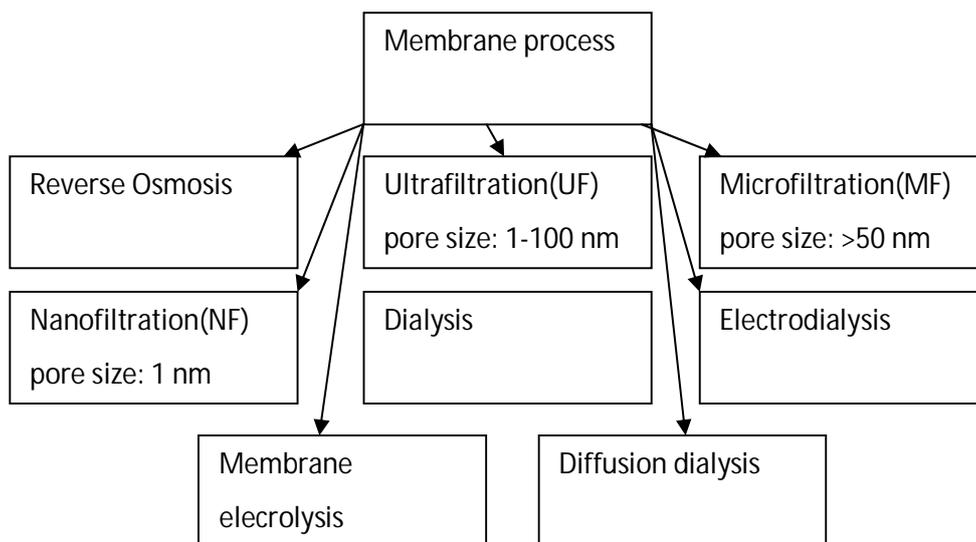


Figure 2.1. Schematic vision of the membrane processes.

According to literature data, UF, RO, MF and electrodialysis are the most popular separation processes for today. First three are pressure-drive processes and concept of separation (except the solution-diffusion model for RO) is practically the same for them. But the pore sizes in these three types of the membranes are different. MF can be used for colloidal particles and bacteria. UF retains macromolecules, such as proteins. RO (because of dramatically small pores) are used in desalination of the sea water.[4] “Work” areas for different membrane processes are presented on the Figure 2.2:

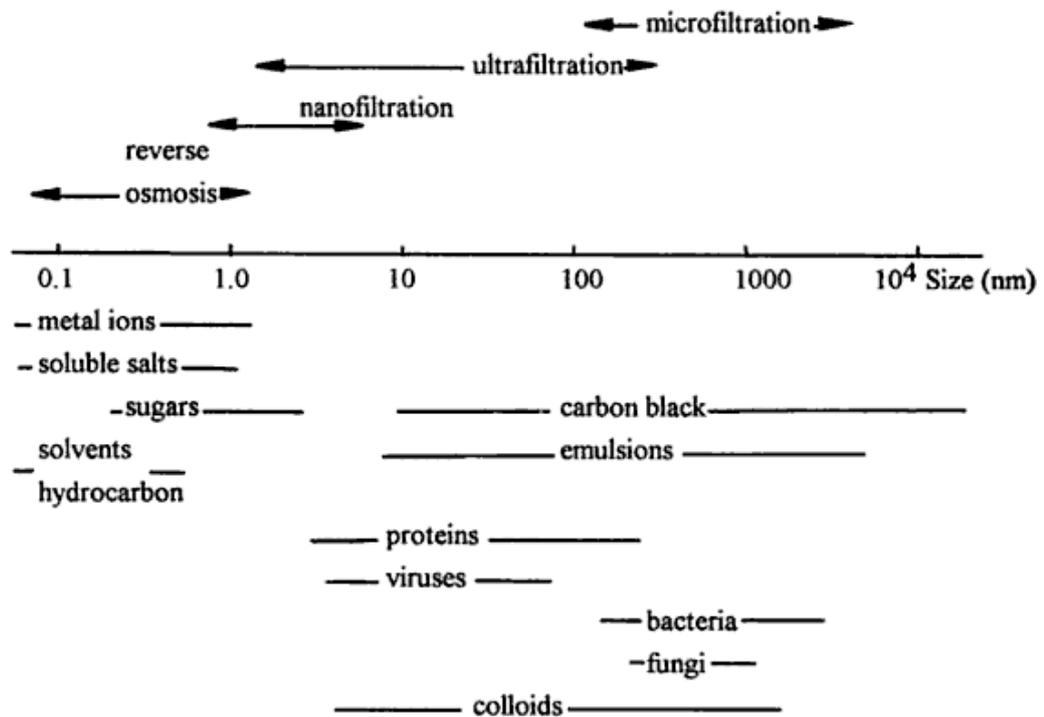


Figure 2.2. Schematic representation of the “work” areas of the different membrane types.[22]

All membrane processes can be also split into two groups: cross-flow and dead-end filtration. In the dead-end type liquid (feed stream and permeate) flows perpendicular to membrane surface. This type usually is used in the laboratories, for small amounts of liquid. MF membranes usually operate in the dead-end mode. Filtered particles in this case gathered near the membrane surface and form a filter cake. Because of it, flux through the membrane decrease with time. [6]

The cross-flow filtration is more popular, due to higher (much higher) flux through the membrane. Feed flows tangentially to the membrane surface and through. Permeate flows through the membrane surface, as it shown on Figure 2.3:

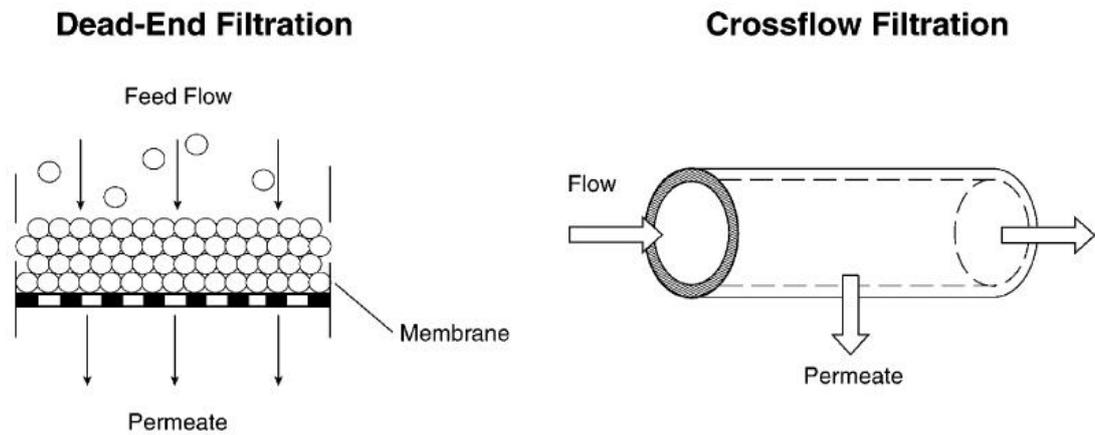


Figure 2.3. Schematic representation of dead-end and cross-flow filtration. [7]

2.4 Ultrafiltration

Ultrafiltration is popular method of the purification and separation. Ultrafiltration (UF) is a cross-flow filtration process. UF-membrane acts as a selective barrier: large molecules stay from one side and small ones pass through the membrane with solvent. Nowadays, UF-membranes representing a useful and commercially available tool for separation processes (especially in water treatment industry) and have a wide range of applications (medicine, biotechnology, food-industry, water-treatment, etc.)[8]

UF is a pressure-driven process. The typical operation pressure is 1-10 bars. Important characteristics for UF-membranes are: thickness of the top-layer and the pore structure of the skin-layer.

The main steps in the Ultrafiltration process development are presented in the Table 2.3:

Table 2.3. Steps in UF membranes development.

Time of invention, year Name of author (or company)	Short description
Bechold, Zsigmondy, Bachmann, Ferry, Elfort	First synthetic UF membrane is obtained from nitro cellulose. Bechold used term “ultrafilter”. Nitro cellulose filters were patented by Bachmann and Zsigmondy in 1918.
1920s	UF membranes are used as laboratory equipment.
1960	UF membranes found industrial applications.
1963 Loeb, Sourirajan, Michaels	UF asymmetric membranes from cellulose acetate were prepared for RO. Michaels described RO technique and prepared UF membranes from different polymers.
1969 Abcor Company	UF membranes tubular modules found their industrial application.
1973 Romicon	UF hollow fibers were commercialized.
1979-1980	Spiral-wounds UF membranes were commercialized.

Different types of polymers are used to prepare UF membranes (such as, polysulfone, polyetherimide, polycarbonate, cellulose acetate). As the result, researchers get the

membranes with good mechanical and chemical resistance, high-flux and selectivity and low operation costs. [9]

That is why, the main aim for nowadays is to obtain the UF-membrane with non-defected top- layer, extend the “membrane lifetime” and increase the flux and selectivity parameters.

The meaning of “membrane lifetime” is a work-time with high flux and selectivity. Membrane fouling strongly affects these two parameters. Today, membrane fouling is the reason that highly decrease “membrane lifetime”. Membrane fouling leads in a serious flux decline and increases the cost of membrane separation.

Interactions between the membrane and components of the solution cause the loss in flux with time. In other words, because of interaction between membrane and solution, we will have a pore blockage or membrane surface fouling. Membrane fouling can be inside the membrane pores (internal fouling) or on the surface (molecules accumulate near the membrane surface and decrease the flux).[9] The mechanism of the membrane fouling is presented on the Figure 2.4:

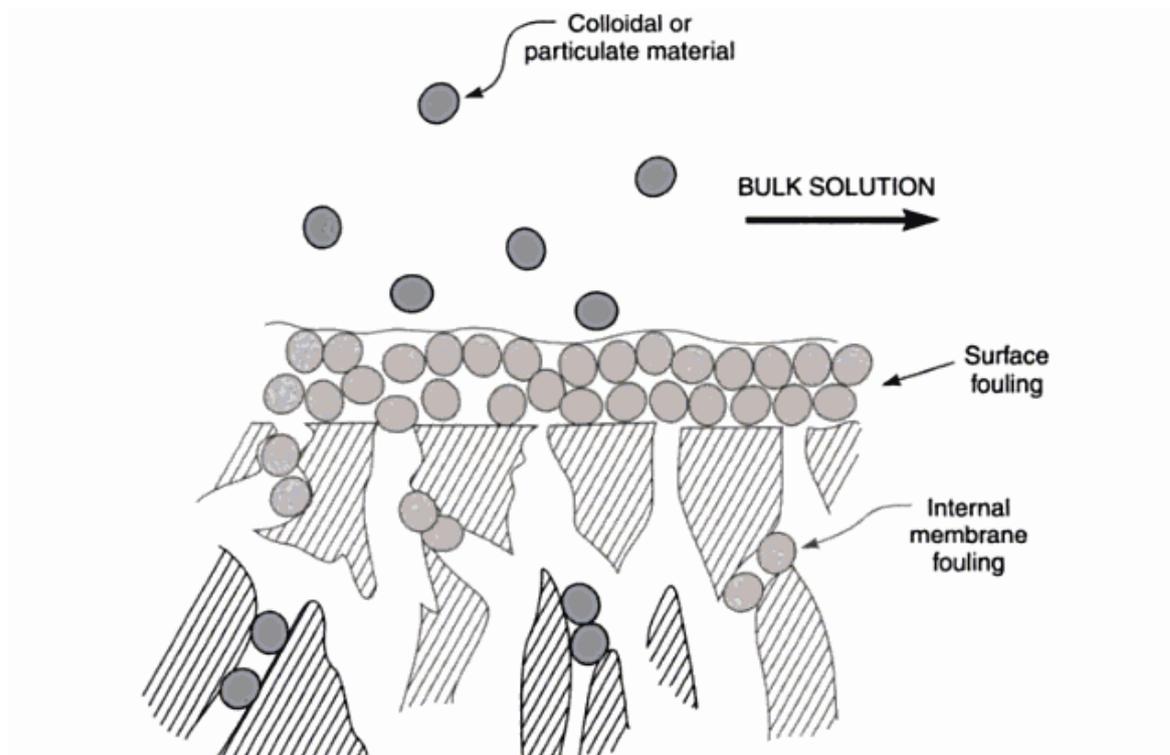


Figure 2.4. Schematic representation of the membrane fouling. [4]

Several researchers have shown, that membrane properties (morphology, charge, polymer type) play a huge role in fouling process. Also filtering solution properties (pH, concentration, molecular weight, density) have influence on the membrane fouling. [10] Pore blockage and flux decline happens because membranes are hydrophobic, have low surface porosity and wide distribution of the pore sizes.

Several methods have been used to prevent the loss in the permeate flux:

- Membrane pretreatment with surfactants or polymers to make membrane hydrophilic and to increase the flux. (Actually, it helps only for a short time)
- Prefiltration of the solution, to take away large-size molecules from it. (This method is not good, because of increasing in operation costs. And technically, one separation process divided into two.)
- Backwashing of the membrane pores. (This method can strongly decrease the time of the membrane life).[9]
- Optimization of operation conditions (*e.g.* cross-flow velocity).

Still, there is no good solution for this problem.

2.5 Description of membrane preparation methods

At first, it should be noted, that many materials (organic and inorganic) can be used to prepare membranes. There are a number of techniques, which allow preparing membrane from the current material. Preparation method always depends on the material and the type of membrane separation process. There are three types of the membranes, according to separation processes: porous, nonporous and liquid.

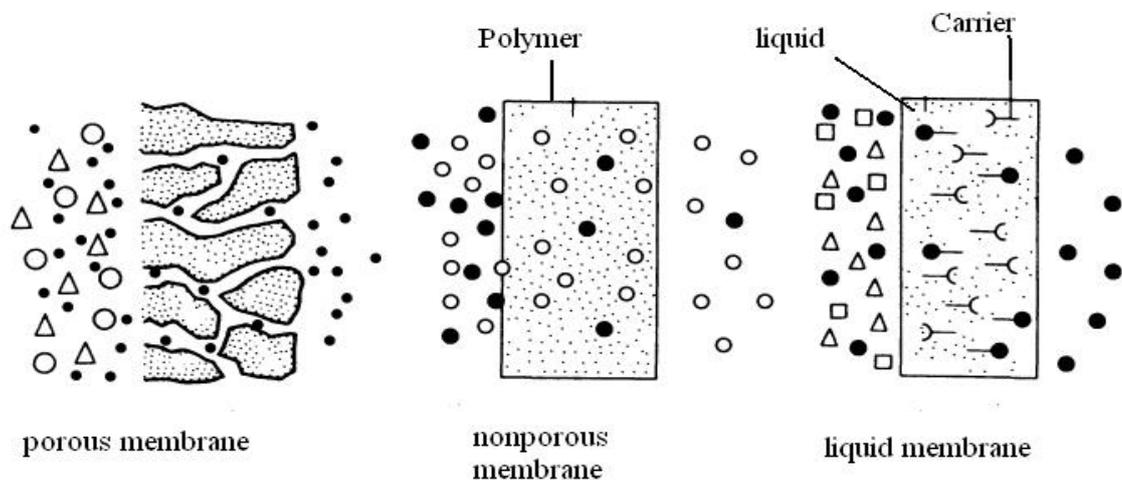


Figure 2.5. Schematic drawing of the three basic types of membrane.[1]

A number of different techniques are available to prepare porous polymeric films, such as sintering, stretching, track-etching, phase separation, sol-gel process, vapor deposition and solution coating. But, since the earliest 1950s (the invention of asymmetric polymer membranes by Loeb and Sourirajan [11]), phase inversion (polymer dissolved in a current solvent, settled on a suitable support and phase separation is introduced by a non-solvent casting solution) has been a common technique for the preparation of polymer membranes with asymmetric structure. After placing in coagulation bath (filled with non-solvent), polymer film is formed (solidified) and membrane with symmetric or asymmetric structure obtained. Structure depends on the polymer properties, coagulation conditions and type of ion-exchange between solvent in cast film and non-solvent in coagulation bath. Phase separation can be performed by liquid-liquid phase separation, solid-liquid phase separation, or both in the same time.[12]

Phase separation process can be divided into four principal methods:

- immersion precipitation /wet phase inversion (Polymer/solvent/non-solvent systems, where the polymer dissolved in suitable solvent and, after time, placed in coagulation bath with non-solvent. Non-solvent replaced solvent and thin polymer film formed) [13]
- vapor-induced phase separation (Thin film, made from solvent and polymer , positioned in a vapour atmosphere, which consist of solvent and non-solvent. Membrane formed, when non-solvent diffused into the film. And a high concentration of solvent in the vapour, prevents the evaporation of it from the film.) [1]
- dry-casting (This method is one of the major phase inversion techniques. In the method of dry-casting, homogeneous polymer solution consisting of solvent and non-solvent is cast on a support, after that the evaporation of the casting solution starts). [14]
- thermally-induced phase separation (This type of phase inversion is used, if the tradition way of membrane obtaining cannot be used (a lot of polymers have problems with solubility). In the thermally-induced phase separation process, only two-component system has been mainly used. It's the simplest technique, in which hot casting solution is

cooled down to phase separation and formed a membrane film. The main parameter in this process is the rate of cooling. It determines the membrane type. If the cooling rate is high, then membranes with small pores obtained. First, this process was commercialized by Akzo, with microporous membranes named Accurel®). [15, 16]

In the process of membrane formation two classes of phase inversion can be appropriate: dry phase inversion and wet phase inversion. The first one takes place in the atmosphere by evaporation of the vaporous solvent and/or by absorption of water as a non-solvent from the air moisture. The second one is carried out by embedding the polymer solution film into a coagulation bath of a non-solvent (water). Membrane formation takes place, when exchange of solvent (in the polymer film) and non-solvent has started. A combination of both processes, dry and wet, is also possible. The final membrane structure and its properties are depended on the experimental parameters[17]:

- the composition of the polymer solution
- the composition of the support material (glass, polymer, metal)
- the thickness of the cast polymer film
- the composition of the non-solvent or the mixture of non-solvents
- the temperature of the polymer solution, the coagulation bath or the environment
- the persistence of a dry phase inversion before the wet phase inversion (combination of processes)
- air moisture

In this case, structure of membranes, prepared by phase inversion methods, is highly depended on change in preparation conditions. [18]

2.6 Polysulfone (characteristics, properties)

Polysulfone, as polymer material, has been produced since 1960s. It is one of the important materials in the membrane technology. The reason for it is the appliance of polysulfone to a class of high-Tg polymers of high mechanical, thermal and chemical resistances. Polysulfones are used in the manufacture of asymmetric membranes with different pore sizes (microfiltration and ultrafiltration membranes) in the active layer.[19]

PSU polymers have an SO₂ group in the backbone. Four main types of this polymer exist: standard, polyaryl, polyether, polyphenyl. Standard PSU is produced by the reaction between the sodium salt of 2,2 – bispropane and 4,4´-dichloridiphenyl sulfone.

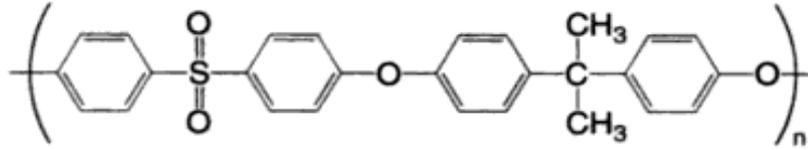


Figure 2.6. General chemical structure of PSU. [20]

There are different PSU, which are commercially available.

1) Udel® Polysulfone. It is non-toxic and has extensive regulatory clearance.

In its natural and unmodified form Tg= 190°C;

HDT/A (heat deflection temperature) = 174°C;

RTI (relative temperature index) = 160°C

Polysulfone has:

- excellent resistance to inorganic acids and bases
- withstands repeated exposure to steam sterilization
- resistance to hot water
- good thermal properties
- can be used for food, water and medical applications

Polysulfone Udel®

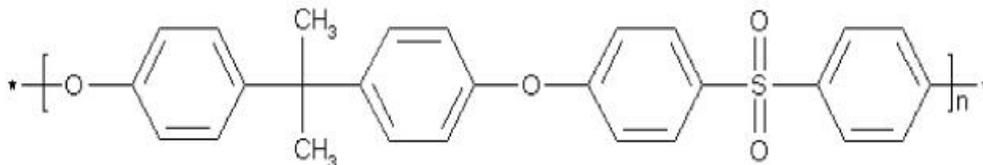
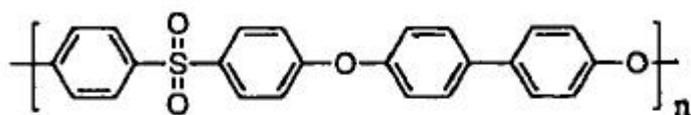
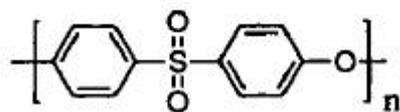


Figure 2.7. Chemical structure of Udel® Polysulfone. [19]



Radel®



Victrex®

Figure 2.8. Chemical structure of Radel® and Victrex® PSU. [21]

Although Udel®, Radel® and Victrex® are aromatic polysulfones containing an ether link in the backbone, they differ in the nature of the aliphatic carbon situated between the two *p*-phenolate rings. That is why, these PSU have difference in their physico-chemical properties. In the Udel® type, the carbon atom bears two phenyl groups and in the Victrex® type, aliphatic carbons are absent in the backbone.

2.7 Polysulfone membranes.

Polysulfone is one of the most popular materials for UF-membrane preparation (due to PSU properties, described in 2.4). Polysulfone membranes find applications in different industries: food industry (juice clarification), dairy industry, biotechnology, water purification, medicine. Also, according to Blanco *et.al* [19]: “Asymmetric polysulfone membranes are also used as a support layer for a thin film of cross-linked polyamide made by interfacial polycondensation of two bifunctional reactants dissolved in two non-miscible liquids in the preparation of reverse osmosis and nanofiltration membranes”.

PSU-membranes performed in two different forms: flat/sheet (used in this master thesis) and tubular. Spiral membranes are produced from flat membranes, and hollow fibers made from tubular form. [1] A form can be chosen due to the separation process (liquid concentration, particle size, time consuming, operation costs).

The main membranes characteristics are: flux (volume flowing through the membrane per unit area and time [1]) and selectivity (performed by retention in this master thesis). R varies between 100% and 0 %.

$$\text{Retention: } R = (1 - c_p / c_f) \times 100\% , \quad (1)$$

c_f – the solute concentration in the feed

c_p – the solute concentration in the permeate.

On other hand, PSU-membranes are sensitive to organic solvents and fouling by aqueous solutions (because PSU is hydrophobic material). They are easily fouled and have a poor water-flux through the pores. That is why polysulfone membranes need to be improved.

2.8 Effect of casting parameters on the membrane performance

In membrane technology, the most important factors to control are: membrane structure and thus membrane performance (flux and rejection). Both these factors are highly depended on different parameters in the manufacturing process (like polymer type and concentration, composition and temperature of coagulant and dope solution and evaporation time).

-Influence of polymer concentration.

In the work of Yoram Cohen *et al.* [22] showed that, that “flux decreases while solvent rejection rate increases with the increase of the concentration of casting solution.” It can be explained like: with increase in concentration, polymer molecules would be packed closer and the spiky chains would like to go into each other (form a coil), thus they take a configuration with smaller free space for solvent that is why smaller pores are formed across the film. And, “as a result, diffusive force increases remarkably and the permeation flux decreases largely while solvent rejection rate is increased.”[22]

In the work of Tweddle *et al.*[23] three types of polymer (Udel®, Radel® and Victrex®) were used for the flat polysulfone membranes formation. The main aim of this work was to determine the effect of polymer concentration on the membrane performance. Results of the work are presented on the Figure 2.9:

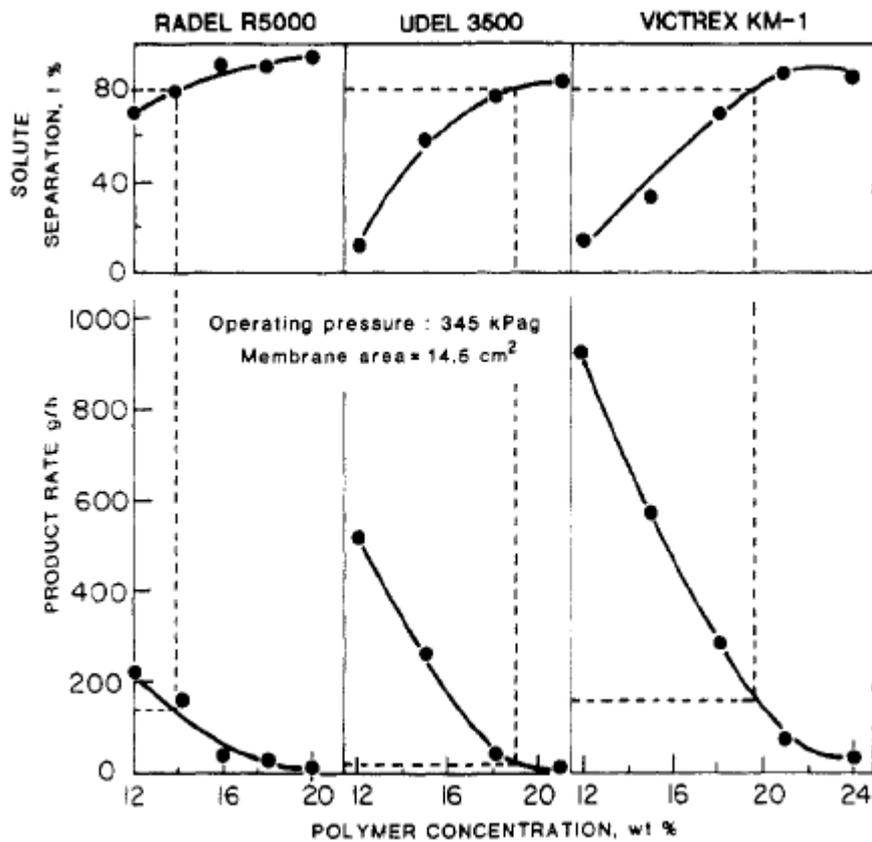


Figure 2.9. Effect of polymer concentration in the casting solution on the performance of resulting membranes. [23]

Tweddle *et al.*[23] made a conclusion, that the flux decreased while the polymer concentration increased. Also the solute separation increased. This effect can be explained with dependence of the membrane pore size from the polymer concentration. Example for this conclusion is showed on the Figure 2.10:

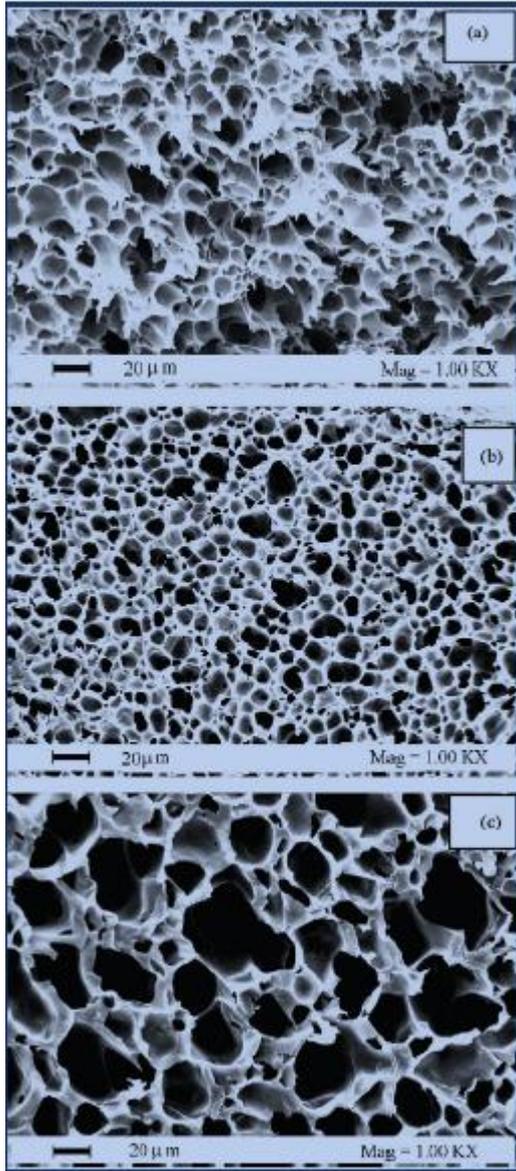


Figure 2.10. Effect of polysulfone concentration on membrane cells and pores. (a)30%,(b)20%,(c)15%. [24]

As can be seeing from the Figure 2.10 with increasing the polymer concentration the diameter of the membrane cells decreases.

It should be mentioned, that not only the concentration, but also the terms of preparing of the casting solution are very important. As it was noted in [25], interfusion of the polymer solution has an minor influence on the membrane structure. Membrane, prepared from good-mixed solution, has a small increase in flux and retention. The reason is that the interfusion can increase the solubility of the solids in the polymer solution, and make the

pore size distribution of the membrane uniform during the process of coagulation, that is why the retention will grow.

Also in the work of Cadotte *et al.* [26] was noted, that their casting solutions (PSU with N,N-dimethylformamide (DMF)) were not shelf-stable. Phase separation in this solutions occurred after two weeks at room temperature. Membranes prepared from that kind of solutions were strongly defected. That is why, the clarity of casting solution is indispensable for good membrane formation. Cadotte *et al.* [26] offered to keep casting solutions in a 65°C oven to prevent the phase separation.

-Influence of evaporation time.

The evaporation of the solvent from the casting solution has influence on the structure of the membrane surface. Thick and almost defect-free skin-layer is obtained, when evaporation time is increased. When the evaporation time is getting longer, permeation flux is decreased and the rejection increased. [27]

-Influence of the coagulation bath temperature.

In the work of Wei Li *et al.* [27] reported, that temperature of coagulation bath strongly affects the membrane pore size. If the temperature is high, then the flux through the obtained membranes increased while their rejection rate decreased. Movement of molecules in solvent and non-solvent becomes faster with growth of the temperature (i.e. diffusion rate increases). We can conclude that temperature of the coagulation bath affect on the membrane structure (pores formation). With high temperatures even macrovoids can form. That is why some scientists preferred to use ice-cold water as a coagulation media. [23]

In 1991, Lin Yizheng improved Loeb-Sourirajan preparation process for asymmetric membranes. He offered dual-bath coagulation method. In this method, casting solution is placed in two different coagulation baths in turn. The conditions (temperature and composition) of the first bath are changed. By this, pore structure and membrane surface structure can be controlled. [28]

-Influence of the additives.

According to Reuvers theory, there are two types of demixing, during the phase inversion process: delayed and instantaneous. Two different types of membranes are obtained from these processes.

Membranes, obtained with delayed demixing, have a macrovoid-free, porous structure with dense thick skin-layer. “Instantaneous” membranes have a porous structure with macrovoids. Skin-layer is thin and highly porous.

Additives are the shortest way to obtain the membrane with desirable properties: good structure and high flux. Additives can change phase separation kinetic, solvent capacity or thermodynamic properties of the solution. Different additives provide different effects. For example, some can form the macrovoids, another suppress their formation. [12]

Machado *et al.* [29] explained the influence of additives on the membrane structure. On the Figure 2.11 two types of the phase separation are presented. First simple separation takes place in the three-component system (solvent-polymer-non solvent). Second type of separation occurred in the systems with additives. Machado *et al.* [29] use the Reuvers theory as the explanation of these systems behavior.

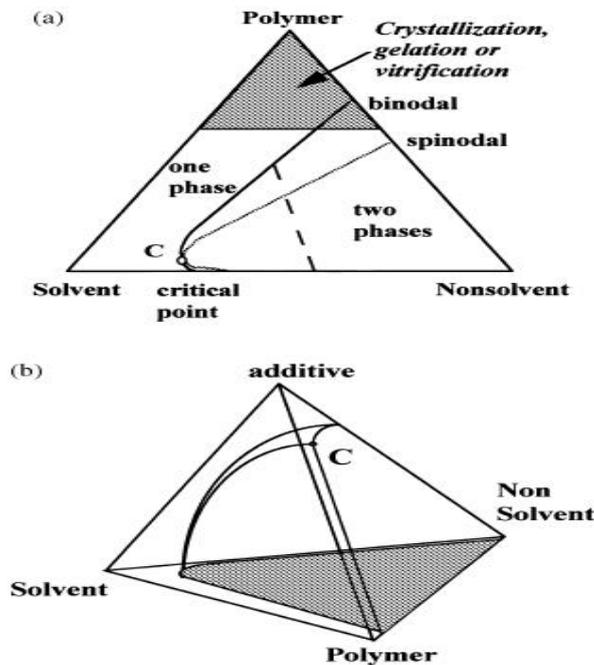


Figure 2.11. Schematic phase diagram. [29]

According to the work of Myeong-Jin Han *et al.* [30] additives plays a role of the non solvent for the membrane polymer. Through the decreasing of the polymer solubility additives reduce the diffusion between solvent and coagulation media. Because of this the pore formation improves.

As an example of the additives effect the results of Tweddle *et al.*[23] work can be presented: two types of membranes were obtained. First type was obtained from the casting solution polymer Victrex®-NMP (25%-75%). Second type was precipitated from the casting solution polymer Victrex®-NMP-PVP(polyvinylpyrrolidone)(25%-69%-6%).

Membranes from the first type gave following results for the retention and product rate: 90% and 15g/h. Membranes from the second type gave the same results for the retention but the product rate was much higher-115g/h.

Plenty of works were done about this topic. [31-33] And all scientists resulted, that non-solvent additives have a strong effect on the membrane structure and properties.

3. EXPERIMENTAL PART

3.1 Objectives

The aim of the experimental part of this work was to study how:

- concentration of the polymer in the casting solution affects the permeability and retention of the obtained membranes.
- precipitation time affects the membrane properties.

3.2 Materials

Casting solutions were prepared from polysulfone Udel® (polymer) and 1-methyl-2-pyrrolidone (solvent). Casting solutions of the following concentrations: 5%, 8%, 10%, 12%, 15%, 17%, and 20% of polysulfone were made. Data for the solution preparation is performed in the Table 3.1

Mass of the standard solution sample was 50 grams.

Table 3.1. Data for Polysulfone solutions.

Solution concentration, %	Polymer mass, gram	Solvent mass, gram
5	2,5	47,5
8	4	46
10	5	45
12	6	44
15	7,5	42,5
17	8,5	41,5
20	10	40

Solutions containing 5–20 wt. % of polymer in 1-methyl-2-pyrrolidone (NMP) were prepared by mild stirring for one day. Model compounds used for retention tests were polyethylene glycol or PEG (M=35000) and dextran (M= 150000).

Note: main testing solution was polyethylene glycol 200 ppm (in the water). But for the membranes with concentration of the polymer 8 % dextran was used.

3.3 Methods

Different methods and analyzing procedures are mentioned in the literature survey. In this thesis the procedure was as follow:

1. Preparation of the flat polysulfone membrane by immersion precipitation.
2. Testing of the obtained membranes (for flux) on the Amicon Millipore Model cell equipment.
3. Measuring the TC (total carbon) on the TOC-machine (Total Organic Carbon Analyzer).

In this thesis the membranes washing procedure did not carry out.

3.3.1 Membrane formation by phase inversion

In these experiments all the membranes were prepared manually. Solution with essential concentration were cast on the glass plate (support) with a special knife, and, after that, placed into coagulation bath. Coagulation bath was filled with 5 liters of distilled water. Temperature of water was the room temperature (22-23° C approximately). Minimal precipitation time was 5 minutes, maximum- 1 hour. 5, 10, 15, 45 and 60 minutes precipitation time was tested. After fixed time in the coagulation bath, membrane was cut with a knife and prepared for a next step.

The short description of the obtained membranes is shown in the Table 3.2

Table 3.2. Classification of the obtained membranes.

Membrane code	Solution concentration, %	Precipitation time, min	Name	Notes
M1	15	45	M1-15	
M2	15	5	M2-15	
M3	15	5	M3-15	
M4	10	5	M4-10	
M5	10	45	M5-10	
M6	10	5	M6-10	
M7	10	5	M7-10	
M8	10	10	M8-10	
M9	10	DRY	M9-10	*
M10	15	60	M10-15	
M11	15	DRY	M11-15	*
M12	15	15	M12-15	

(Table 3.2 continuation)

Membrane code	Solution concentration, %	Precipitation time, min	Name	Notes
M13	15	DRY	M13-15	gap
M14	10	45	M14-10	
M15	15	5	M15-15	
M16	10	5	M16-10	
M17	15	5	M17-15	
M18	15	5	M18-15	
M19	15	60	M19-15	
M20	15	5	M20-15	
M21	15	DRY	M21-dry	*
M22	15	45	M22-15	
M23	10	10	M23-10	
M24	15	45	M24-15	
M25	15	DRY	M25-dry	*
M26	15	10	M26-15	
M27	15	DRY	M27-dry	*
M28	10	45	M28-10	
M29	10	45	M29-10	
M30	10	DRY	M30-dry	*
M31	12	5	M31-12	
M32	12	5	M32-12	
M33	12	5	M33-12	
M34	12	10	M34-12	
M35	12	DRY	M35-dry	*
M36	12	60	M36-12	
M37	12	DRY	M37-dry	*
M38	12	10	M38-12	
M39	12	10	M39-12	
M40	12	60	M40-12	
M41	15	10	M41-15	
M42	15	10	M42-15	
M43	12	45	M43-12	
M44	12	45	M44-12	
M45	10	10	M45-10	
M46	10	15	M46-10	
M47	15	15	M47-15	
M48	15	60	M48-15	gap
M49	12	45	M49-12	
M50	12	15	M50-12	

(Table 3.2 continuation)

Membrane code	Solution concentration, %	Precipitation time, min	Name	Notes
M51	12	15	M51-12	
M52	10	60	M52-10	
M53	17	5	M53-17	*
M54	10	15	M54-10	
M55	17	60	M55-17	*
M56	10	15	M56-10	
M57	17	60	M57-17	*
M58	10	60	M58-10	
M59	8	5	M59-8	
M60	12	60	M60-12	
M61	12	15	M61-12	
M62	8	5	M62-8	
M63	17	60	M63-17	gap
M64	8	60	M64-8	
M65	8	5	M65-8	
M66	8	5	M66-8	
M67	8	15	M67-8	
M68	8	10	M68-8	
M69	8	15	M69-8	
M70	8	10	M70-8	
M71	8	15	M71-8	
M72	8	45	M72-8	
M73	8	45	M73-8	

Note: solution of the polymer starts to form membrane film immediately after the placing into the coagulation medium. Visible defects of the membrane top-layer are possible: bubbling, gaps and rippling. Conditions of the preparing have an influence on the membrane formation.

According to the work of Tweddle *et al.* [23], water in the coagulation bath has a strong influence on the membrane structure.

*- these membranes did not show any results for the flux.

A dry membrane means the membrane, which was made and dried in the air after that.

3.3.2 Preparation of the model solution for the filtration experiments

Testing solution for this work was 200 ppm polyethylene glycol. For preparation we took 0, 2 g of this material and dissolve in 1 liter of distilled water.

For the testing of 8% PSU membranes dextran solution (170000 g/mol) was used. Preparation steps were the same.

3.3.3 Flux determining (filtration experiments)

The Amicon Corporation Model cell was used to determine flux through the obtained membranes. The schematic representation of this filter is presented in Figure 3.1 , where:

1. Glass tube (350 ml).
2. Stirring unit.
3. Cover with bolts.
4. Gas-supply tube.
5. Vent for testing solution.
6. Temperature control valve.
7. Stirring unit controller.
8. Pressure indicator.
9. Gate valve.
10. Filter.
11. Permeate selection.
12. Glass (500 ml)
13. Dormant scale.

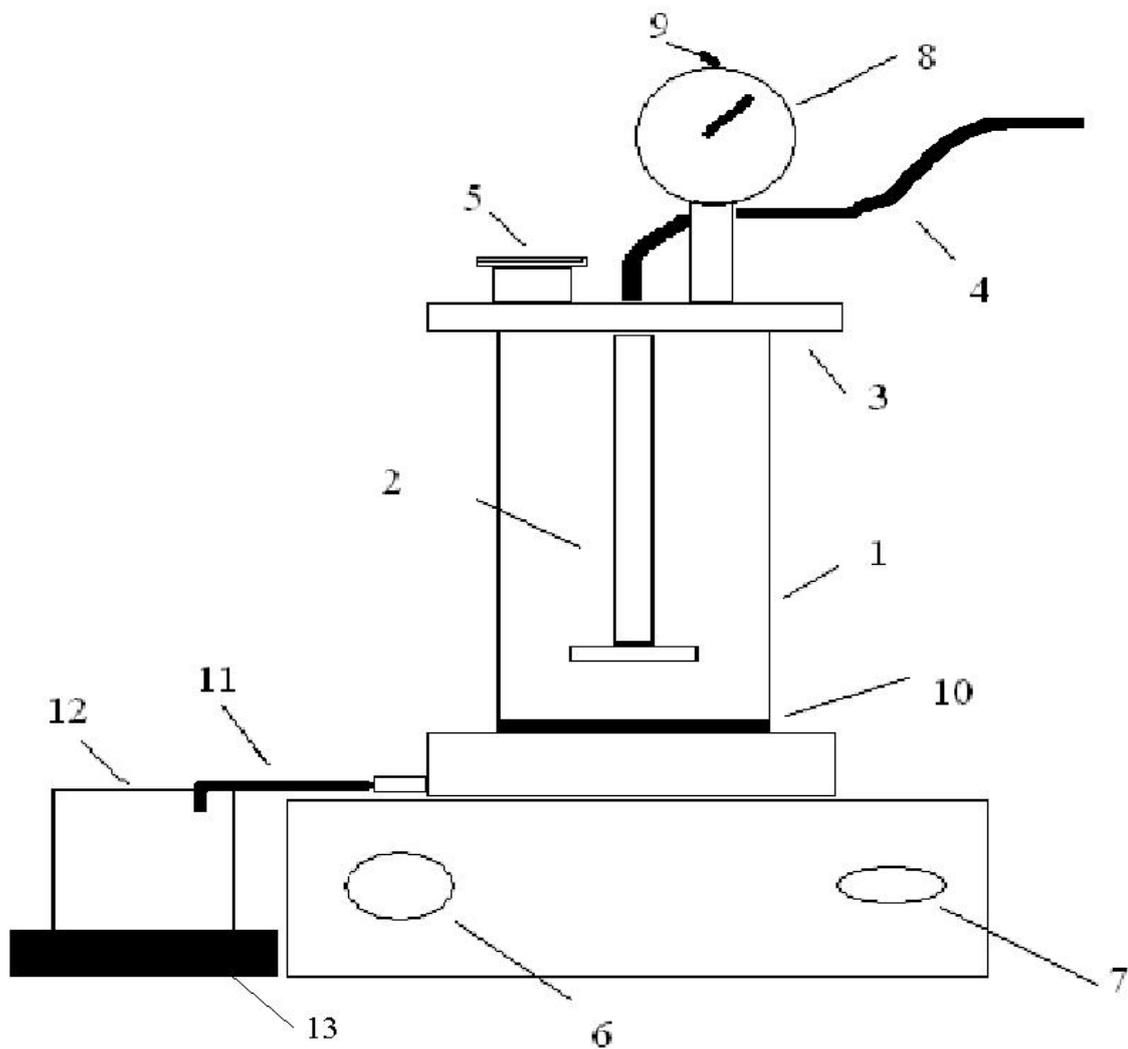


Figure 3.1. Schematic drawing of the Amicon Corporation Model cell.

Experiment description: We took the obtained membranes and cut round samples from them. These samples were placed in the cell on the filter(10) (to prevent membrane adhesion to the cell) and testing solution of the polyethylene glycol in water (300 g) was put in the cell(1). After that vent for testing solution was closed (5) and gas valve (4) was opened. The test was held with mixing (2) and rotation number of the stirring unit (2) was 500 revolutions per minute (solution, passed through the membrane is called permeate. Solution left in the cell is called concentrate).

Permeate (11) was collected in the glass (12) and weight was recorded every 30 seconds (13) to determine the flux through the membrane. After 225 g of the permeate was

collected, cell was stopped. Permeate and concentrate were placed in the plastic bottles, marked and put in the fridge until the TOC-measuring.

This operation was done for all obtained membranes and some dry samples.

Note: when cell is working, the gate valve (9) on the pressure indicator (8) should be turn left (to indicate the pressure). When we need to take the concentrate from the cell, gate valve (9) should be turn right to prevent oil-leak into the sample.

Operation pressure should be stable in the range from 0 to 6 bar. In this work we used pressure from 0, 4 bar to 3 bar (for the testing of the dry membranes), because high pressure can instigate the membrane break.

3.3.4 Analysis of the total carbon

For the measuring of the TC (Total Carbon) in the permeate and concentrate samples Shimadzu TOC-5050A (Figure 3.2) was used. All measurements were done automatically.



Figure 3.2. Photo of the Shimadzu TOC-5050A.

A very small amount of the permeate and concentrate samples of different membranes were placed into auto sampler ASI-5000A. Total Carbon (TC) was measured by injecting the sample into the sample port, which connected directly to a furnace, heated to 800°C. Carbon in the sample was converted into the carbon dioxide and detected by infra-red

detector. Detector produced the signal which was proportional to the carbon concentration. At the end of the session all the results were printed and used in the estimation of the membrane retention.

3.3.5 Example of the calculation

Calculation for current work was divided into 3 steps:

1) To determine the flux (2) we need to know operation membrane area (for this experiment it was 0,004 m²), mass of the permeate passed through the membrane in 30 seconds and operation time (in hours). As an example, calculation data for the membrane M62-8 is shown in the Table 3.3

$$\text{Flux [kg} \backslash (\text{m}^2\text{h)]} = \text{av.mass} \backslash 0,00833 \backslash 0,004 \quad (2)$$

Table 3.3. Calculation data for membrane M62-8.

time,h	mass,kg	av. mass,kg	flux (kg\h\m ²)	p, bar	permeability M62-8
0	0.02			0.4	0
0.00833	0.0492	0.0292	876	0.4	2190
0.01667	0.0742	0.025	750	0.3	2500
0.025	0.1016	0.0274	822	0.5	1644
0.03333	0.1261	0.0245	735	0.4	1837.5
0.04167	0.1531	0.027	810	0.4	2025
0.05	0.1793	0.0262	786	0.4	1965
0.05833	0.2042	0.0249	747	0.4	1867.5

For the flux estimation average mass was taken (av. mass= mass₂- mass₁, mass₃- mass₂...mass_{n+1}-mass_n)

2) After the flux determining, permeability was estimated with formula (3).

$$\text{Permeability} = \text{Flux} \backslash \text{pressure (operating pressure)} = \text{kg} \backslash \text{h} \backslash \text{m}^2 \backslash \text{bar} \quad (3)$$

3) Retention.

Data, which was collected from TOC-analyzer, was used to calculate the retention (1).

4. RESULTS AND DISCUSSION

4.1 Filtration test results

Filtration experiments were carried on the Amicon Corporation Model cell.

4.1.1 Precipitation time 5 minutes:

In 5-minute precipitation time 8, 10, 12 and 15% Polysulfone solution (PSU) was used in the membrane preparation.

-8% PSU membranes had top-layer with defects (gaps, bubbles). They were weak and extremely thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 2500 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$ till 1644 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$. Filtration time was about 4, 5 minutes.

-10% PSU membranes had defects in the top-layer. They were weak and thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1400 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$ till 300 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$. Filtration time was about 7 minutes.

-12% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1000 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$ till 500 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$. Filtration time was about 11 minutes.

-15% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thick. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 400 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$ till 200 $\text{kg} \cdot \text{h} / \text{m}^2 \cdot \text{bar}$. Filtration time was about 11 minutes.

Results of the filtrations are shown on the Figure 4.1:

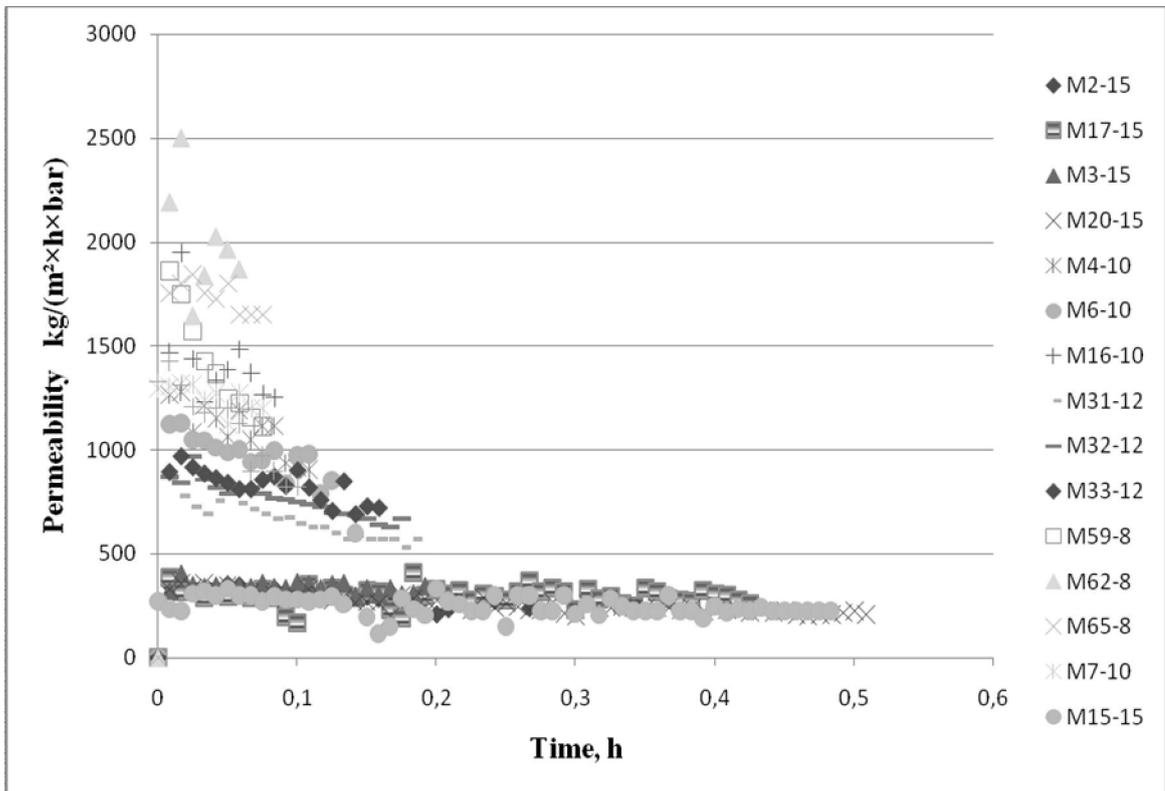


Figure 4.1. Permeability as a function of filtration time for the 5-minutes precipitation membranes.

Note: As we can see from the Figure 4.1, the most stable membranes are the 15% PSU membranes. These samples showed low (in the range from 0 to 400 $\text{kg}\backslash\text{h}\backslash\text{m}^2\backslash\text{bar}$) permeability for PEG 200 ppm. The best permeability results (in the range 1500-2500 $\text{kg}\backslash\text{h}\backslash\text{m}^2\backslash\text{bar}$) were achieved with 8% PSU solution membranes.

4.1.2 Precipitation time 10 minutes:

Visual inspection did not show any difference between 5 and 10 minute precipitation PSU membranes. Permeability of the 8% and 10% PSU membranes were almost the same when 10 minutes precipitation time was used.

-8% PSU membranes had top-layer with defects (gaps, bubbles), were weak and extremely thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 2250 $\text{kg}\backslash\text{h}\backslash\text{m}^2\backslash\text{bar}$ till 1200 $\text{kg}\backslash\text{h}\backslash\text{m}^2\backslash\text{bar}$. Filtration time was about 6 minutes.

-10% PSU membranes had defect top-layer, were weak and thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1750 kg\ h\ m²\bar till 1065 kg\ h\ m²\bar. Filtration time was about 7 minutes.

-12% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1065 kg\ h\ m²\bar till 660 kg\ h\ m²\bar. Filtration time was about 9,5 minutes.

-15% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thick. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 465 kg\ h\ m²\bar till 247 kg\ h\ m²\bar. Filtration time was about 25,5 minutes.

Results of the filtrations are shown on the Figure 4.2

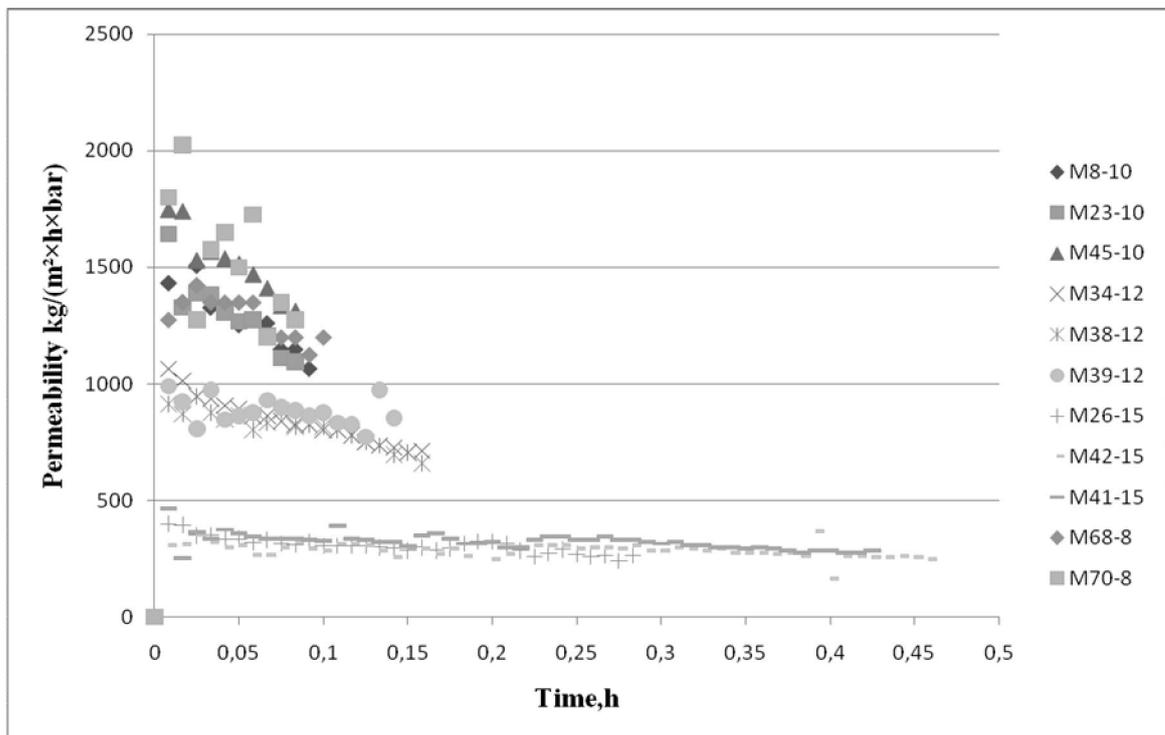


Figure 4.2. Permeability as a function of filtration time for the 10-minutes precipitation membranes.

Note: According to Figure 4.2, 10% PSU membranes have shown the best results for the Permeability.

4.1.3 Precipitation time 15 minutes:

Permeability of the 8% and 10% and 12% PSU membranes were almost the same.

-8% PSU membranes had top-layer with defects (gaps, bubbles). They were weak and extremely thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1860 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 975 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 7 minutes.

-10% PSU membranes had defect top-layer, were weak and thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1800 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 630 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 9 minutes.

-12% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1100 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 360 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 10,5 minutes.

-15% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thick. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 430 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 225 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 27,5 minutes.

Results of the filtrations are shown on the Figure 4.3:

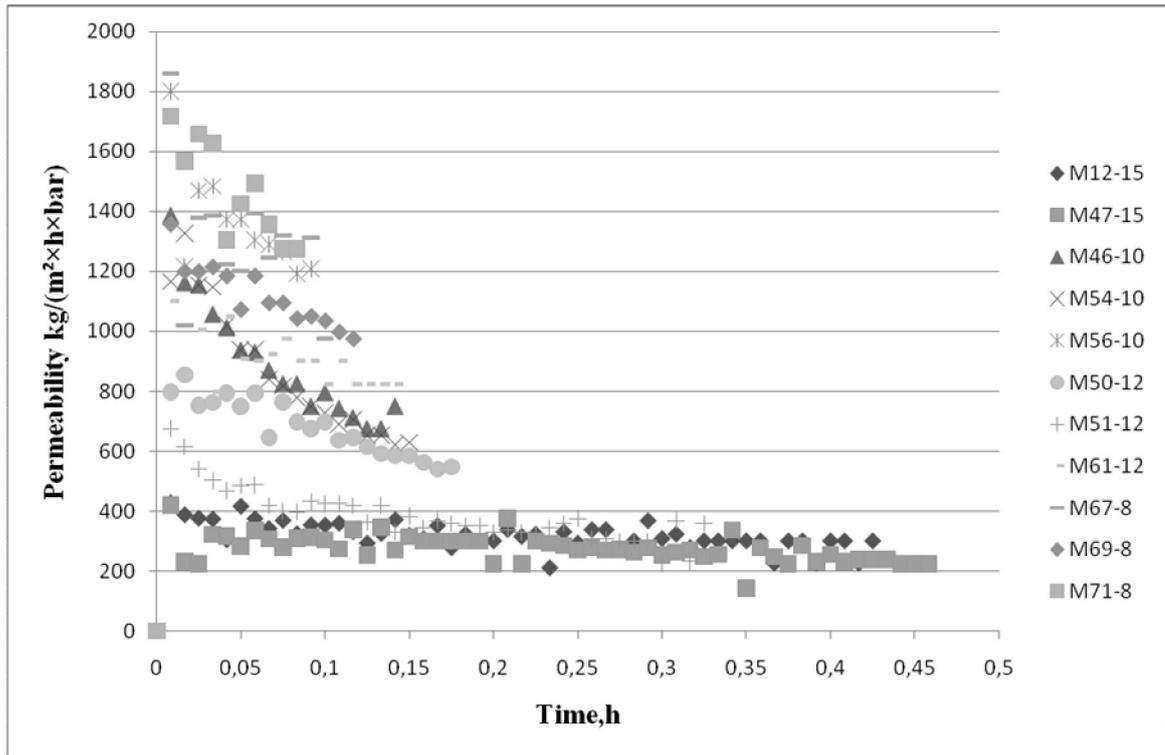


Figure 4.3. Permeability as a function of filtration time for the 15-minutes precipitation membranes

4.1.4 Precipitation time 45 minutes:

Permeability of the 8% and 10% PSU membranes were almost the same.

-8% PSU membranes had top-layer with defects (gaps, bubbles), were weak and extremely thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from $1650 \text{ kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}^{-1}$ till $1125 \text{ kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}^{-1}$. Filtration time was about 5,5 minutes.

-10% PSU membranes had defect top-layer, were weak and thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from $1875 \text{ kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}^{-1}$ till $1130 \text{ kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}^{-1}$. Filtration time was about 5,5 minutes.

-12% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thin. According to permeability and retention measurements,

permeability through these membranes was high and lay in the field from 1100 kg\ h\ m²\bar till 740 kg\ h\ m²\bar. Filtration time was about 9,5 minutes.

-15% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thick. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 460 kg\ h\ m²\bar till 130 kg\ h\ m²\bar. Filtration time was about 22,5 minutes.

Results of the filtrations are shown on the Figure 4.4:

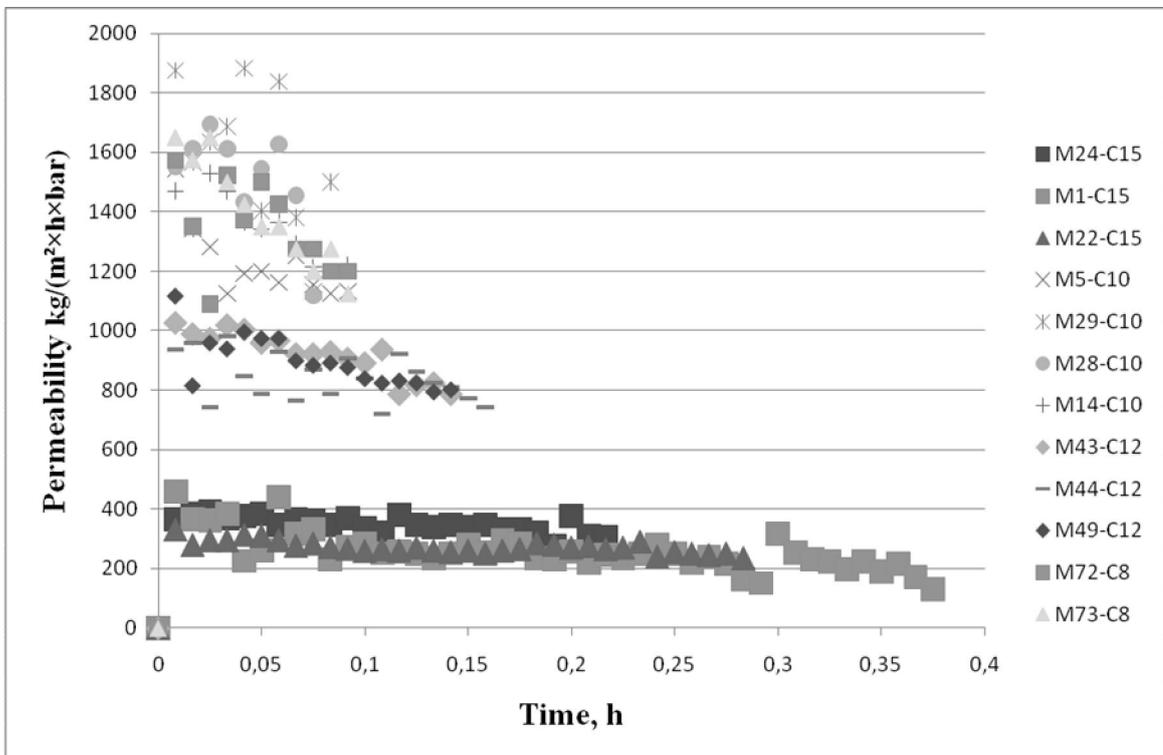


Figure 4.4. Permeability as a function of filtration time for the 45-minutes precipitation membranes

4.1.5 Precipitation time 60 minutes:

Permeability of the 8% and 10% PSU membranes were almost the same.

-8% PSU membranes had top-layer with defects (gaps, bubbles). They were weak and extremely thin. According to permeability and retention measurements, permeability

through these membranes was high and lay in the field from 2500 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 1400 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 3,5 minutes.

-10% PSU membranes had defect top-layer, were weak and thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1350 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 375 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 16, 5 minutes.

-12% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thin. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 1130 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 675 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 10 minutes.

-15% PSU membranes had the top-layer without any visible defects, had good mechanical resistance and were thick. According to permeability and retention measurements, permeability through these membranes was high and lay in the field from 580 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$ till 230 $\text{kg} \cdot \text{h} \cdot \text{m}^2 \cdot \text{bar}$. Filtration time was about 19 minutes.

Results of the filtrations are shown on the Figure 4.5:

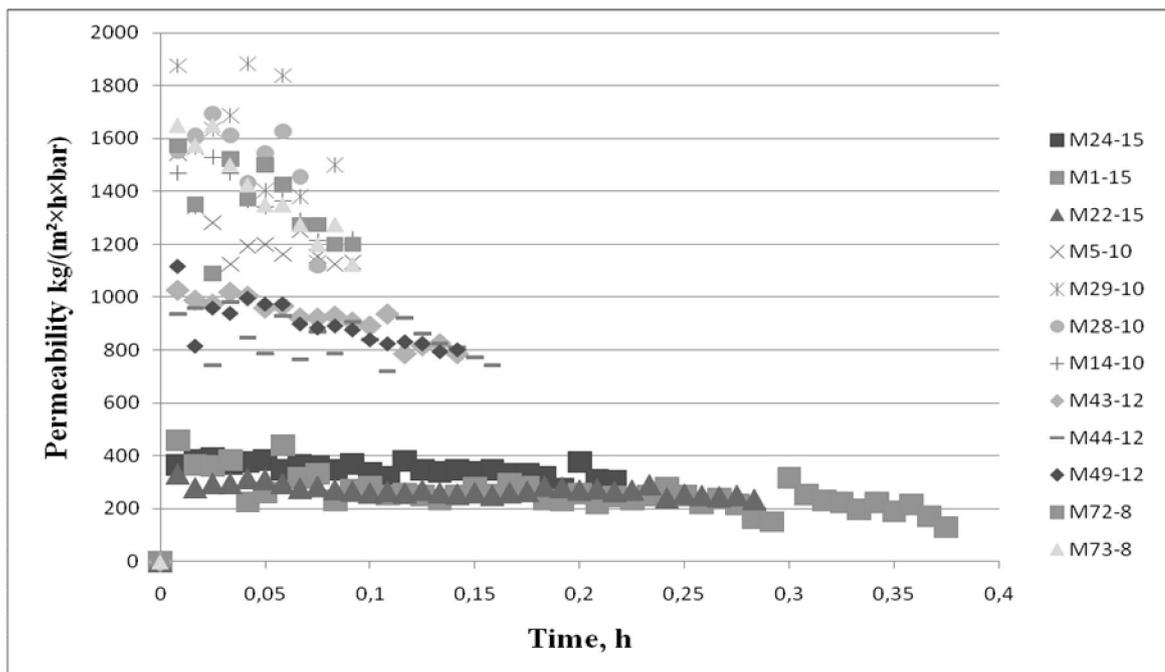


Figure 4.5. Permeability as a function of filtration time for the 60-minutes precipitation membranes.

4.2 Retention Results

Note: We took the results of flux at 0,075 hours for the all membranes from the Figures 4.1-4.5, and combined them in the Tables 4.1-4.5:

- Retention results for the 5-minutes precipitation membranes:

Table 4.1. Retention for the 5-minutes precipitation membranes.

Membrane	Retention,%	Flux(kg\h\m ²) 0,075 h
M3-15	no result	216
M18-15	62	200
M17-15	14	132
M2-15	6	201
M20-15	2	120
M15-15	36	120
M4-10	1	447
M6-10	1	381
M16-10	0	507
M31-12	2	276
M32-12	1	315
M33-12	2	342
M59-8	1	444
M62-8	0	-
M65-8	-14	660

8%, 10%, 12% PSU membranes showed negative retention results. It can be explained with size of the molecules in the test-solution (polyethylene glycol). But when solution was changed (Dextran), the results remained the same.

Another idea was about the washing operation that did not carry out for the obtained membranes. Usually, membranes prepared by immersion precipitation are washed with water to delete the monomer compounds from the membrane pores. These compounds have an influence on the retention, because they increase the concentration of the carbon in the permeate. That is why, without this operation, during the TOC-measuring wrong data can be obtained. Some calculations were made and placed in Appendix 1.

- Retention results for the 10-minutes precipitation membranes:

Table 4.2. Retention for the 10-minutes precipitation membranes.

Membrane	Retention,%	Flux(kg\h\m ²) 0,075 h
M26-15	4	189
M41-15	14	135
M42-15	22	120
M34-12	1	336
M38-12	-1	354
M39-12	1	360
M8-10	2	459
M23-10	2	444
M45-10	3	534
M68-8	-10	480
M70-8	12	540

The best retention was achieved with 15% of polysulfone membranes.

- Retention results for the 15-minutes precipitation membranes:

Table 4.3. Retention for the 15-minutes precipitation membranes.

Membrane	Retention,%	Flux(kg\h\m ²) 0,075 h
M12-15	19	147
M47-15	23	112
M50-12	7	306
M51-12	27	160
M61-12	-16	390
M46-10	2	330
M54-10	2	327
M56-10	1	507
M67-8	7	528
M69-8	- 24	438
M71-8	-6	510

8%, 10%, 12% PSU membranes showed negative retention results. The best retention was achieved with 15% of polysulfone membranes.

- Retention results for the 45-minutes membranes:

Table 4.4. Retention for the 45-minutes precipitation membranes.

Membrane	Retention,%	Flux(kg\h\m ²) 0,075 h
M24-15	3	216
M14-15	0	486
M22-15	3	170
M43-12	1	369
M44-12	2	348
M49-12	2	354
M5-10	1	462
M29-10	2	453
M28-10	1	447
M14-10	0	486
M72-8	-2	510
M73-8	0	480

All the membranes showed bad retention results.

- Retention results for the 60-minutes precipitation membranes:

Table 4.5. Retention for the 60-minutes precipitation membranes.

Membrane	Retention,%	Flux(kg\h\m ²) 0,075 h
M10-15	3	168
M19-15	14	179
M36-12	1	390
M40-12	1	369
M60-12	0	324
M52-10	16	198
M58-10	1	441
M64-8	-6	

The best retention was achieved with 15% of polysulfone membranes.

4.3 Results for the Permeability and Retention.

In this part results for the Permeability and Retention for the different membranes were collected and combined into the tables 4.6-4.10:

-5 minute precipitation:

Table 4.6. Total results for the 5 minute- precipitation membranes.

Membrane PSU concentration, %	Permeability, (kg\h\m ² \bar)	Retention, %	Time of filtration, min
8	2500-1644	-14-1	4.5
10	1400-300	0-1	7
12	1000-500	1-2	11
15	400-200	2-62	11

From this data we can make a conclusion that only 15% membranes work with polyethylene glycol solution.

-10 minute precipitation:

Table 4.7. Total results for the 10 minute- precipitation membranes.

Membrane PSU concentration, %	Permeability, (kg\h\m ² \bar)	Retention, %	Time of filtration, min
8	2250-1200	-10-12	6
10	1750-1065	2-3	7
12	1065-660	-1-1	9.5
15	465-247	4-22	25.5

In this testing group 15% membranes also showed the best results.

-15 minute precipitation:

Table 4.8. Total results for the 15 minute- precipitation membranes.

Membrane PSU concentration, %	Permeability, (kg\h\m ² \bar)	Retention, %	Time of filtration, min
8	1860-975	-24-7	7
10	1800-630	1-2	9
12	1100-360	-16-27	10.5
15	430-225	19-23	27.5

In this testing group 10% membranes also showed results, but for high permeability their retention results were too small.

-45 minute precipitation:

Table 4.9. Total results for the 45 minute- precipitation membranes.

Membrane PSU concentration, %	Permeability, (kg\h\m ² \bar)	Retention, %	Time of filtration, min
8	1650–1125	-2-0	5.5
10	1875–1130	0-2	5.5
12	1100–740	1-2	9.5
15	460–130	0-3	22.5

In this testing group all membranes showed bad retention results.

-60 minute precipitation:

Table 4.10. Total results for the 60 minute- precipitation membranes.

Membrane PSU concentration, %	Permeability, (kg\h\m ² \bar)	Retention, %	Time of filtration, min
8	2500–1400	-6	3.5
10	1350–375	1-16	16.5
12	1130–675	0-1	10
15	580–230	3-14	19

In this testing group 10 and 15 % membranes showed the best results.

After observing the Tables 4.6-4.10 following conclusion can be made:

- With increasing the polymer concentration in the casting solution permeability declined while the retention rose (negative retention can be explained with the manual method of the membrane preparation or with influence of the feed solution composition).

4.4 Membranes description.

8% PSU membranes and 10% PSU membranes are not good even for the laboratory work. They are easily tearing and thin. Negative retention through these membranes can be explained with molecules form of the polyethylene glycol. As it was described in the literature part of this master thesis, these linear molecules can “sneak” through the membranes. However, mass balances showed that some materials were also came off from the membrane matrix during the filtration. This increased the carbon concentration in the permeate sample and might be the reason for negative retentions.

-5% PSU/solvent.

Membrane from this solution did not form. This happens, because concentration of the polymer was too small.

-8% PSU/solvent.

Membranes, prepared from this solution were extremely thin. Easy to tear, they did not have any mechanical stability. These membranes had defects of the top-layer.

-10% PSU/solvent.

Formed membranes were with defects of the top-layer and without mechanical strength.

-12% PSU/solvent.

Thin membranes were formed without any defects of the top-layer, but films did not have any mechanical resistance.

-15% PSU/solvent.

Membranes from this solution were thin but they had a good mechanical resistance. Top-layer of these films was without any defects.

-17% PSU/solvent.

Thick, mechanically resistant membrane films were formed without any top-layer defects.

-20% PSU/solvent.

Thick, not transparent and mechanically resistant membrane films were formed without any top-layer defects.

Note: 17% PSU/solvent and 20% PSU/solvent membranes did not show any result during filtration test, because the pressure (4 bar) was not enough high.

4.5 Discussion

To determine the potency of the obtained membranes, results of this master thesis work were compared with the results of another works in this field.

The work of Soon Hong Lee *et al.* [34] was about the preparation of polysulfone membranes. The concentrations of the polymer in the NMP were: 2,5%, 5%, 10%, 12,5%, 15%, and 20% (almost the same, as in this work). Results of the comparison presented in the Table 4.11:

Table 4.11. Results of comparison.

PSU concentration, %	This work results	Soon Hong Lee et al. results [34]	Notes
2.5	no membrane formation	no membrane formation	
5	no membrane formation	no membrane formation	
10	imperfect and weak	imperfect and weak	
12	without any defects	satisfactory thick and dense	*
15	satisfactory thick and dense	satisfactory thick and dense	
20	very thick and dense	very thick and dense	

* In this case, Soon Hong Lee *et al.* [34] used 12,5% PSU concentration in the casting solution. Maybe, the difference in the membrane formation results can be explained with this.

Solution of PEG 35000 in the water (200ppm) was used in this master thesis work for the testing of the Retention. Soon Hong Lee *et al.* [34] used solution of PEG 18500 in the water (2000ppm). Retention results are presented in the Table 4.12:

Table 4.12. Results for the retention tests. [34]

PSU concentration, %	Retention, %
2.5	-
5	-
10	91
12.5	95
15	93
20	-

According to the article [34], membranes with 12,5 % of PSU showed the best results for the Retention and flux (flux was 45 l/m²/h). Whereas the best results for this work membranes with 15% of PSU showed. It can be explained with the difference in the testing solutions and operation pressure (almost 4 bar in [34]).

5 CONCLUSIONS

The aims of the work in this thesis were:

- to study the process of the flat polysulfone membranes formation by immersion precipitation.
- to determine the influence of the polymer concentration in the casting solution on the membrane properties
- to find out, how the precipitation time affects the membrane properties

In this work 73 flat polysulfone membranes were obtained by immersion precipitation. Precipitation time and polymer concentration in the casting solution were studied as factors, affecting the membrane permeability and retention.

According to experimental and literature data polymer concentration in the casting solution plays a huge role in the membrane performance. Membranes that were obtained from the solution with high concentration of PSU (15%, 12%) had a non-defect membrane surface and good mechanical resistance. Membranes with low concentration of PSU (8% and 10%) had defect on the surface (gaps, wrinkles). It can be concluded that with the increase of polymer concentration the membrane quality increases. But high concentration of the polymer in the casting solution is not good: membranes with 20% PSU did not show any results during the filtration experiments (because operating pressure was not high enough).

Membrane properties (permeability and retention) also depend on the polymer concentration in the casting solution. Samples with low concentrations (8%, 10%) showed high results for the permeability but low (sometimes negative) results for the retention. The best retention results, 67% for PEG (30000 g/mol), were measured with the 15% PSU membranes. It can be concluded, that with the increase of polymer concentration in the casting solution the permeability decreases whereas retention increases.

Also, it should be noted, that the membranes with low concentration of polysulfone in the casting solution, have “open” pores. These membranes (8%, 10% PSU membranes) had high permeability (in the range 2000-1500 l/m²/h) distinctive to microfiltration, but not to ultrafiltration.

Low retention can be explained with absence of washing operation for the 15% PSU membranes and structure for the 8-10% PSU membranes. Because of this, some monomer compounds fouled the membranes pores and distort the retention test results.

Precipitation time also has an influence on the membrane structure and properties. The highest retention was measured for membranes with short precipitation time (5 minutes). But there is no distinct dependence between precipitation time and membranes retention. This question need to the further work.

As the result of this work, 15% PSU membranes with good retention properties were precipitated. To improve the permeability through these membranes different additives can be used.

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APPENDIX 1

Table. Retention results for the membranes with a glance to mass balance.

Membrane code	Retention. %	Retention results (with a glance to mass balance), %
M1	27	9
M2	9,9	6
M3	No result	No result
M4	-3,9	1
M5	1,6	1
M6	-3,9	1
M7	0	1
M8	1	2
M10	7	3
M12	43	19
M14	1	0
M15	67	36
M16	1	0
M17	33	14
M18	83	62
M19	67	14
M20	4,4	2
M22	12	3
M23	1,6	2
M24	7	3
M26	12	4
M28	0,2	1
M29	-0,3	2
M31	-3	2

(Table continuation)

Membrane code	Retention. %	Retention results (with a glance to mass balance), %
M32	-7	1
M33	-8	2
M34	-12	1
M36	-0,5	1
M38	-3	-1
M39	-9,7	-1
M40	2	1
M41	37	14
M42	43	22
M43	4	1
M44	-4	2
M45	-3	3
M46	3	2
M47	40	23
M49	2	2
M50	-7	7
M51	54	27
M52	32	16
M54	3	2
M56	-2	1
M58	1,9	1
M59	-7,3	1
M60	1,4	0
M61	-84	-16
M62	24,4	0

(Table continuation)

Membrane code	Retention. %	Retention results (with a glance to mass balance), %
M64	-33,9	-6
M65	-5,6	-14
M66	-10,3	-20
M67	3,4	7
M68	-3,9	-10
M69	-55,5	-24
M70	15,7	12
M71	-3,3	-6
M72	0,72	-2
M73	0,85	0