Solvent and Thermally Resistant Polymeric Membranes for Different Applications

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Committee members: Professor Peng Wang, Professor Alexander Rothenberger, Professor Robert Schucker
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ABSTRACT

Solvent and Thermally Resistant Polymeric Membranes for Different Applications

Taghreed Adnan Jalal

In this work polymeric materials were developed to be used as a solvent and heat resistance membrane for different applications.

In ultrafiltration, poly (ether imide sulfone) membranes were manufactured by combining phase inversion and functionalization reaction between epoxy groups and amine modified polyether oligomers (Jeffamine®). Polysilsesquioxanes or oligo silsesquioxanes containing epoxy functionalities were in-situ grown in the casting solution and made available for further reaction with amines in the coagulation/annealing baths. Water permeances up to 1500 l m$^{-2}$ h$^{-1}$ bar$^{-1}$ were obtained with sharp pore size distribution and a pore diameter peak at 66 nm, confirmed by porosimetry, allowing 99.2 % rejection of γ-globulin. The membranes were stable in 50:50 dimethylformamide/water, 50:50 N-methyl pyrrolidone/water and 100 % tetrahydrofuran.

In pervaporation, Novel hydrophobic Hyflon®/Extem® and Hyflon®/PVDF were developed and investigated for ethylene glycol dehydration and n-butanol dehydration respectively. For ethylene glycol different Extem® concentrations were evaluated with regard to both flux and amount of water in the permeate side. Eighteen (18) wt% gave more than 90 wt% water in the permeate. Increasing feed temperature from 25 to 85°C increased the water flux from 31 to 91 g m$^{-2}$ h$^{-1}$ when using 5 wt% water in ethylene glycol as feed. The water flux of 40 wt%
water:ethylene glycol at 45°C was found to be 350 g m$^{-2}$ h$^{-1}$. And for n-butanol dehydration the coating protocols for thin defect-free Hyflon® selective layer on the PVDF support was optimized. Water and n-butanol transport was measured, analyzing the effect of operating conditions. The water flux through the newly developed membranes was higher than 150 g m$^{-2}$ h$^{-1}$ with selectivity for water higher than 99 wt%. The membrane application can be extended to other solvents, supporting an effective and simple method for dehydration with hydrophobic membranes.

In membrane distillation, PVDF membrane before and after coating with Hyflon® were examined for ionic liquid dehydration on 23.6 mS cm$^{-1}$ feed concentration. Different feed temperatures and flow rates were evaluated for flux as well as rejection.

High flux was obtained at 70°C and increased at high flow rate from 2 Kg m$^{-2}$ h to 10 Kg m$^2$ h.
ACKNOWLEDGMENTS

I am thankful to Allah who in his infinite blessing and mercy has guided me to complete this PhD.

Big thanks to my respected professor Dr. Suzana P. Nunes for giving me this opportunity to work under her supervision and for her helping and supporting in my PhD journey here in KAUST. Thanks to my kind research group for their helping and for their supporting.

I would like to thank my respected committee members: Dr. Peng Wang and Dr. Alexander Rothenberger from KAUST and to Dr. Robert Schucker from SABIC.

I will extend my thankful to SABIC Company for sponsoring me and for SABIC people for their support.

My great parent, my sweet daughter, my sweet sisters and brothers, the whole family and my friends’ thank you for your love, care and your support.
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<td>Ultrafiltration</td>
</tr>
<tr>
<td>PV</td>
<td>Pervaporation</td>
</tr>
<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyetherimide</td>
</tr>
<tr>
<td>PVDF®</td>
<td>Poly (vinylidene fluoride)</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrrolidone</td>
</tr>
<tr>
<td>DCMD</td>
<td>Direct contact membrane distillation</td>
</tr>
<tr>
<td>SGMD</td>
<td>Sweeping gas membrane distillation</td>
</tr>
<tr>
<td>AGMD</td>
<td>Air gap membrane distillation</td>
</tr>
<tr>
<td>VMD</td>
<td>Vacuum membrane distillation</td>
</tr>
<tr>
<td>Extem®</td>
<td>Poly (ether imide sulfone)</td>
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Chapter 1: Introduction

1.1 General Introduction

Membranes are attractive for many industrial applications due to their benefits. They save energy, are easy to scale-up, can operate at ambient temperature, are technically simple to operate, and no chemical additives are required, which make them environmentally friendly. Membrane technology is utilized to separate mixtures of gases and vapours, miscible liquids and dissolved solids and solutes from liquids. Therefore we can see membranes in different processes including microfiltration (MF), ultrafiltration (UF), dialysis, vapour permeation (VP), reverse osmosis (RO), electrodialysis (ED), membrane electrolysis (ME), gas separation (GS), membrane distillation (MD), nanofiltration (NF), membrane contactor (MC) and pervaporation (PV). Membranes play an important role in various industrial applications. They are used to produce potable water from the sea, concentrate or purify macromolecular mixtures in food and drugs industries, minimize air pollution and treat hazardous industrial waste, separate proteins and microorganism, and are present in wide range of processes in chemical industries.

The propitiate membrane to use must have good permeation flux, good selectivity, long life time and low cost.

Some membrane processes involve organic solvents or require increased temperature. This is a challenge due to the demand of an appropriate membrane material with specific properties such as high thermal stability, mechanical properties and solvent resistance. Organic solvents are utilized in many sectors
like: automotive industry, agriculture, cleaning industry, food processing and packaging, paints coatings, personal care, pharmaceutics and household.

Polymeric membranes are the most widely used as they are inexpensive materials for fabrication and easy to scale up\textsuperscript{2-4}, but their thermal stability and solvent resistance are poor due to their nature. Ceramic membranes can better withstand aggressive solvents and high temperature systems, but their fragility, shaping properties and relatively high prices limit their application. Moreover, their upscaling is less straightforward than in case of polymeric membranes\textsuperscript{5}. Therefore, more research is required in order to make polymeric membranes thermally and solvent stable.

In my research, I focused on the development of new polymeric membrane materials possessing thermal and solvent stability for ultrafiltration, pervaporation and membrane distillation.
1.2 Theory and Background

1.3 Membrane definition

A membrane is a selective barrier between two phases, which allows one or more components of a mixture to pass through, while the other components will remain in the feed side. The permeation of a selective component can be caused by differences in concentration, pressure, temperature or electrical potential as driving force\(^6\) (Scheme 1.1). The performance of a membrane is determined by its permeance, estimated by the rate of mass or volume flowing through the membrane per unit area (m\(^2\)) per unit time (h) per pressure difference, and by its selectivity, which is generally expressed by retention or separation factor, depending on the applied process\(^6\). Membranes can be classified according to its material, morphology, geometry, transport theory, driving force and others. Table 1.1 summarize some general classification of membranes\(^7\)

![Scheme 1.1 basic principle of membrane permeation.](image)

\(\Delta C, \Delta P, \Delta T, \Delta E\)
<table>
<thead>
<tr>
<th>Membrane separation</th>
<th>Membrane type</th>
<th>Feed phase/permeate phase</th>
<th>Driving force</th>
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<tr>
<td>Microfiltration</td>
<td>Symmetric and asymmetric microporous</td>
<td>Liquid/liquid</td>
<td>Hydrostatic pressure</td>
<td>Clarification, sterile filtration\textsuperscript{8}</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Asymmetric microporous</td>
<td>Liquid/liquid</td>
<td>Hydrostatic pressure</td>
<td>Separation of macromolecular solutions\textsuperscript{9}</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Asymmetric</td>
<td>Liquid/liquid</td>
<td>Hydrostatic pressure</td>
<td>Separation of small organic compounds and selected salts from solutions\textsuperscript{10}</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Asymmetric, composite, homogeneous skin</td>
<td>Liquid/liquid</td>
<td>Hydrostatic pressure</td>
<td>Separation of micro-solutes and salts from solutions\textsuperscript{11}</td>
</tr>
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<td>Gas permeation</td>
<td>Asymmetric or composite, homogenous or porous polymer</td>
<td>Gas/gas</td>
<td>Hydrostatic pressure concentration gradient</td>
<td>Separation of gas mixtures\textsuperscript{12}</td>
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<tr>
<td>Process</td>
<td>Membrane Type</td>
<td>Phase Combination</td>
<td>Mechanism</td>
<td>Description</td>
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<tr>
<td>Dialysis</td>
<td>Symmetric microporous</td>
<td>Liquid/liquid</td>
<td>Concentration gradient</td>
<td>Separation of micro-solutes and salts from macromolecular solutions(^6)</td>
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<tr>
<td>Pervaporation</td>
<td>Asymmetric, composite non-porous</td>
<td>Liquid/vapor</td>
<td>Concentration gradient, vapour pressure</td>
<td>Separation of mixtures of volatile liquids(^{13})</td>
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<td>Composite non-porous</td>
<td>Vapor/vapor</td>
<td>Concentration gradient</td>
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<td>Membrane distillation</td>
<td>Microporous</td>
<td>Liquid/vapor</td>
<td>Temperature</td>
<td>Separation of water from non-volatile solutes(^{15})</td>
</tr>
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<td>Electrodialysis</td>
<td>Ion exchange, homogeneous or microporous polymer</td>
<td>Liquid/liquid</td>
<td>Electrical potential</td>
<td>Separation of ions from water and non-ionic solutes(^{16})</td>
</tr>
<tr>
<td>Electrofiltration</td>
<td>Microporous charged membrane</td>
<td>Liquid/liquid</td>
<td>Electrical potential</td>
<td>De-watering of solutions of suspended solids(^{1})</td>
</tr>
</tbody>
</table>

In my research I focused on three of them: ultrafiltration, pervaporation and membrane distillation.
1.3.1 Membrane transport theory

Two models represent the permeation process through membranes (Scheme 1.2) pore-flow and solution diffusion model.

![Scheme 1.2 Membrane transport theory](image)

1.3.1.1 Pore-flow model

In porous membrane depending on pore size of the membrane, molecular size of the feed components, molecular orientation and operation condition the separation will affect. A hydrostatic pressure difference between two phases caused the separation. It is based on the molecular sieving where one component with smaller size will permeate through the pores while the other will exclude and stay as retentate like in microfiltration and ultrafiltration\(^6\). There is a tradeoff between pore size which is directly proportional to flux as well as to molecular weight cut-off and between the rejections as it shown in Scheme 1.3.
1.3.1.2 Solution diffusion model

In non-porous dense membrane, membrane materials, chemical potential of feed components and membrane free volume are the factors can affect the separation performance. The difference of concentration or chemical potential gradient which caused difference in vapor pressure caused the separation. Five steps represented the transportation mechanism in reverse osmosis, pervaporation and gas separation by polymeric membranes\(^\text{18}\) (i) Diffusion of the permeant through the boundary layer on the feed side of the membrane, (ii) absorption of the permeant from the feed into the upstream side of the dense membrane, (iii) diffusion of the permeant across the membrane, (vi) desorption of that component from the membrane and (v) evaporation of that component into the gas phase on the downstream side of the membrane\(^\text{19}\). The permeation depends on the chemical interaction or solubility between membrane material and feed component; operating conditions and on permeate diffusivity which is vary for different polymeric systems and materials. In different polymeric membrane materials the transport depends on 1. The free volume within the polymer and 2. On the

Scheme 1.3 Relation between pore size, flux, molecular weight cut-off and selectivity.
segmental mobility of the polymer chain which affected by extent of unsaturation, degree of crosslinking, degree of crystallinity and nature of substitutions\textsuperscript{20}. Different polymeric systems can be rubbery or glassy. For rubbery polymer the most significant characteristics are unsaturation, segmental mobility and the amount of free volume between molecules while in glassy polymers hard and brittle moiety with restricted chain mobility are the diffusion characteristics. The permeability of the component defined as diffusivity multiplied by solubility. In the case of non-glassy (rubbery) polymer the decrease of diffusivity is less than the increase of solubility, therefore the contribution of solubility is dominant, while for glassy polymer the permeability is determined mainly by diffusion contribution\textsuperscript{21}.

1.3.2 Membrane filtration operation modes

Two operation modes can be used for filtration: cross flow filtration mode, where the feed is pumped parallel to the membrane surface, and dead end filtration mode or batch filtration, where the feed flow through the membrane by applied pressure perpendicular to the membrane surface\textsuperscript{6} (Scheme 1.4).

![Scheme 1.4](image)

Scheme 1.4 Different membrane filtration designs a. dead-end mode, b. cross-flow mode.
1.3.3 Ultrafiltration (UF)

UF is a size exclusion-based pressure-driven membrane separation process. It is typically used to remove macromolecules with size of 1,000 to 300,000 molecular weight, for a wide range of applications. Some of them are listed in Table 1.2.

Table 1.2 Applications of UF

<table>
<thead>
<tr>
<th>process</th>
<th>Separation / Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrophoretic paint</td>
<td>Rinse water process, recycle of paint to dip tank to allow reuse of rinse water</td>
</tr>
<tr>
<td>Cheese whey</td>
<td>Concentration/fractionation of proteins from lactose and inorganics</td>
</tr>
<tr>
<td>Juice clarification</td>
<td>Removal of haze components from apple juice</td>
</tr>
<tr>
<td>Textile industry sizing agents</td>
<td>Recovery of polyvinyl alcohol after scouring of woven good or treatment of dye effluents</td>
</tr>
<tr>
<td>Polymer latex</td>
<td>Latex emulsions concentration from wastewater</td>
</tr>
<tr>
<td>Water treatment</td>
<td>Concentration before sludge dewatering</td>
</tr>
<tr>
<td></td>
<td>Treatment of wool scour effluent for water recovery and re-use</td>
</tr>
<tr>
<td>Food</td>
<td>Treatment of food processing waste water</td>
</tr>
<tr>
<td>Biological</td>
<td>Concentration of proteins, enzymes and hormones</td>
</tr>
<tr>
<td></td>
<td>Treatment of blood and plasma</td>
</tr>
<tr>
<td>Pharmaceutical</td>
<td>Manufacturing of antibodies</td>
</tr>
</tbody>
</table>

1.3.3.1 Membrane material

An effective membrane for UF must have good porosity for high permeability and high rejection, thermal stability, chemical resistance, mechanical stability, less tendency to foul, ease of cleaning and low cost.
In literature sets of polymers are used for UF membranes\textsuperscript{6}, such as:

- Cellulose acetate (CA) high hydrophilic material, very sensitive to thermal, chemical and biological degradation and it must be used at room temperature and pH range 4 - 6.5 because of high tendency of hydrolysis\textsuperscript{31}.

- Poly acrylonitrile (PAN) is a common used material for UF\textsuperscript{32}, has good solvent and thermal stability.

- Polysulfone (PSf) and polyethersulfone (PES) are well known as ultrafiltration membrane material and as a support\textsuperscript{33} to prepare composite membrane materials.

- Poly (phthalazine ether sulfone ketone) (PPESK) is a novel amorphous polymer, which has high thermal stability, good chemical stability, solubility and superior mechanical strength\textsuperscript{34}.

- Polyimide (PI) and polyetherimide (PEI) exhibit high chemical\textsuperscript{35}, mechanical, thermal and hydrolytic stability.

- Poly (vinylidene fluoride) (PVDF) is a hydrophobic material, which shows good thermal and chemical stability and it can be soluble in DMF, DMAc, TEP and NMP.

1.3.3.2 Membrane fabrication

Asymmetric membranes consist of a thin top selective layer, followed by a sublayer with larger pores, as it shown in Figure 1-1, normally prepared by phase inversion.
Phase inversion is a liquid-liquid demixing process, where a homogenous polymer solution can be transformed into a membrane by different techniques:

- Precipitation from vapor phase: After casting, a homogeneous polymer solution is placed in a saturated vapor of non-solvent atmosphere and the vapors diffuse into casting film forming porous membrane.
- Precipitation by solvent evaporation: After casting a homogeneous polymer solution, the solvent starts to evaporate in presence of inert gas to avoid existence of water vapor and the dense homogeneous membrane forms.
- Thermally induced phase separation: the polymer solution is cooled to achieve phase separation.
- Immersion precipitation: a cast polymer solution submerged in coagulation bath contains non-solvent (water) and after the exchange between solvent and non-solvent the asymmetric membrane is produced.
Most phase inversion membranes are prepared by immersion precipitation\textsuperscript{6} where the exchange between solvent and non-solvent takes place. To understand the mechanism of membrane fabrication three components are essential (Scheme 1.5)\textsuperscript{36}: polymer, solvent and non-solvent, where the last two should be miscible. In the beginning, the homogenous solution of polymer and solvent is stable.

Demixing by nucleation and growth (A) when polymer solution changed its composition to metastable region or by spinodal decomposition when the polymer solution go to instable region (B) is possible. For nucleation and growth case, for dilute polymer solution a nuclei of the polymer-rich phase is formed. In this case latex type structure with low mechanical strength is formed while for concentrated polymer solution a nuclei of the polymer lean phase is formed. In the other hand the case of spinodal demixing, the phase separation takes place at the surface of the film due to a decline of polymer chemical potential which make a direction of net movement of the polymer perpendicular to the surface results a high polymer concentration in the surface layer (solidification of the concentrated phase) followed by porous membranes with interconnected pores. Instantaneous precipitation occur when the affinity between polymer solvent and non-solvent precipitation path is high.
The membrane structure is affected by factors such as type of polymer, solvent and non-solvent, composition of casting solution, composition of coagulation bath, temperature and evaporation time. Thus there are many parameters that have to be taken into consideration, while preparing polymeric membrane by phase inversion:

- **Nature of polymer**: Thermally and chemically resistant polymers mainly related to the chemical structure of the polymer and the presence of certain structural elements, like aromatic groups, imide bonds or F-atoms.

- **Additives**: Adding extra component to the casting solution has been widely used. Additives can work as a pore former, increase solution viscosity or accelerate the phase inversion process. Inorganic salts like LiCl or organic
like PVP or PEG in the casting solution will improve the membrane morphology and properties\textsuperscript{39,40}.

- Selection of solvents and evaporation time: It strongly affects morphology and properties of cast membranes. Increasing the evaporation time or choosing more volatile solvents in the casting solutions will partially evaporate the solvent before immersion step, thus a top-layer with high polymer concentration will be formed. Then, after immersion, the exchange in the underneath layer will be slower. This influences also the formation of macrovoids\textsuperscript{37,41}.

- Coagulation medium: A strong mutual interaction between solvent and non-solvent increases the exchange rate, enhances the demixing process, and leads to formation of membranes with a thin top-layer and a porous sublayer with macrovoids\textsuperscript{6}. Adding some solvents into aqueous coagulation bath or increasing coagulation bath temperature will help to obtain highly porous membrane, but with less macrovoids\textsuperscript{37}. In the presence of the additives, high temperature promotes formation of an interconnected pore structure. Therefore high permeation rate can be obtained\textsuperscript{42}.

1.3.4 Pervaporation

Pervaporation (PV) is a process to separate liquid mixtures when it partially vaporized and transported through dense membrane under vacuum in the downstream side\textsuperscript{43}. The transport depends on vapor pressure of feed components, downstream pressure, feed temperature and membrane material and thickness. The advantages of using PV are the low operating costs and relatively simple
operation in contrast to adsorption and distillation processes. It can be used in
different applications, for dehydration of aqueous-organic mixtures\textsuperscript{44}, remove trace
amount of organic solvents from aqueous solution\textsuperscript{45} and for separate organic
solvent from organic solvent mixtures\textsuperscript{46}.

1.3.4.1 Membrane materials

The membrane materials are essential in this process in order to have high
separation performance, because they affect the sorption and the diffusion of the
transported permeant. According to that, the choice of the proper membrane
materials depends on the type of mixture and the component that we want to
separate. The requirements for the membrane used in pervaporation in general
are the permeance, which depends on intrinsic permeability and thickness of the
membrane, selectivity and high thermal and chemical stability\textsuperscript{13}.

1. Dehydration of organic solvents is the main application in the industry for
water selective membrane. Different materials have been used for wide
range of different organic aqueous solutions for example:

- In dehydration of aqueous ethanol solution different membranes
  based on polymeric materials have been used, such as cellulose
  acetate\textsuperscript{47}, perfluorinated polymer on polyacrylonitrile support\textsuperscript{48},
  polyacrylonitrile with polyvinylpyrrolidone\textsuperscript{49}, chitosan, chitosan
  acetate and crosslinked chitosan membrane\textsuperscript{50} and carbon
  nanotubes into poly (vinyl alcohol)\textsuperscript{51}.

- In dehydration of aqueous isopropanol solution hydrophilic chitosan-
  modified polybenzoimidazole\textsuperscript{52}, polybenzoxazinone\textsuperscript{53} and poly(vinyl
alcohol) crosslinked with trimesoyl chloride\textsuperscript{54} are an example of materials for this application.

2. Recovery of volatile organic compound from aqueous solution is mainly used for pollution control and recovery of organic compounds

- For ethanol recovery from aqueous solution polydimethylsiloxane (PDMS)\textsuperscript{55}, polydimethylsiloxane on polyamide support\textsuperscript{56}, polyvinylidenefluoride\textsuperscript{57} and poly(1-trimethylsilyl-1-propyne)\textsuperscript{58}, etc. are some materials used for ethanol recovery.

- For butanol recovery from aqueous solution polydimethylsiloxane on ceramic support\textsuperscript{59}, poly(1-trimethylsilyl-1-propyne)\textsuperscript{60} and poly(ether block amide)\textsuperscript{61} are used.

3. Separation of organic compounds from organic mixtures can be categorized according to the type of solvents or organic compound into:

- Polar/non-polar mixtures, for example in methanol/benzene mixtures. Some works reported the use of perfluorosulfonic acid on Teflon\textsuperscript{62}, cellulose, poly(vinyl alcohol), cellulose acetate and cellulose tri-acetate with acrylic acid\textsuperscript{63}.

- Aromatic/ Alicyclic mixtures, for example in toluene/cyclohexane mixtures. Some works are reported using faujasite-type zeolite membrane\textsuperscript{64}, polystyrene with polyacrylamide\textsuperscript{65} and polyurethane\textsuperscript{66}.

- Aromatic/aliphatic mixtures, for example in benzene/n-hexane mixtures. Some works reported the use of poly (vinyl alcohol)\textsuperscript{67},
polyurethane\textsuperscript{68}, sulfonyl-containing polyimide\textsuperscript{69} and high density polyethylene plasma grafted by glycidyl methacrylate\textsuperscript{70}.  

- Aromatic isomers, for example \( p \)-xylene/\( m \)-xylene. Some works report using poly (vinyl alcohol) filled with \( \beta \)-cyclodextrin\textsuperscript{71} and \( \alpha \)-alumina-supported zeolite MFI membranes\textsuperscript{72}.

1.3.5 Membrane distillation

Membrane distillation (MD) is a thermal based process to separate water from ions, macromolecules, colloids, cells and non-volatile compounds and remove trace volatile organic compounds from water\textsuperscript{15}. The transport occurs through porous membranes and depends on the vapor pressure of the components of feed solution. The advantages of MD are its relatively low cost, energy saving capability, no need for larger vapor space compared to distillation and reverse osmosis and better rejection\textsuperscript{15}.

1.3.5.1 Membrane distillation process

A heated feed solution contacts one side of the hydrophobic membrane surface and only vapor will pass through the membrane. Four different configurations can be applied, according to the permeate composition, flux and volatility\textsuperscript{15} illustrate in Scheme 1.6:
Scheme 1.6 Membrane distillation configurations: (a) Direct Contact Membrane Distillation (DCMD); (b) Air Gap Membrane Distillation (AGMD); (c) Vacuum Membrane Distillation (VMD) and (d) Sweep Gas Membrane Distillation (SGMD)\(^7^3\).

- **Direct contact membrane distillation (DCMD)** is the simplest one to operate where the permeate side of the membrane contains water in direct contact with a membrane, in order to condense the permeate. It can be used for desalination or concentration of aqueous solution in food industries. The drawback is the heat lost by conduction.

- **Air gap membrane distillation (AGMD)** can be applied for desalination and removal of volatile compounds from aqueous solution, where the permeate side is separated from the membrane by air gap. The vapor permeate passes through the membrane pores and the air gap and condenses over a cold surface inside the membrane module. The drawback is the additional resistance to mass transfer.

- **Sweeping gas membrane distillation (SGMD)** can be applied for removing volatile compounds from aqueous solution. Inert gas sweeps the permeant vapor at the permeate membrane side and the condensation happens outside the membrane module. The drawback is that small volume of
permeate diffuses in a large sweep gas volume, demanding larger condenser.

- Vacuum membrane distillation (VMD) is used to separate aqueous volatile solutions without almost any heat lost by conduction. Vacuum is created by using a pump in the permeate membrane side.

1.3.5.2 Membrane material and applications

For MD non-wetted (hydrophobic) porous membranes are required with pore size from 1 nm to 1 μm. Table 1.3 lists some materials for different MD applications.

Table 1.3 MD feed, processes and materials

<table>
<thead>
<tr>
<th>Feed solution</th>
<th>MD process</th>
<th>Membrane material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water and humic acid&lt;sup&gt;74&lt;/sup&gt;</td>
<td>DCMD</td>
<td>Microporous polytetrafluoroethylene and poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>Water and NaCl&lt;sup&gt;75&lt;/sup&gt;</td>
<td>DCMD</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>Water and NaCl&lt;sup&gt;76&lt;/sup&gt;</td>
<td>DCMD</td>
<td>Poly(vinylidene fluoride) + LiCl</td>
</tr>
<tr>
<td>Water and ethanol&lt;sup&gt;77&lt;/sup&gt;</td>
<td>VMD</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Contaminated water and benzene traces&lt;sup&gt;78&lt;/sup&gt;</td>
<td>VMD</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Water and methylene blue dye&lt;sup&gt;79&lt;/sup&gt;</td>
<td>VMD</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Water and formic acid&lt;sup&gt;80&lt;/sup&gt;</td>
<td>SGMD</td>
<td>Polytetrafluoroethylene on polypropylene support</td>
</tr>
<tr>
<td>Water and isopropanol&lt;sup&gt;81&lt;/sup&gt;</td>
<td>SGMD</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>Water and acetone / ethanol&lt;sup&gt;82&lt;/sup&gt;</td>
<td>SGMD</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>Water and propane&lt;sup&gt;83&lt;/sup&gt;</td>
<td>AGMD</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>Water and ethanol / methanol / isopropanol&lt;sup&gt;84&lt;/sup&gt;</td>
<td>AGMD</td>
<td>Polytetrafluoroethylene / Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>Water and ethanol&lt;sup&gt;85&lt;/sup&gt;</td>
<td>AGMD</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
</tbody>
</table>
1.4 Objectives of this work

The main objective of this work is the development and characterization of membranes for separation, involving organic solvents and elevated temperatures, for which the availability of polymeric membranes is currently limited. The work is divided in three parts:

- In chapter 2: Development of solvent-resistant asymmetric porous Extem® membranes, modified by silanes and hydrophilic crosslinkers. For this part we propose a new method, the “reactive phase inversion”, in which the crosslinking reactions are simultaneous to the pore formation.

- In chapter 3 and chapter 4: Development of chemically and thermally resistant membranes for separation of water from aqueous alcohol solutions by pervaporation. A dense top layer was formed by dip-coating. Porous Extem® was used as substrate for dehydration of ethylene glycol and PVDF was used as substrate for dehydration of n-butanol. In both works Hyflon® was used as dense thin selective layer.

- In chapter 5. Ionic liquid was purified by removal of water using direct contact membrane distillation. The performance or different conditions were evaluated with PVDF membrane before and after coating with Hyflon®.
Chapter 2: Surface modification and crosslinking of Extem® for ultrafiltration

Part of this work was published as:

2.1 Introduction

Reactive processing is a powerful strategy to compatibilize polymer blends\(^{86}\) during extrusion and produce thermosetting materials with fine geometry molding\(^{87}\). Reactive injection molding is a widespread process in the plastic industry. Reactive processes can be used in quite different ways to induce nanostructures in polymer blends and copolymers. Yamanaka et al.\(^{88}\) described the development of a co-continuous phase separated morphology obtained by reaction-induced spinodal decomposition in mixtures of liquid nitrile rubber and epoxy, which were submitted to cure, leading to incremented damping capacity. Bucknall and Partridge investigated the phase separation during crosslinking of blends of epoxy resins with polyethersulphone\(^{89}\). Grubbs et al.\(^{90}\) reported the incorporation of epoxy functionalized block copolymers to control morphology, inducing order in thermosetting epoxy networks. Landfester\(^{91}\) reported the preparation of nanocapsules by phase separation induced during polymerization. More recently, Seo and Hillmeyer\(^{92}\) combined polymerization-induced phase separation, in situ block copolymer formation and etching to prepare nanoporous structures.
“Phase inversion”, or phase separation induced by immersion of polymer solutions in water, is a well-established manufacture process for asymmetric porous membrane fabrication. Membranes prepared in this way are present in artificial kidneys, reverse osmosis desalination plants and ultrafiltration systems for food industry. Post-functionalization of membranes is frequently performed to improve resistance to fouling, increase stability in organic solvents by crosslinking, to add specific functionalities like catalytic activity. We combine here the advantage and simplicity of the phase inversion process with in-situ functionalization reaction during the membrane formation, leading to membranes with high hydrophilicity, partial crosslinking and incorporation of nanoparticles.

Poly (ether imide sulfone) (Extem® XH1005) was chosen in this work for the membrane manufacture. The chemical structure of Extem® XH1005 combines elements of polysulfone and the polyetherimide Ultem® and has been demonstrated to have superior thermal properties with suitable processability. Ultem® has been frequently used for membrane fabrication, being successful in different applications as a single polymer or as a blend with polysulfone. Ultem® membranes have been tested for gas separation, pervaporation, ultrafiltration and biomedical applications. Extem® XH1005 has been pioneered for membranes by Chung’s group and has been reported so far only for application in gas separation. Here we developed Extem® XH1005 membranes with characteristics, which would allow application in ultrafiltration, also in conditions requiring higher temperature and better solvent resistance than addressed by other polyetherimide or polysulfone membranes.
For achieving high water flux, besides porosity, hydrophilicity is an important factor. Hydrophilicity is governed by the chemical structure of segments exposed to the pore walls and membrane surface. Good wetting characteristics, demonstrated by low water contact angles, facilitate the water penetration even through small capillary channels, maximizing the pore density available for the transport. Hydrophilicity is also known to increase the fouling resistance of membranes, since most of organic fouling agents are rather hydrophobic and tend to primary adhere to hydrophobic surfaces. Hydrophilicity can be improved by surface modification, as explored by different groups in the past and summarized in excellent reviews published by Ulbricht\textsuperscript{104}, Rana and Matsuura\textsuperscript{105}, Whitesides’s\textsuperscript{106} and Belfort’s\textsuperscript{107} groups. Coatings and polymer chemical modifications promoted by UV and plasma treatment are some of the most applied approaches. Grafting of hydrophilic segments on surface is expected to provide a stable modification and is a good strategy as long as reactive groups are available. Effective modifications include growing hydrophilic segments like ethylene oxide and imparting charge, negative or positive, or zwitterionic groups. The strategy we propose here is the preparation of a blend or a semi-interpenetrating polymer network for which one of the polymers is an epoxy-modified polysilsesquioxane. Polysilsesquioxanes are here polymeric or oligomeric chains with the empirical formula of RSiO\textsubscript{1.5}, for which R is an epoxy-terminated segment\textsuperscript{108,109}.

The modification of polymeric membranes, by incorporating ethylene oxide segments has been explored before by our group and others for application in gas separation to increment CO\textsubscript{2} permeation\textsuperscript{110,111}, as well as with the objective of
increasing hydrophilicity and fouling resistance\textsuperscript{112-115} of membranes used for water-based separations. In the latter case modifications have been promoted by activating reactive carboxylic sites by plasma treatment\textsuperscript{115}, by adding an intermediary polydopamine layer to facilitate further reaction\textsuperscript{112}, or by promoting reaction at high temperature directly with imide functionalities in the polymer backbone. Our proposal is the incorporation of ethylene oxide by reaction of polyether diamines with the epoxy groups of polymerized silsesquioxanes.

2.2 Materials

Poly (ether imide sulfone), Extem\textsuperscript{®} XH1005, XH1015 and UX1006 shown in Scheme 2.1 – a, was kindly provided by SABIC. N-methyl pyrrolidone (NMP), dimethylformamide (DMF), tetrahydrofuran (THF), hydrochloric acid (HCl) and N,N-Dimethylformamide (DMF) were supplied by Sigma Aldrich. Rejections tests were performed with 1 wt% of γ – globulins from bovine blood from Sigma Life Science in 0.1M NaCl, from Alfa Aesar; 3-Glycidyloxypropyl trimethoxy silane, trimethoxy (octadecyl) silane and O,O'-bis (2-aminopropyl) polypropylene glycol – block – polyethylene glycol – block –polypropylene glycol 500 (Jeffamine®) was supplied by Aldrich and Acros Organics, used as received has chemical structure shown in Scheme 2.1 – b and c respectively.
2.3 Different grades of Extem®

Different grades mean different polymer lengths subsequently different molecular weights in range of 41000 g/mol\textsuperscript{116}. Some physical and thermal properties of available Extem®’s in our lab listed in Table 2.1\textsuperscript{117}

<table>
<thead>
<tr>
<th>Properties</th>
<th>UH1006</th>
<th>HX1015</th>
<th>HX1005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm\textsuperscript{-3})</td>
<td>1.37</td>
<td>1.31</td>
<td>1.31</td>
</tr>
<tr>
<td>Melt temperature (°C)</td>
<td>400-415</td>
<td>380-410</td>
<td>380-410</td>
</tr>
<tr>
<td>Tensile stress break, 5mm/min (MPa)</td>
<td>107</td>
<td>74</td>
<td>70</td>
</tr>
</tbody>
</table>

2.4 Experimental procedures
2.4.1 Membrane manufacture

Plain poly (ether imide sulfone) membranes: Membranes were prepared by phase inversion, by casting 16-20 wt % solutions of Extem® in NMP or DMF on a glass plate, using a doctor blade with 150 to 200 μm gap and immersing in a non-solvent bath. The non-solvent was water at room temperature or at 65°C.

In order to enhance hydrophilicity as well as water flux of the membranes, 3-glycidyloxypropyl trimethoxy silane (1:10 volume to volume ratio of silane to Extem®) was added to the 18-20 wt % Extem® casting solution in DMF. The solution was stirred for two hours, after that 0.1M HCl was added to the mixture in 3:2 (HCl to silane) molar ratio. The resulting mixture was stirred for three days in order to promote the silane polymerization into an epoxy-functionalized silica network.

Different approaches were then followed, as specified in the results and discussion session, mainly based on (i) immersion in water (room temperature or 65°C) or (ii) solutions of hydrophilic amino-tethered segments (O,O′-Bis (2-aminopropyl) polypropylene glycol – block – polyethylene glycol – block –polypropylene glycol)

2.4.2 Scanning electron microscope (SEM)

The morphology of the membranes was investigated by using a (FEI Quanta 200) Field Emission Scanning Electron Microscope. Imaging was carried out at 2-5 kV with a working distance of 10 – 5 mm. The membrane samples were mounted on aluminum stubs using aluminum tape and coated with Au/Pd before imaging for 45s at 20mA. The samples for cross-sectional images were previously fractured in liquid nitrogen.
2.4.3 Contact angle

Contact angle was measured on a (KSV CAM200) equipment in static mode at ambient temperature. Membranes formed by immersion in water bath were used to investigate the hydrophilicity with different functionalizations. Each contact angle was reported as the average of three measurements.

2.4.4 Pore size distribution

Gas-liquid displacement through pores was conducted with (Porolux™ 1000 IB-FT – Germany), at pressure range 0 to 34.5 bar and a membrane diameter of 18.5 mm, after dipping the membrane samples for 15 min in perfluoroether (Porefil, surface tension of 16 dynes cm\(^{-1}\)) in order to measure mean flow pore size (MFP) and pore size distribution.

2.4.5 Thermal analysis

Thermogravimetric analysis (TGA) was performed on a (TA instrument Q50). Temperature was increased from 30 °C to 800 °C, under nitrogen constant flow of 60 mL/min with heating rate of 0.5 K/min.

The glass transition temperature (Tg) was obtained by using DMA by measuring the storage and loss modulus in range of temperature to 350 °C with ramp temperature rate 3 °C/min and 1Hz frequency.

2.4.6 Rheology

Rheology measurement was carried out in order to determine the properties of polymer solutions by using an AR-1500 ES rheometer (TA Instruments) with cone angle of 1° and plate fixture of diameter 25mm.
2.4.7 Membrane performance: solvent and water flux and rejection

The solvent flux was measured by using a home-made dead-end metal filtration cell. The flux of different solvents was tested for few hours, by applying 2 bar pressure and using effective area of membrane 1 cm$^2$. Water flux was measured by using a Millipore Amicon dead-end stirred filtration cell (Model 8010, 10 mL) for ultrafiltration. Milli Q water was used as feed. The effective membrane area was 3.49 cm$^2$ and the pressure was adjusted to 1 to 2 bar.

The membrane rejection for γ- Globulin was measured by filtering a 1 wt % solution of the protein in 0.1M NaCl in the same set-up used for the water flux measurement. The first 2 mL permeate were discarded. After that samples of permeate and retentate were collected and the protein concentration was analyzed by measuring UV absorption ($C_p$ and $C_r$, respectively) in a Shimadzu UV-2550 at 280 nm. The rejection, $R$, was calculated as

$$R = \left(1 - \frac{C_p}{C_r}\right) \times 100$$

(2.1)

The experiment was repeated with poly (ethylene oxide) aqueous solutions of molecular weights ranges from 35 to 1000 kg/mol.

2.5 Results and discussion

2.5.1 Plain poly (ether imide sulfone) membranes

2.5.1.1 Viscosity of different grades of Extem® solutions

Figure 2-1 represents viscosity versus shear rate for solutions of different grades of Extem®, which were prepared with fixed polymer concentration in NMP.
Different viscosity values are related to different molecular weights of different grades of Extem®.

2.5.1.2 Mechanical properties of membranes from different concentrations of Extem® XH1015

Membranes were prepared from solutions with different concentrations of Extem® (16 to 20 wt%) in NMP and the mechanical properties were evaluated. Figure 2-2 shows that strain as well as stress gradually increase with the increase of polymer concentrations.
2.5.1.3 Water flux and permeance of Extem® 1015 membranes from different polymer concentrations

Solutions with 16, 18 and 20 wt% of Extem® 1015 in NMP were prepared by phase inversion method, using water as a non-solvent. Pure water flux was measured for the membranes by applying 2 bar pressure. The flux declined as the polymer concentration was increased, as noted in Table 2.2. The permeances were measured from the slope as illustrated in Figure 2-3.
Figure 2-3 Fluxes of membranes prepared from different concentrations of Extem®.

Table 2.2 summarizes the water permeance of membranes prepared from solutions with different polymer concentrations at 2 bar and the slope from Figure 2-3 and calculated membranes resistance. The increase of polymer concentrations led to increase of the thickness of the skin layer and/or smaller pore sizes.

Table 2.2 Permeance of membranes prepared from solutions with different polymer concentrations

<table>
<thead>
<tr>
<th>Polymer concentration (wt %)</th>
<th>Water permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Slope (bar)</th>
<th>Membrane resistance (bar l⁻¹ m² h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>14.2 ± 2.6</td>
<td>9.1629</td>
<td>0.109</td>
</tr>
<tr>
<td>18</td>
<td>3.7 ± 1.1</td>
<td>3.3314</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>0.58 ± 0.1</td>
<td>0.048</td>
<td>20.83</td>
</tr>
</tbody>
</table>
2.5.1.4 Effect of coagulation bath temperature on membrane morphology and membrane performance

The level of porosity was highly dependent on the temperature of the coagulation bath. Hot water bath at temperature of 65°C led to large pores, as confirmed by scanning electron microscopy in Figure 2-4. For membranes prepared at room temperature the pore size was below the detection limit of the porometer (around 20 nm) and could not be clearly seen by FESEM either.

![Figure 2-4 FESEM top surface image of membrane from 18wt% Extem® solution in DMF cast in 25°C and 65°C water coagulant temperature.](image)

The effect of the immersion bath temperature can be understood in the following way. When the polymer solution is cast and immersed in water, pores are formed following a phase separation mechanism, which can be spinodal decomposition or nucleation and growth, depending on the thermodynamic conditions and the corresponding phase diagram (ruled by temperature, polymer concentration, solvent and non-solvent composition), as well as on the kinetics of solvent-non-
As the phase separation proceeds, if the concentration of the polymer rich phase is high enough and the thermodynamic interaction between polymer and the surrounding solvent mixture is adequate, the polymer mobility will decrease and gelation will be observed. The phase separation is then frozen at this stage and the polymer-dilute phase will give rise to the final membrane pores. If phase separation is allowed to proceed till later stages, before gelation occurs, the pores are expected to be larger. If we compare the pore formation in water baths at 25 and 65°C Figure 2-4, a combination of the following effects is probably leading to larger pores at higher temperature:

(i) The polymer mobility is higher at higher temperature and gelation will only start at later stage of phase separation; this might be the predominant factor;

(ii) The surface tension of water changed with temperature and the solvent-water exchange kinetics might be slightly different;

(iii) Different temperature might slightly change the phase diagram favoring slightly different routes of phase separation.

A broad distribution of pore sizes was observed for those prepared by immersion in hot water Figure 2-5.
Figure 2-5 Pore size distribution for 18wt% Extem® solution in DMF cast at 65°C water temperature.

The pore size distribution was estimated by immersing each membrane in perfluoroether as wetting liquid and measuring nitrogen flow rate as the membrane is submitted to increasing pressures. The bubble point gives an idea of the largest available pores, identified by the minimum pressure needed to dislocate the wetting liquid. The mean flow pore size corresponds to the point at which 50% of the total gas flow can be accounted\textsuperscript{118}.

The water permeance (flux normalized by pressure) of membranes prepared in hot water was confirmed to be $30.7 \pm 4.5 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and $130.5 \pm 3.5 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, for those prepared at room temperature and 65°C respectively. The water flux measurements demonstrate that even for those prepared at room temperature, porosity is enough for water permeance of $30.7 \pm 4.5 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, although the
pores are smaller than the resolution of the methodology (FESEM and porosimetry) applied for evaluation.

2.5.2 Membrane modification with epoxy-modified polysilsesquioxane

In this section the modifying agent was 3- glycidyloxypropyl trimethoxy silane. If we now compare the membranes in absence and presence of 3- glycidyloxypropyl trimethoxy silane, differences in pore sizes can be explained, by considering the silane as an additional component of the solvent mixture, affecting the phase diagram. By comparing Figures 2-4 and 2-6 we see how the polysilsesquioxane affects the membrane morphology, slightly increasing the pore size.

![SEM image of membrane](image)

Figure 2-6 SEM top surface image of membrane cast from 18wt% Extem® solution in DMF with epoxy-modified polysilsequioxane (1:10 Extem®:silane precursor), immersed in water at 25 and 65°C.
Figure 2-7 Pore size distribution for 18wt% Extem® solution in DMF with epoxy-modified polysilsequioxane (1:10 volume to volume ratio of silane precursor: Extem®), immersed in water at 65°C.

By comparing Figures 2-5 and 2-7 we confirm the increase in average pore size, when the silane is added. A broad peak of pore sizes can be seen at 47-61 nm. The bubble point was 294 nm for membranes prepared at 65°C. The water permeance was 284.8 l m⁻² h⁻¹ bar⁻¹, 7-fold higher than when the membrane was prepared at room temperature.

NMR measurements confirmed that the epoxy groups does not open during stirring of the casting solution, before immersion in the coagulation bath (Figure 2-8). Only the polymerization of the silane precursor to polysilsesquioxane takes place under acid catalysis, promoted by addition of HCl (FTIR spectra in Figure 2-9). The reaction between diamine and epoxy groups is promoted at 65°C.
Figure 2-8 1H NMR (600MHz, 297K, CDCl₃, ppm) spectrum of Extem® membrane with and without polysilsesquioxane.

Figure 2-9 FTIR spectra of glycidoxy propyl trimethoxysilane (GMS) before and after the hydrolysis and condensation at R=1.5 (H₂O/Si molar ratio) with 0.1M HCl.
Peaks at 3700-3100 cm\(^{-1}\) (\(-\)OH from condensation reaction), 1700-1600 cm\(^{-1}\) (deformation mode of H\(_2\)O molecules, absorbed in siloxane network), 1050-950 cm\(^{-1}\) (Si-OH stretching vibration), 650-800 cm\(^{-1}\) (Si-O-Si vinding vibration).

2.5.3 Membrane functionalization with poly (ether diamine) segments

The next approach was the incorporation of hydrophilic polyether segments to the membrane. Epoxy-polysilsesquioxane, was previously generated and blended with Extem® as part of the casting solution. Epoxy is known to react with amino groups. Bis (2-aminopropyl) polypropylene glycol – block – polyethylene glycol – block –polypropylene glycol (Jeffamine®) was chosen as diamine for later reaction with epoxy. A partial crosslinking is obtained at least on the membrane surface and inside the pores, anchoring the hydrophilic segments. This approach was demonstrated for Extem®-based membranes, but could be extended to other polymer systems. Table 2.3 demonstrates that the addition of polysilsesquioxane itself already contributed for the increase of hydrophilicity (low contact angle) and for the formation of larger pores. As a result the water flux increased about twice by adding silane to the casting solution, as seen for membranes prepared at 65°C.

Extem®/polysilsesquioxane solutions were cast and immersed directly into 1M Jeffamine® aqueous solution at 65°C as coagulant bath, but did not form a membrane. By decreasing the temperature to 45°C and the Jeffamine® concentration to 0.5 M, a membrane was formed, but it was fragile. The morphology is shown in Figure 2-10.
Stable membranes were obtained by first promoting the pore formation by coagulation in water, followed by immediate immersion in Jeffamine® solution. The membrane morphology can be seen in Figure 2-11.
Figure 2-11 SEM image of (a) surface and (b) cross section of a membrane cast from 18wt% solution in DMF, with epoxy-modified polysilsesquioxane (1:10 Extem®:silane precursor), briefly immersed in water at 65°C and transferred to a 0.1M Jeffamine® bath for 2 days.

When poly (ether diamine) was added to the water bath, polyether segments were incorporated into the membrane, decreasing the contact angle even more. As a result the water permeance increased to 461.8 l m⁻² h⁻¹ bar⁻¹. A broad peak of pore size between 100 and 140 nm was then detected in Figure 2-12. Additional pore size characterization can be seen in Table 2.3.
Figure 2-12 Pore size distribution for membrane cast from 18wt% Extem® solution in DMF, with epoxy-modified polysilsequioxane (1:10 Extem®:silane precursor), briefly immersed in 65°C water and transferred to 0.1 M Jeffamine® bath for 2 days.

The best results were obtained by casting the solution only 10 minutes after adding the Jeffamine®, immersing briefly in hot (65°C) water and soaking the formed membrane into a 45°C water bath for one night. The resulting membrane morphology can be seen in Figure 2-13.
Figure 2-13 SEM surface image of membrane cast from 18wt% Extem® solution in DMF, with epoxy-modified polysilsesquioxane (1:10 Extem®:silane precursor), stirred for 3 days immersed in water at 65°C after after 10min of adding 1:5 Jeffamine®:Extem® to polymer solution.

Figure 2-14 Pore size distribution of membrane cast from 18wt% Extem® solution in DMF, with epoxy-modified polysilsesquioxane (1:10 Extem®:silane precursor), stirred for 3 days immersed in water at 65°C after after 10min of adding 1:5 Jeffamine®:Extem® to polymer solution.
High water permeance was obtained: $1500 \pm 400 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The pore size distribution in Figure 2-14 showed an unusually sharp peak at 65 nm with bubble point of 223 nm. The achievement of much higher flux with smaller pore size indicates that the porosity as a whole is much higher and probably also the pores hydrophilicity.

Table 2.3 Bubble point, mean flow and smallest pore size characterized by porosimetry and contact angle

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Bubble point (µm)</th>
<th>Mean flow pore size (µm)</th>
<th>Smallest pore size (µm)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extem®</td>
<td>0.092 ± 0.001</td>
<td>0.022 ± 0.002</td>
<td>0.015 ± 0.006</td>
<td>79.6 ± 0.4</td>
</tr>
<tr>
<td>Extem® + epoxy polysilsesquioxane</td>
<td>0.294 ± 0.037</td>
<td>0.050 ± 0.029</td>
<td>0.029 ± 0.008</td>
<td>61.4 ± 1.6</td>
</tr>
<tr>
<td>Extem® + Jeffamine®</td>
<td>0.328 ± 0.127</td>
<td>0.119 ± 0.044</td>
<td>49.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Extem® + Jeffamine® c</td>
<td>0.223 0.066</td>
<td>0.020</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Note</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a membranes coagulated in water at 65°C</td>
<td></td>
</tr>
<tr>
<td>b membrane cast from Extem® solution with polysilsequioxane immersed first in water then in 0.1 M Jeffamine® solution</td>
<td></td>
</tr>
<tr>
<td>c membrane cast from Extem® solution with polysilsesquioxane and Jeffamine®, coagulated in water at 65°C</td>
<td></td>
</tr>
</tbody>
</table>

2.5.4 Thermogravimetric analysis of different membranes

Extem® membranes remained thermally stable above 400°C even after the modification, as confirmed by TGA measurements (Figure 2-15 and Table 2.4).
Figure 2.15 Thermogravimetric analysis of Extem® membranes cast from (black) plain Extem® solution; (red) Extem® solution with polysilsesquioxane coagulated in 65°C water and (green) Extem® solution Extem® solution with polysilsesquioxane coagulated in 65°C water.

Table 2.4 Membrane thermodegradation

| Weight loss (%) | Temperature (°C) | Extem® | Extem® + polysilsesquioxane | Extem® + polysilsesquioxane + Jeffamine®
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43</td>
<td>69</td>
<td>334</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>494</td>
<td>470</td>
<td>434</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>507</td>
<td>493</td>
<td>465</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>512</td>
<td>505</td>
<td>485</td>
<td></td>
</tr>
</tbody>
</table>

*a* the membrane was immersed directly after the formation in 1M Jeffamine® bath for 2 days
2.5.5 Rheology of polymer solutions with Jeffamine®

The highest water flux was obtained by adding the Jeffamine® directly to the casting solution, after optimizing the preparation conditions. 18 wt % Extem® solution in DMF with 1.8 wt % epoxy silane stirred for 24 h at room temperature and then having and 0.9 wt % addition led to a crosslinked gel.

![Graph showing rheological characterization](image)

Figure 2-16 Rheological characterization: storage and loss moduli of the Extem® with polysilsesquioxane casting solution as a function of time with and without addition of Jeffamine®.

Figure 2-16 shows how the storage and loss moduli of the casting solution at 25°C changes with time after adding Jeffamine®. The viscosity of the casting solution is below 2 Pa s and clearly increases with addition of Jeffamine® due to crosslinking reaction. After 45 minutes the storage modulus becomes higher than the loss modulus, indicating that a gel with strong elastic characteristics has been formed. At shorter periods the solution has still liquid consistence and can be easily used
for casting membranes. By casting the solution 10 to 15 minutes after adding Jeffamine® and immersing in hot (65°C) water however a fragile membrane was formed. The optimum time of reaction before casting is therefore 15 minutes.

2.5.6 Protein rejection

γ-Globulin retention of 99.2 % was confirmed. After protein filtration and washing with water, a water flux recovery of 77.5 % was achieved. Figure 2-17 shows the determination of molecular weight cut-off for this membrane, being around 150,000 g mol⁻¹. This is close to the molecular weight of γ-globulin. Measurements with poly (ethylene oxide) (PEO) were done with diluted solutions of 35, 100, 300, 600 and 1000 Kg/mole, while the measurement with γ-globulin was performed with 1 wt % solution. It must also be considered that PEO is a linear polymer, which is usually more easily transported through pores than globular proteins with the same molecular weight.
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Figure 2-17 Molecular weight cut-off determined by filtering diluted solutions (100 ppm) of poly (ethylene oxide) of different molecular weights; γ-globulin rejection obtained with 1 wt% feed solution in 0.1 M NaCl.

2.5.7 Solvent resistance membrane

20 wt% of Extem® membranes were soaked in different solvents for 1 week. In case no physical change was observed, further solvent filtration experiments were performed with membranes based on plain Extem® under 2 bar during a few hours. Table 2.5 shows that toluene has high permeance.

Table 2.5 Solvent permeation of membranes prepared from 20 wt% Extem® solutions

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Toluene</th>
<th>Ethanol</th>
<th>Methanol</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeation</td>
<td>327 ± 21</td>
<td>6.1 ± 0.6</td>
<td>7.7 ± 1.9</td>
<td>4.8 ± 0.8</td>
</tr>
</tbody>
</table>

(L m⁻² h⁻¹ bar⁻¹)
The stability of the membranes was extended to more polar solvents after the modification. They did not show any visible change when immersed in 50:50 DMF/water, 50:50 NMP/water and 100 % THF. This is a strong advantage, which allows the application in the presence of high concentration of polar solvents, even 100 % THF. It however dissolved in 100% DMF and 100 % NMP.

2.6 Conclusion

Membranes based on poly (ether imide sulfone) (Extem®), which are highly stable even at temperatures as high as 260°C were modified by blending with an in-situ polymerized silsesquioxane, containing epoxy groups. The epoxy groups were further used for attachment of poly (ether diamine) oligomers. The contact angle decreased from 80 to 49°, after the modification with polyether, demonstrating in this case a high increase of hydrophilicity.

A new approach was demonstrated, combining phase inversion and simultaneous functionalization reaction during the membrane formation (“reactive phase inversion”). The method was used for crosslinking with incorporation of hydrophilic segments.

By adding now Jeffamine® directly to the casting solution of Extem® and preformed epoxy-functionalized polysilsesquioxane, membranes with sharp pore size distribution (peak at 65.3 nm pore size) were obtained, with high water permeance (1500 l m⁻² h⁻¹ bar⁻¹), molecular weight cut-off of 150 kg/mol and stability in solutions with high concentration of organic solvents. The water flux in experiments with proteins was 77.5 % recovered after simple washing.
The same approach applied in this work is expected to be successful with other polymer systems, since it does not depend on the polymer backbone functionalities for reaction.
Chapter 3: Dehydration of ethylene glycol using Hyflon®/Extem® for pervaporation

3.1 Introduction

Dehydration of ethylene glycol (EG) is an important process in many industrial applications. Ethylene glycol is industrially produced by hydrolysis of ethylene oxide and hence an excess amount of water is generally added to enhance the production yield. EG has many industrial applications as an antifreeze in internal combustion engines, an industrial heat transfer agent, and as a heat transfer fluid in aircraft due to its high heat transfer capability, high boiling point (197.6 °C), and low freezing point (-13 °C) which can be lowered when mixed with water\textsuperscript{119}. Moreover, it is an essential chemical in plastic industries for polyester fibers and resins.

Although EG does not form an azeotrope with water all over ranges and distillation is considered as a conventional way to purify EG\textsuperscript{120}, this process has a critical drawback of high energy consumption due to the high boiling point of EG\textsuperscript{121}. Membrane-based separation technologies have attracted great interests due to their low energy consumption, small footprint and low-cost modular construction\textsuperscript{11}. Among them, pervaporation is an effective technique to separate liquid-liquid mixtures. Its advantages are simplicity, relatively low energy consumption, use of low-grade steam\textsuperscript{17} and no additional chemicals needed\textsuperscript{13}. These advantages make pervaporation a promising full-scale process in industries\textsuperscript{122}.

For pervaporation process of EG-water mixtures, different polymeric materials have been widely studied to fabricate hybrid, composite and dense membranes.
Examples of hybrid membranes are gamma glycidyloxypropyl trimethoxy silane (GPTMS) or tetraethoxy silane (TEOS)/poly(vinyl alcohol) (PVA)\textsuperscript{123}, mordenite/chitosan-PAA\textsuperscript{124}, zeolite/cellulose-chitosan\textsuperscript{125}, carbon nanotube/poly vinylamine (PVAm)-PVA\textsuperscript{126} and zeolite NaA/PVA membranes\textsuperscript{127}.

Examples of composite membranes are crosslinked poly vinyl alcohol (PVA) coated on porous polyethersulfone supports\textsuperscript{128}, chitosan coated on porous polysulfone supports\textsuperscript{129}, crosslinked chitosan coated on porous polyethersulfone supports\textsuperscript{130}, crosslinked poly (N,N-dimethyl amino ethyl methacrylate-polysulfone) with p-xylylene dichloride\textsuperscript{131}, PVA-polysulfone crosslinked by trimesoyl chloride (TMC)\textsuperscript{132}, layer by layer self-assembly of polyethyleneimine and PAA (polyacrylic acid)\textsuperscript{133} and dual-layer polybenzimidazol (PBI)-polyetherimide (PEI) hollow fiber membranes\textsuperscript{134}.

Dense membranes have also been reported for dehydration of EG such as the interpenetrating polymer network (IPN) of (PAA)-PVA and polyacrylamide (PAAM)-PVA\textsuperscript{135}, sulfonated polyether etherketone\textsuperscript{136}, crosslinked chitosan with phosphoric acid\textsuperscript{137}, crosslinked PVA with glutaradehyde\textsuperscript{138} and chitosan-PVA blend membranes crosslinked with TMC\textsuperscript{139}.

In this work, Extem® membranes coated with Hyflon® AD® were chosen for dehydration of ethylene glycol. Extem® (poly ether imide sulfone) is an amorphous thermoplastic and easily processable commercial polymer\textsuperscript{117}. It exhibits high thermal and chemical resistance with a high glass transition temperature (267°C), good mechanical properties, strong stiffness and high creep resistance\textsuperscript{117}. In
membrane-based applications, Extem® can be easily prepared in dense films for
gas separation\textsuperscript{94,103} or in porous membranes for ultrafiltration\textsuperscript{140}.

On the other hand, Hyflon® AD® is an amorphous perfluoropolymer copolymer of
tetrafluoroethylene (TFE) and 2,2,4 trifluoro, 5 trifluoromethoxy 1,3 dioxide (TTD). It
has high gas permeability and selectivity, excellent hydrophobicity, high thermal
and chemical resistance, and an ability to form uniform and thin films\textsuperscript{141}. It has
been used as dense and porous membranes and showed excellent properties and
performance\textsuperscript{142} for various applications such as ultrafiltration\textsuperscript{143}, gas and vapor
separations\textsuperscript{142,144-152} and pervaporation\textsuperscript{48,153,154}. It has been also employed as a
coating layer on PVDF membranes in membrane contactor\textsuperscript{155,156}, membrane
distillation\textsuperscript{157} and pervaporation\textsuperscript{153}.

In general, hydrophilic materials are used for pervaporation dehydration and hence
crosslinking agents or additives are required to reduce the swelling effect. In this
study, a simple method of using hydrophobic materials as a coating layer was
proposed. The effects of support structures, feed temperature and concentration
will be investigated.

3.2 Materials

Poly (ether imide sulfone) Extem® 1015 was kindly provided by SABIC and N-
methylpyrrolidone (NMP) from Sigma-Aldrich was used as a solvent. Hyflon®
AD®60X was provided by Solvay Plastics and Galden HT200 from Solvay-Solexis
was used as a solvent. Ethylene glycol (\textgeq 99\% purity) was purchased from Sigma-
Aldrich, and Milli-Q water produced by a Millipore unit was used for all experiments.
3.3 Experimental procedure

3.3.1 Membrane preparation

Different weight percentages of polymer solutions in NMP were prepared from 14-18 wt% solution, cast on a glass plate and immersed in water coagulation bath at 25°C. The formed membranes were then air dried and dip-coated by immersion in 2 wt% Hyflon® AD® solution in Galden HT200 for 10 s. They were then dried at room temperature for 1 day, then put in the oven at 65°C for one day to remove all solvent residue.

3.3.2 Membrane characterization

The morphology of Extem® flat sheet membranes surfaces before and after coating with Hyflon® AD® and cross-section of different polymer concentration was characterized by using a field emission scanning electron microscope (FESEM, Quanta 200). The membrane samples were prepared on aluminum stubs and coated with Iridium for 3 nm thickness (Quorum, Q105T ES). Dynamic mechanical analysis (DMA, Q800, TA) instrument was used to measure the mechanical properties of the membranes. The contact angles of water on different membrane surfaces were measured by a (Kruss EasyDrop) equipment. Porosity ($\varepsilon$) of the membrane support were determined by taking the weight of wet membrane after remove the excess of water from the surface ($m_1$) and the weight of the dried membrane after overnight oven dry ($m_2$) in order to estimate the amount of absorbed water into the polymer pore. By applying eq.3.1 the porosity was calculated.
$$\varepsilon = \frac{(m_1 - m_2)/\rho_W}{(m_1 - m_2)/\rho_W + m_2/\rho_P}$$  \hspace{1cm} (3.1)

3.3.3 Pervaporation experiments

A laboratory pervaporation system was built with a metal cell having an effective membrane area of 3.14 cm$^2$. The downstream pressure was kept < 0.1 mbar by applying a vacuum pump. Permeate was collected in a cold trap, immersed in a liquid-nitrogen-containing Dewar flask to condense its vapor to the liquid phase. The weight of the collected permeate (g) at a certain time (h) was measured by using a 4-digital balance and the flux was calculated using eq.3.2

$$J = \frac{Q}{A \times t}$$  \hspace{1cm} (3.2)

where Q is the weight of the permeate (g), A is the membrane surface area (m$^2$) and t is the time (h). The composition of water-ethylene glycol mixtures was measured using a refractometer (KRUSS AR2008, Germany).

Activation energy was calculated by using the Arrhenius plot with flux from the following equation

$$J = A \times \exp \left(-\frac{E_p}{RT}\right)$$  \hspace{1cm} (3.3)

where $J$ is the permeation flux, $A$ is a constant, $E_p$ is the activation energy, $T$ is the absolute temperature and $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$).

3.4 Results and discussion
3.4.1 Vapor liquid equilibrium

Figure 3-1 and Figure 3-2 show the diagram of vapor-liquid equilibrium obtained by using the Aspen NRTL-RK method for water and ethylene glycol at 25°C and their saturated vapor pressure at different temperatures.

![Figure 3-1 Water and ethylene glycol vapor liquid equilibrium at 25°C.](image)
Figure 3.2 Saturated vapor pressures of water and ethylene glycol at different temperatures.

3.4.2 Support characterizations

Figure 3.3 shows the surface morphology and cross-section of the supports prepared from different polymer solutions. The polymer concentration can affect membrane morphology in terms of porosity, particularly surface pore size and cross-sectional morphology. Figure 3.3 illustrates that increasing polymer concentration from 14 wt% to 16 wt% can narrow surface pore size and increase membrane thickness, which may favor the defect-free coating layer of Hyflon® in the later step and increase the thickness of the final membrane. Increase polymer concentrations lead to an increase in the viscosity of the casting solutions which as a result reduce the mobility of polymer chain during phase inversion, which control the exchange between solvent and non-solvent leading to denser membrane structure. Porosity value presented in Table 3.1 proved that increasing
polymer concentrations will reduce the porosity. The higher the polymer concentration is, the stronger it is, as shown in Table 3.2

![Images of different polymer concentrations](image1)

Figure 3-3 Surface morphology and cross-section of the Extem® support prepared from different polymer concentrations.

<table>
<thead>
<tr>
<th>Membrane concentration (wt%)</th>
<th>14</th>
<th>16</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Porosity (%)</strong></td>
<td>84 ± 0.4</td>
<td>82 ± 0.3</td>
<td>80 ± 0.6</td>
</tr>
</tbody>
</table>

Table 3.1 Porosity of different membrane support concentrations

<table>
<thead>
<tr>
<th>Membrane concentration (wt%)</th>
<th>14</th>
<th>16</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stress (MPa)</strong></td>
<td>2.3</td>
<td>2.5</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Strain (%)</strong></td>
<td>5.3</td>
<td>5.9</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Table 3.2 Mechanical properties of Extem® supports
The contact angles of all supports, which reflect their hydrophilicity and roughness, were measured and listed in Table 3.3. All values are lower than 90° which indicates the inherently hydrophilic nature of Extem® material. Increasing polymer concentration from 14 wt% to 16 wt% slightly reduces the contact angle of supports from 75.2° to 67.5°. This minor decrease may be due to the change in surface roughness, which is seen in Table 3.3.

Table 3.3 Contact angles of support membranes

<table>
<thead>
<tr>
<th>Polymer concentration (wt%)</th>
<th>Before coating (°)</th>
<th>After coating (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>75 ± 2</td>
<td>111.6 ± 0.2</td>
</tr>
<tr>
<td>16</td>
<td>72 ± 1</td>
<td>113.2 ± 0.1</td>
</tr>
<tr>
<td>18</td>
<td>68 ± 2</td>
<td>116.1 ± 0.1</td>
</tr>
</tbody>
</table>

3.4.3 Membrane characterization

The contact angles of the membranes were measured and listed in Table 3.3 in comparison with those of the supports before coating. All the membranes have much higher contact angles than their supports, which demonstrates that the Hyflon® layer is successfully coated. High contact angle values of > 110° reflect the hydrophobic nature of Hyflon®, which is consistent with previous studies. Increasing polymer concentration leads to the higher contact angle value of the membranes, which may imply a more perfect and less defective coating layer.
3.4.4 Effect of support concentration

Different polymer concentrations from 14 to 18 wt% were employed to fabricate the supports for membranes and their effects on pervaporation performance are listed in Table 3.4. As the polymer concentration increased, the flux decreased from 87 g m\(^{-2}\) h\(^{-1}\) to 26 g m\(^{-2}\) h\(^{-1}\) but the water concentration in the permeate increased from about 85.2 wt% to 93.4 wt%. These changes in performance are attributed to the change in membrane morphology. Increasing polymer concentration may lead to lower porosity, which increases the permeation resistance and hence reduces the flux. On the other hand, the pore size of the surface can be narrowed, which supports a smooth and defect-free Hyflon® coating layer, enhances membrane selectivity and hence water concentration in permeate.

Table 3.4 Pervaporation performance of Hyflon®/Extem® membranes prepared from different polymer concentrations

<table>
<thead>
<tr>
<th>Support concentration (wt %)</th>
<th>Total flux (g m(^{-2}) h(^{-1}))</th>
<th>Water concentration in permeate (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>87 ± 13</td>
<td>85 ± 12</td>
</tr>
<tr>
<td>16</td>
<td>71 ± 20</td>
<td>86.1 ± 0.1</td>
</tr>
<tr>
<td>18</td>
<td>26 ± 7</td>
<td>93 ± 4</td>
</tr>
</tbody>
</table>

Coating condition: 2wt% Hyflon® AD® for 10s

Feed concentration: water:ethylene glycol 5:95 (wt%)
3.4.5 Effect of operating temperature

Figure 3-4 presents the water, EG and total fluxes through Hyflon® AD/Extem® membranes as a function of feed temperature. The results show that all the permeation fluxes increase with feed temperature. The temperature dependence of the flux can be characterized by the Arrhenius equation as eq. 3. The plot of the logarithmic permeation flux versus the reciprocal of feed temperature is depicted in Figure 3-4. From this plot, the activation energies for permeating molecules, i.e. water and EG, can be calculated and listed in Table 3.5 as 18.0 and 54.2 kJ/mol, respectively. Their positive values reflect the trend of permeation fluxes increasing with temperature as shown in Figure 3-4. The flux increases are attributed to the increases in their saturated vapor pressure (as in Figure 3-2), which leads to increment in their driving force.
Figure 3-4 Pervaporation performance of Hyflon®/Extem® membranes at different feed temperatures. The Extem® supports were prepared from 18wt% polymer solution and the feed composition is water:ethylene glycol 5:95 (wt%).

Figure 3-5 Plot of logarithmic permeation flux versus the reciprocal of feed temperature.
Table 3.5 The activation energies of water and ethylene glycol

<table>
<thead>
<tr>
<th>Activation energy</th>
<th>Water</th>
<th>Ethylene glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPa.mole⁻¹</td>
<td>18.0</td>
<td>54.2</td>
</tr>
</tbody>
</table>

Figure 3-4 also indicates that increasing the feed temperature decreases water concentration in permeate, i.e. membrane selectivity. This decrease may be due to the interaction between water and ethylene glycol molecules.

3.4.6 Effect of water concentration in the feed

Different feed water concentrations varying from 5 wt % to 40 wt % have been investigated. Figure 3-6 indicates that increasing the feed water concentration can significantly enhance the flux from around 35 g m⁻² h⁻¹ to 414 g m⁻² h⁻¹, while moderately reducing the permeate water concentration from 88 wt% to 85 wt%. When the feed water concentration increases, the dilution or concentration of water/EG governs the change in formation of molecule clusters and in interaction among water, EG and the membrane. These changes will determine the flux and selectivity trends.
3.5 Conclusion

In this study, Hyflon®/Extem® membranes have been developed for ethylene glycol dehydration. The following conclusions can be made:

1. The polymer concentration in the dope solution can affect the support’s porosity and its surface pore size. Increasing polymer concentration narrows surface pore size, supports a smoothing coating layer of Hyflox® and hence improves membrane selectivity.

2. Increasing feed temperature enhances the fluxes of both water and ethylene glycol, mainly due to the increases in their saturated vapor pressure with temperature. However, the membrane selectivity decreases at high temperatures.
because of the interaction between water molecules and ethylene glycol increases with increase the temperature.

3. Operation at high feed water concentration favors EG dehydration because it can significantly improve the flux while the decrease in membrane selectivity is trivial.
Chapter 4: Hydrophobic Hyflon®/PVDF Membranes for Butanol Dehydration via Pervaporation


4.1 Introduction

Perfluorinated polymers have been attractive to applications for which the most common polymers are not suitable due to their higher hydrophobic character and higher resistance towards most common solvents, acids, alkalis and strong oxidizing agents. While crystalline fluorinated Teflon® is opaque, amorphous polymers such as Teflon HF® and Cytop® are highly transparent to light from far UV to near infrared waves increasing their potential for optical applications, semiconductor industry, and photocatalysis. Hyflon® AD, Cytop® and Teflon® HF with high hydrophobicity and high free volume have attracted interest for membranes-based gas separation and contractor devices. Perfluorinated/sulfonated polymers such as Hyflon® Ion and Nafion® are well explored for PEM fuel cells. Hyflon® AD was recently employed as a protective layer on a hydrophilic membrane for ethanol dehydration to enhance the membrane selectivity and control water-induced plasticization by preventing the hydrophilic membrane from the direct contact with the feed.

Other than Hyflon® AD, the perfluorinated polymer perfluoro-2,2-dimethyl-1,1,3-dioxole copolymerized with tetrafluoroethylene (PDD–TFE) has been used in pervaporation for separating different pharmaceutical solvents. Bhattacharyya
et al.\textsuperscript{48} were the first to employ PDD-TFE for water/solvent separation by pervaporation. They also proposed separation mechanism of water from ethanol, isopropanol, ethyl acetate and ethanol ethyl acetate. Tang and Sirkar\textsuperscript{162} found that the performance of PDD–TFE surpassed that of NaA zeolite for separating water from different aprotic solvents, such as dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc). However, their large membrane thickness of 25 µm-100 µm may limit their application potential due to the high cost of perfluorinated polymers.

Butanol is considered as an alternative fuel for gasoline\textsuperscript{163,164}, diesel and kerosene\textsuperscript{165}, which can be produced from the fermentation process\textsuperscript{163,164,166}. It is also used in the manufacture of urea resin, cleaning fluids, reaction with acids to form esters, etc\textsuperscript{167}. Presence of water in such media is highly expected and hence it is essential to explore effective and energy-saving techniques to remove water from butanol. Membrane-based pervaporation has emerged as a potential technology for such separation because of its energy efficiency, small footprint, low maintenance cost, simple operation and ease of control\textsuperscript{168}. Selection of appropriate membrane materials in pervaporation process can control the efficiency of the process\textsuperscript{21}.

For n-butanol dehydration, both ceramic and polymeric membranes have been studied\textsuperscript{169}. Hybrid silica membranes with organic links were investigated for dehydration of 5/95% water/n-butanol solution. It displayed a high water flux and high permeate water content of about 98 wt% for a long test duration of 1000 days\textsuperscript{170,171}. By changing the operating temperature to 95°C, the permeate water content
increased to 99.5 wt%. Paradis et al. concluded that combination of bridging and terminating organic compounds increased the hydrophobicity leading to the decrease in permeate water content from ~99wt% to ~40wt%. On the other hand, polymeric membranes have been studied by Chung et al for butanol dehydration. They employed the commercial hydrophilic membrane Pervap®2510 and achieved the permeate water content of around 93wt% at 60°C. Polyether block amide (PEBA), polydimethylsiloxane (PDMS), and polyurethane (polyether based, PUR) have been used for the dehydration of the 1/99 wt% water/n-butanol solution at 50°C and achieved the water fluxes of 222, 44, 78 g m⁻² h⁻¹ and the relatively low enrichment factors of 20, 37, 9, respectively.

In this study, our aim is to (1) explore hydrophobic Hyflon® AD coating on poly (vinylidene fluoride) (PVDF) membranes for dehydration; (2) optimize the coating protocols for thin defect-free Hyflon® AD selective layer on the PVDF support; and (3) analyze the effects of the pervaporation operating conditions. By using a thin coating of Hyflon® AD on the lower-cost PVDF support, the composite membrane would be feasible for industrial application.

4.2 Materials

Polyvinylidene fluoride (PVDF, Kynar® HSV900), was kindly provided by Arkema. The polyester non-woven support fabric (05TH-100) was purchased from Hirose.
Hyflon® AD60X with an average molecular weight of 500,000 g/mol, density of 1.93 g/cm³, and glass transition temperature of 125°C, was provided by Solvay Plastics. Its chemical structure is shown in Scheme 4.1. N-methyl pyrrolidone (NMP) from Sigma-Aldrich was used as solvent for PVDF, while Galden® HT200 from Solvay-Solexis was employed as the solvent for Hyflon® AD. N-butanol (≥ 99.7% purity) was purchased from Sigma-Aldrich and Milli Q water was used for all experiments, generated using a Millipore unit.

### 4.3 Experimental procedure

#### 4.3.1 Membrane preparation

The support was prepared by casting 10 wt% of PVDF in NMP on polyester non-woven support followed by phase inversion in water. Further, an ultra-thin layer of Hyflon® AD on the top support surface was obtained by dip coating, using 0.5, 2 and 4 wt% solutions. The layer was dried at room temperature overnight followed by vacuum drying at 130°C overnight.
4.3.2 Pervaporation experiment

A lab-scale pervaporation system was built as shown in Scheme 2.1 with effective membrane area of $3.14 \text{ cm}^2$. Downstream pressure was kept $< 0.1 \text{ mbar}$ by applying a vacuum pump. Permeate was collected in a cold trap, immersed in liquid nitrogen containing Dewar flask to condense its vapor to the liquid phase.

Scheme 4.2 Pervaporation experimental set-up.

4.3.3 Characterization

The membrane morphology was observed by scanning electron microscope (SEM) using a FEI Quanta 200 Field Emission Scanning Electron Microscope (FESEM).

The support pore size and the pore size distribution were estimated by using a Porolux™ 1000 IB-FT instrument from Germany at the pressure range of $0$–$34.5$ bar and using perfluoroether (Porofil) with the surface tension of $16$ dynes cm$^{-1}$ as the pore filler. The hydrophobicity of the support and membrane surfaces was determined by measuring their contact angles using a KSV CAM200 equipment at
ambient temperature. Sorption measurements for the support and membranes in pure water, pure n-butanol and 5 wt% water/n-butanol solution were carried out at room temperature. The pre-dried support or membrane strips were weighed before immersed into sorption solutions, which were kept in a closed vessel for 30 days.

The swollen strips were then taken out, blotted with tissue paper and then weighed using the four digits balance (AND GH-202, Japan). The degree of sorption was calculated by using following equation:

$$Ds = \frac{W_e - W_o}{W_o}$$

(4.1)

Where $W_o$ and $W_e$ refer to the weights of the strips before and after immersed in solution.

4.3.4 Membrane performance

The membrane performance was evaluated through flux and separation factor. Flux is the rate of mass transfer through the membrane in a unit of time as following equation:

$$J = \frac{w}{A \times t}$$

(4.2)

Where $W$ is the weight of permeate collected in g, $A$ is the membrane surface area in m$^2$, and $t$ is the time in h.

Separation factor provides information on the quality of the permeate. It can be calculated from the following equation:

$$\alpha = \frac{y_1/y_2}{x_1/x_2}$$

(4.3)
Where \( y_1 \) and \( y_2 \) are the water concentrations in permeate and feed respectively, \( x_1 \) and \( x_2 \) is the n-butanol concentrations in the permeate and in the feed, respectively. They are determined by using a chromatography (GC) instrument (Agilent 7890A) connected to a thermal conductivity detector (TCD) with a HP – INNOWAX column of 60 m in length, 0.320 mm in diameter.

To understand the membrane intrinsic properties, permeance \((P_i/l)\) and selectivity \((\beta)\) were analyzed\(^{134,180}\). The permeance can be calculated from the following equation:

\[
\frac{P_i}{l} = \frac{J_i}{x_i y_i P_{i \text{ sat}} - y_i P_p} \tag{4.4}
\]

where \( x_i y_i P_{i \text{ sat}} \) is the feed fugacity.

Fugacity is the driving force for the component \( i \) transferring through the membrane, when the permeate pressure \( P_p \) is negligible. The fugacity is independent of the membrane properties. The saturated vapor pressure \((P_{\text{sat}})\) can be calculated from the Antoine equation:

\[
\ln P_{\text{sat}} = A - \frac{B}{C + T} \tag{4.5}
\]

where \( A, B \) and \( C \) can be obtained from Lange’s handbook of chemistry\(^{181}\). \( P_{\text{sat}} \) and \( T \) are calculated in kPa and \(^\circ\)C, respectively. The values are listed in Table 4.1

Table 4.1 A, B, C parameters of Antoine equation for water and n-butanol

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The activity coefficient $\gamma_i$ can be determined by applying the Wilson equation:

$$\ln \gamma_i = -\ln (x_i + A_{ij} x_j) + x_j \left( \frac{A_{ij}}{x_i + A_{ij} x_j} - \frac{A_{ji}}{A_{ji} x_i + x_j} \right) \quad (4.6)$$

Hence $x_i$ and $x_j$ are the mole fractions of water and butanol, respectively, while $A_{ij}, A_{ji}$ are Wilson equation parameters. The selectivity of water over butanol is defined as the ratio of their respective permeances:

$$\beta = \frac{P_i}{P_j} \quad (4.7)$$

4.4 Results and discussion
4.4.1 Membrane characterization

4.4.1.1 Pore size distribution

Figure 4.1 Pore size distribution of PVDF support measured using Porolux, Inset: SEM image of the PVDF support surface.

Figure 4.1 shows the SEM image of the support surface and its pore size distribution. It can be seen that the support has relatively large pores with an average diameter of 111 nm, which was measured by Capillary Flow Porometry. This method detects the active permeating pores. SEM gives a good estimation of pore size and distribution, however depicts only the surface and not necessarily distinguishes impermeable closed pores from continuous open pores. A relative low concentration of PVDF in NMP as casting solution and water as a non-solvent led to supports with large pores. The high porosity reduces the resistance for vapor transport under pervaporation operation. In addition, the pore size distribution is
sharp, convenient for a homogeneous Hyflon® AD coating layer on the support surface.

4.4.1.2 Support and composite membrane morphologies

Figure 4-2 shows the SEM images of the PVDF support coated with Hyflon® AD under different procedures. The surface of the membrane prepared with 2 wt % coating solution was not fully covered by Hyflon® AD with large open pores still evident. The surfaces of the membranes coated twice with a 2 wt % solution or with a single coating using 4 wt % solution are dense and no obvious pores can be observed anymore. The latter is smoother and therefore the subsequent results were obtained with coatings using 4 wt % Hyflon® AD solution.

![SEM surface images of porous PVDF support coated with (a) 2 wt%, (b) 2 wt% (twice) and (c) 4 wt% Hyflon®(R) AD solutions.](image)

4.4.1.3 Contact angle measurement

The PVDF support has a contact angle of 91.7° ± 0.8°, which indicates an inherently hydrophobic nature. After coating with Hyflon® AD, the hydrophobicity
of the resultant membrane increased, reflected by an increment in contact angle to \(119.6^\circ \pm 0.8^\circ\).

4.4.1.4 Sorption

The sorption behavior reflects the affinity between water and n-butanol and the membrane material. The sorption data in Figure 4-3 show that both the support and the coated membrane have much higher affinity towards n-butanol than water. The n-butanol sorption degrees are 44 % and 34 % for the support and the coated membrane, respectively, while those for water sorption are negligible. This result is consistent with the contact angle data, both of which confirm the hydrophobicity of PVDF and Hyflon® AD. Compared to the support, the sorption of the coated membranes is lower. This should be more a consequence of the higher support porosity than of thermodynamic interaction or solubility.
4.4.1.5 Thermal stability

The thermal stability of the support and coated membrane was determined by TGA analysis. The results in Figure 4-4 show that the polyester non-woven, PVDF support and Hyflon® AD coated membrane have high degradation temperatures of around 340°C. Although this indicated high chemical stability, the operation at high temperatures is limited by the PVDF melting temperature, which is around 177°C.
4.4.1.6 Pure water and n-butanol properties

Besides the membrane properties, the thermodynamics of the penetrating molecules significantly affect their transport\textsuperscript{18}. Figure 4-5 demonstrates the diagram of the vapor liquid equilibrium for water/n-butanol mixtures at 21°C by using the Aspen NRTL-RK method. It shows broad positive deviation from the Raoult’s law at low water compositions. When the water concentration in n-butanol is lower than 18 wt %, the slope of the curve is sharper, which implies higher water vapor fractions in the vapor mixture and hence higher separation efficiency towards water. From 18 to 76 wt % of water in n-butanol, the vapor pressure is constant which implies a two-phase system, and hence it is not necessary to conduct pervaporation on this region.
Figure 4-5 The diagram of vapor liquid equilibrium for water/n-butanol mixture at 21°C.

Table 4.2 lists the activity coefficient, saturated vapor pressure and flux of water and n-butanol at 21°C. These values of water are much higher than those of n-butanol, which indicates higher driving force for water permeation. When the temperature increases, the increment in saturated vapor pressure of water is higher Figure 4-6, which suggests that high temperatures may be beneficial for the separation.

Table 4.2 Characteristics of pure components

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>n-Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity coefficient</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Saturated vapor pressure</td>
<td>2.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Flux (g m⁻² h⁻¹)</td>
<td>710 ± 157</td>
<td>222 ± 69</td>
</tr>
</tbody>
</table>
4.4.1.7 Effect of different coating procedures on the membrane performance

Different coating protocols with various coating solution concentrations and coating time have been tested, starting from 0.5 wt% Hyflon® AD for 1 min. The resultant membrane did not have an adequately dense layer of Hyflon® AD, and consequently the pervaporation process was not satisfactory, with the feed solution leaking to the permeate side. Although the pervaporation process was feasible with a membrane coated with 2 wt% solution for 4 min, it has insufficient mechanical stability under vacuum. The membrane can resist the vacuum only for 30-40 min with high flux but very low separation factor as shown in Table 4.3. This result is consistent with its SEM image, which displayed the support partially covered by Hyflon® AD. Double coating with the same condition decreases the flux significantly and did not enhance the separation factor. Although double
coating is able to fill the large pores as its SEM image verified, it may not efficiently 
seal minor defects while increasing transport resistance due to the formation of the 
thicker coating layer. Increasing the coating concentration to 4 wt % was the best 
option, which enhances the separation factor to more than 1550 with a reasonably 
high flux of 156 g m\(^{-2}\) h\(^{-1}\). Hence coating with 4 wt % concentration was used for 
further investigation with respect to coating time.\(^{183}\)

These results indicate the dehydration capability of the Hyflon® AD /PVDF 
membranes although both materials are hydrophobic as confirmed by contact 
angle measurement and sorption data.

The separation efficiency is attributed to the occurrence of at least two 
simultaneous conditions, a high driving force for water permeation (as discussed 
in the pure water and n-butanol properties) and a low, but not negligible, selectivity 
to water. As well-known, the transport mechanism of pervaporation is governed by 
the solution-diffusion model, where the performance is determined by the affinity 
of membrane materials towards the permeate molecules (solubility) and their 
diffusion across the membrane (diffusivity). Although the Hyflon® AD /PVDF 
membranes have higher affinity towards n-butanol, Hyflon® AD is known for its 
high free volume. The diffusivity is critical for the selectivity in this case because of 
high driving force of water comparing to n-butanol. Water has also much smaller 
kinetic diameter than n-butanol (2.6 vs. 5.1 Å)\(^{183,184}\). Dehydration with the high free 
volume hydrophobic membrane with small degree of swelling with water is then 
very effective.
Table 4.3 Pervaporation performance for membranes coated by different procedures

<table>
<thead>
<tr>
<th>Coating solution concentration (wt%)</th>
<th>Time (min)</th>
<th>Total flux (g m$^{-2}$ h$^{-1}$)</th>
<th>Water in the permeate (wt%)</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>12758 ± 146</td>
<td>27 ± 5</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>4 (twice)</td>
<td>500 ± 64</td>
<td>30 ± 7</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>149 ± 2</td>
<td>82 ± 1</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>156 ± 3</td>
<td>98.8 ± 0.3</td>
<td>1564</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>156 ± 17</td>
<td>95 ± 4</td>
<td>361</td>
</tr>
</tbody>
</table>

Feed composition: 5 (wt):95 (wt) water:n-butanol

4.4.2 Effect of different coating times on membrane performance

In order to further optimize the coating procedure, different coating times, varying from 2 to 6 min, have been tested. The data in Table 4.3 shows that the total flux is similar for all the membranes coated with three different coating times, but the water permeate concentration increases from 80 wt % to 99 wt %. These results imply that no much change in the performance occurs after 4 min coating with 4 wt %, which was then adopted for all further membrane preparations.

4.4.3 Effect of feed water concentration on pervaporation performance

Different feed water concentrations varying from 5 wt % to 17.5 wt % have been investigated. The maximum solubility of water in n-butanol is about 20.1 wt % at 20 °C. Figure 4-7 shows how the flux of each component changes with increasing feed water concentration. From eq. 4.4, flux is determined by the
intrinsic membrane permeance and the external driving force, which is feed-concentration dependent. Table 4.4 shows the activity coefficients and feed fugacity as a function of mole fraction. Saturated vapor pressure for water and n-Butanol respectively is 2.5 and 0.64 kPa. A higher mole fraction of water leads to a lower activity coefficient, but the corresponding feed fugacity for water increases sharply with increasing feed water concentration. In case of n-butanol, despite the increase in activity coefficient with the increase in feed water concentration, its fugacity slightly decreases due to the higher decline in its mole fraction. However, both water and n-butanol fluxes do not follow the trends of their fugacity. To better understand the reasons behind the flux variation with feed concentration, we calculate the membrane permeance and selectivity according to eqs. 4.4 and 4.7.

![Figure 4-7 Effect of feed water concentration on flux.](image-url)
Table 4.4 Mole fraction, activity coefficient and fugacity of water and n-butanol with different feed water concentrations

<table>
<thead>
<tr>
<th>Water / n-butanol in feed (wt%/wt)</th>
<th>Mole fraction (mol %)</th>
<th>Activity coefficient</th>
<th>Feed fugacity (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>n-Butanol</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>(mol %)</td>
<td>(mol %)</td>
<td>(mol %)</td>
</tr>
<tr>
<td>5.0/95.0</td>
<td>0.18</td>
<td>0.82</td>
<td>3.9</td>
</tr>
<tr>
<td>7.5/92.5</td>
<td>0.25</td>
<td>0.75</td>
<td>3.2</td>
</tr>
<tr>
<td>13.5/86.5</td>
<td>0.39</td>
<td>0.61</td>
<td>2.3</td>
</tr>
<tr>
<td>17.5/84.5</td>
<td>0.47</td>
<td>0.53</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 4-8 Effect of feed water concentration on water and n-butanol permeance.
Figure 4-8 shows the water and n-butanol permeances of the membranes as a function of feed concentration. Both their permeances follow a similar trend, where there is a peak at the feed water concentration of 7.5%. When the feed water concentration increases, the dilution or concentration of certain molecules governs the change in formation of molecule clusters and in interaction among water, n-butanol and the membrane. The combination of these changes determines the trend of permeance.

Figure 4-8 also indicates that water permeance is much higher than 1-butanol permeance, expressing that the intrinsic property of the membranes is water-selective. Despite their hydrophobicity, the higher diffusivity of water leads to its preferential permeation. Figure 4-9 shows that both separation factor and selectivity decrease with an increase in feed water concentration. However, the separation factor still remains high (> 200), leading to a permeate water concentration > 90 wt%.
4.4.4 Effect of feed temperature on membrane performance

Figure 4-10 presents the water, n-butanol, and total fluxes through Hyflon® AD/PVDF membranes as a function of feed temperature. The results indicate that all the permeation fluxes increase with feed temperature. The temperature dependence of the flux can be analyzed by the Arrhenius equation\textsuperscript{186}:

\[ J = J_0 \exp\left(\frac{-E_J}{RT}\right) \]  

(4.8)

where \( J_0 \) is the pre-exponential factor, \( R \) is the universal gas constant, \( T \) is the operating temperature in K, and \( E_J \) is the apparent activation energy of the flux, which determines the overall temperature dependence on flux. The plot of the logarithmic permeation flux versus the reciprocal of feed temperature is shown in Figure 4-11. From this plot, the activation energies can be calculated and listed in
Table 4.5, as 6.6 and 85.7 kJ/mol for water and n-butanol, respectively. Their positive values reflect permeation fluxes increasing with temperature as shown in Figure 4-10. For other polymeric membranes it has been explained by the enhancement in thermal motion of polymer chains, leading to more accessible free volume in the polymer matrix and improved diffusion coefficients of the permeating molecules\textsuperscript{187,188}.

Table 4.5 Activation energies of water and n-butanol fluxes and permeances for Hyflon® AD /PVDF membranes

<table>
<thead>
<tr>
<th></th>
<th>$E_J$ (kJ/mol)</th>
<th>$P_J$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>6.6</td>
<td>-37.2</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>85.7</td>
<td>34.9</td>
</tr>
</tbody>
</table>

However in order to thoroughly understand the reason behind, the effects of feed temperature on membrane intrinsic property and external driving force have to be analyzed separately. According to eq. 4.4, the driving force for each component depends on its feed fugacity if the permeate pressure is negligible. Table 4.6 shows that the driving forces of both water and n-butanol increase remarkably with increasing temperature due to the rapid increase in their saturated vapor pressures. On the other hand, the water trend of permeance vs. temperature as shown in Figure 4-12 is opposite to that of its flux, where water permeance decreases with increasing feed temperature. Therefore, the increase in its flux is
mainly attributed to the increase in its driving force (saturated vapor pressure), rather than any intrinsic change in membrane property.

Figure 4-10 Effect of feed temperature on flux.
Figure 4-11 Plot of the logarithmic flux versus the reciprocal of feed temperature.

Figure 4-12 Effect of feed temperature on permeance.
Similarly, the permeance dependence on temperature follows the Arrhenius relationship and its activation energies $E_P$ are also listed in Table 4.5 as $-37.2$ and $34.9$ kJ/mol for water and $n$-butanol, respectively. By definition, $E_P$ is the combination of the activation energy of diffusion ($E_D$) and the enthalpy of dissolution ($\Delta H_S$). $E_D$ generally has a positive value, while $\Delta H_S$ is negative because of exothermic sorption. Since typically diffusion enhances but sorption declines with increasing temperature, the negative value of $E_P$ for water expresses that a more decrease in solubility than the increment in diffusivity for the water molecules at high temperatures. Similar observations have also been reported in previous studies\textsuperscript{131,174}. The opposite trend is observed for $n$-butanol, where a positive value of $E_P$ is obtained.
Table 4.6 Activity coefficient, saturated vapor pressure and fugacity of water and n-butanol at different feed temperature (T)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Activity coefficient</th>
<th>Saturated vapor pressure (kPa)</th>
<th>Feed fugacity (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>n-Butanol</td>
<td>water</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
<td>5.7</td>
</tr>
<tr>
<td>45</td>
<td>3.9</td>
<td>1.06</td>
<td>9.6</td>
</tr>
<tr>
<td>55</td>
<td></td>
<td></td>
<td>15.8</td>
</tr>
</tbody>
</table>

Mole fraction (mol %) of water 0.18 and for n-butanol 0.82

Figure 4-13 illustrates the temperature effects on separation factor and membrane selectivity and indicates that by increasing the temperature both separation factor and selectivity decrease. The membrane selectivity comprises diffusivity selectivity and solubility selectivity, and their values change with increasing temperature. As afore mentioned, Hyflon® AD membranes is characterized by diffusion selectivity towards water and sorption selectivity towards n-butanol. Increasing temperature enhances the mobility of polymeric chains, creating more and larger free volume available for both water and n-butanol, so the diffusion selectivity towards the smaller-sized molecule, i.e. water, decreases. On the other hand, both Hyflon® AD and PVDF are hydrophobic, which means the membrane displays solubility selectivity towards n-butanol. A temperature increase may increase solubility
selectivity towards n-butanol. The combined effects contribute to decrease in both separation factor and membrane selectivity.

4.5 Conclusion

In this study, Hyflon® AD /PVDF membranes have been developed for n-butanol dehydration. The following conclusions can be made:

1. The large and uniform pores of the PVDF support reduce the resistance for vapor transport and enable a homogeneous coating of the Hyflon® AD layer on its surface.

2. Water has higher driving force than n-butanol, which is the main contribution to its higher flux.

3. The coating condition of 4 wt% for 4 min was the most suitable to form a defect-free Hyflon® AD layer on the PVDF support.

4. The resultant membrane has a comparably high performance in terms of both flux and separation factor.

5. The partial fluxes and total flux follow a Λ-shape with increasing feed water concentration, which was attributed to the combination of the change in fugacity and the increase in permeability. In addition, increasing the water content in the feed results in lower separation factor and lower selectivity.

6. An increase in feed temperature leads to an increase in driving force and flux. However, water permeance decreases with increasing temperature due to the decrease in permeants’ sorption. By increasing the temperature, the membrane
separation factor and selectivity also decrease, due to the lower diffusion selectivity associated to the enhanced polymer chain mobility, free volume and solubility selectivity in the polymeric matrix.
Chapter 5: Purification of aqueous ionic liquid solution using membrane distillation

5.1 Introduction

Ionic liquid (IL) is a fluid of an organic salt in range of temperature from -96°C to around or below 100°C \(^{189}\) which are air and moisture stable. Ionic liquids have no effective vapor pressure, non-flammable, good chemical and thermal stability and good chemical conductivity. They can be used as a solvent for clean synthesis and catalytic reactions for industrial processes \(^{190-192}\), because they can dissolve wide range of organic and inorganic materials. They can be used as acidic catalyst in alkylation reaction, as solvent for liquid-liquid extraction \(^{193}\), as conductive material for electrodeposition of metals and semiconductors, electrochemical system and energy bio-device \(^{194,195}\).

To purify ionic liquid different techniques have been used depending on the ionic liquid like, distillation \(^{196-198}\), cooling crystallization \(^{199,200}\), liquid-liquid extraction \(^{196,201}\), adsorption by activated carbon \(^{202}\), pervaporation \(^{203}\), drying of the ionic liquid \(^{204}\). Membrane distillation (MD) is a new technique with a low cost, low operating pressure and temperature \(^{15}\), less requirement of membrane mechanical properties \(^{73}\), can be used for high solute concentration and no need for add chemicals \(^{205}\). For MD there are different configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). Although the main disadvantage of DCMD is heat lost by conduction, it is the most studied
among the configurations because it is the simplest one, whereas there is no need for an external condenser, and because of relatively high flux.

Purification of ionic liquid by membrane distillation is relatively new. Preliminary results have been only reported very recently, using PVDF and PTFE.

In this work PVDF membrane before and after coating with Hyflon were evaluated. Different feed temperatures and flow rates were investigated.

5.2 Materials

Poly (vinylidene fluoride) (PVDF, Kynar® HSV900) was kindly provided by Arkema. The polyester non-woven support fabric (05TH-100) was purchased from Hirose. Hyflon® AD60X with an average molecular weight of 500,000 g/mol and density of 1.93g/cm³ was purchased from Solvay Plastics. N-methyl pyrroloidone (NMP), from Sigma-Aldrich, was used as solvent for Extem® and PVDF, while Galden® HT200 from Solvay-Solexis was employed as the solvent for Hyflon® AD. 1-Ethyl-3-methylimidazolium acetate (≥ 95.0% purity) was purchased from Sigma-Aldrich and Milli Q water was used for all experiments, generated using a Millipore unit.

5.3 Experimental procedure

The DCMD lab-scale set-up for flat-sheet membranes was illustrated in Scheme 5.1, using membrane effective area of 50 cm². The conductivity was measured using conductive meter (Cond 3310, WTW). Initial feed conductivity was 23.6 mS/cm and the experiments run for 24 hours.
Scheme 5.1 Flat sheet membrane DCMD set-up (C1, C2 are conductivity sensors; P1, P2 are pressure sensors; T1, T2, T3, T4 are temperature sensors).

5.3.1 Membrane preparation

Phase inversion was the way to prepare 10wt% PVDF and 18wt% Extem® in water as a non-solvent. Each membrane was dip-coated in 0.5 wt% of Hyflon for 60 second and dried in room temperature overnight, followed by overnight vacuum oven at 65°C.

5.4 Results and discussion

5.4.1 Effect of operating feed temperature

Different feed temperatures, fixed permeate temperature of 20°C, permeate and feed flow rates fixed at 100 mL/min were chosen as operation conditions. A feed solution of ionic liquid/water with conductivity of 23.6 mS/cm was tested. MD is a thermal process and it is highly depended on the temperature. Figure 5-1 illustrates that the increase of feed temperature, and therefore the temperature difference
across the membrane, will enhance the flux. The rejection remains high (≥ 99.8 wt%).

Figure 5-1 Effect of feed temperature on flux and rejection for PVDF membrane at 100 mL/min feed and permeate flow rate and permeate temperature at 20°C.

5.4.2 Effect of operating feed flow rate

By adjusting the feed temperature at 70°C, permeate temperature at 20°C and permeate flow rate at 100 mL/min, different feed flow rates, varying from 50 to 1000 mL/min were tested. Figure 5-2 shows that flux increases five-fold with flow rate increasing from (2 kg m⁻² h⁻¹ to 10 kg m⁻² h⁻¹) because it increased the turbulence and reduced the boundary layer on membrane surface. The rejection remains high at high feed flow rate, because the hydrostatic trans-membrane pressure is lower than the liquid entry pressure (LEP), which is for PVDF = 4.4 bar. This ensures that the membrane pores will not be wetted.
5.4.3 Effect of PVDF/Hyflon® membrane

When the membrane is coated with Hyflon, surface hydrophobicity is increased. The contact angle of the membrane increased from \((91.7 \pm 0.8)°\) to \((119.6 \pm 0.8)°\).

The performance was evaluated after coating the PVDF membrane with Hyflon® for different feed temperatures and flow rates. In Figure 5-3 and Figure 5-4 similar behavior was observed for PVDF before coating. Excellent rejection, but lower flux was observed, due to the added coating layer, which reduced the pore sizes.

Figure 5-2 Effect of feed flow rate on flux and rejection of PVDF membranes, under the following conditions: 70°C feed temperature, 20°C permeate temperature and 100 mL/min permeate flow rate.
Figure 5-3 Effect of feed temperature on flux and rejection for PVDF/Hyflon membrane at 100 mL/min feed and permeate flow rate and permeate temperature at 20°C.

Figure 5-4 Effect of feed flow rate on flux and rejection of PVDF/Hyflon membrane at 70°C feed temperature, 20°C permeate temperature and 100 mL/min permeate flow rate.
5.5 Conclusion

Membrane distillation is a new effective way to dehydrate ionic liquid. High rejection is obtained over wide range of temperature and feed flow rate. Water flux increases with increase of feed flow rate. New porous hydrophobic material can be applied to separate water from ionic liquid in membrane distillation.
CONCLUSION

In this work simple and effective ways to control and enhance the membrane performance for applications in the chemical industry have been proposed.

In chapter 2, ultrafiltration membranes based on Extem® were improved, by blending the polymer casting solution with *in-situ* polymerized silsesquioxane, containing epoxy groups. The epoxy groups were further used for attachment of poly (ether diamine) oligomers or anchoring of amine-functionalized nanoparticles.

A new approach was demonstrated, combining phase inversion and simultaneous functionalization reaction during the membrane formation ("reactive phase inversion"). The method was used for crosslinking with incorporation of hydrophilic segments. Other approaches, mixing the crosslinker directly with the polymer solution containing preformed poly epoxy-functionalized polysilsesquioxane, led to membranes with sharp pore size distribution with high water permeance.

In chapter 3 and 4, Hyflon®/Extem® and Hyflon®/PVDF membranes have been developed by dip-coating porous supports with Hyflon® for ethylene glycol and alcohol dehydration, by pervaporation. By increasing the feed temperature, flux could be enhanced. By increasing the temperature, the membrane separation factor and selectivity decreased, due to the lower diffusion selectivity, associated to the enhanced polymer chain mobility, free volume and solubility selectivity in the polymeric matrix.
In chapter 5, porous hydrophobic membranes were developed for membrane distillation used for dehydration ionic liquid. By varying the operating parameters the permeate flux could be optimized.
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