Membrane Technology for the Regeneration of Supercritical Carbon Dioxide

PROEFSCHRIFT

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To my family, my inspiration
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Summary

For many applications the use of supercritical fluids provides effective possibilities to replace organic solvents. However, one of the main problems in supercritical fluid applications is the regeneration of the supercritical fluid. Generally, the regeneration is performed by decreasing the solubility of the solute in the supercritical fluid. Regeneration by expansion or cooling is accompanied by extensive energy consumption, as the fluid needs to be repressurized and reheated to supercritical conditions. Selective membrane separation of supercritical fluids could open new and economically attractive possibilities for the regeneration step.

In this thesis, three different types of composite membranes have been tested for use in supercritical fluids. Polymeric membranes consisting of a polyethersulfone ultrafiltration membrane as a base membrane and two different selective polymeric top layers have been used. One top layer consists of polyvinyl alcohol (PVA) and the other top layer consists of a polyamide polymer. The ceramic membrane consists of support layers of $\alpha$– and $\gamma$–alumina with silica as the selective layer. Finally, membranes consisting of a selective titania layer with different molecular weight cut-off on a $\alpha$-alumina support have been tested.

The performance of the different membranes has been evaluated by measuring the fluxes of different species as a function of feed pressure, the temperature and the pressure difference across the membranes. Furthermore, the different types of membranes have been tested for the regeneration of supercritical carbon dioxide. The solubility of oil-like components in supercritical carbon dioxide has been studied using a cloud point method. Knowledge of the phase equilibria is important to maintain a homogeneous supercritical phase during the regeneration. Phase separation of the solutes and the $\text{CO}_2$ should be avoided, because this reduces the membrane performance. In the development of the polymeric membranes swelling and plasticization effects of $\text{CO}_2$ on the polymers have been studied as well.

With respect to the permeation behaviour, a general picture has appeared that at supercritical conditions the main mechanism for mass transport across the different membranes is by viscous flow. For all the three types of membranes a maximum is observed for the permeance of $\text{CO}_2$ and $\text{SF}_6$ as a function of the feed pressure. For permeation experiments conducted at a temperature just above the temperature where $\text{CO}_2$ and $\text{SF}_6$ become supercritical, a maximum is observed in the permeance at the
pressure where the species become supercritical. It is observed that the permeance of the two supercritical fluids obtained for different conditions can be described by a single mobility constant, which is independent of temperature and pressure. At supercritical conditions the mass transport across the membranes is mainly determined by the phase behavior of the fluid. It is observed that at high pressures CO
\textsubscript{2} has a plasticization effect on the two polymeric membranes, which reduces the stability of the membranes. Increasing the degree of crosslinking of the top layer improves the stability considerably; however, this is at the cost of a reduction in the CO
\textsubscript{2} permeance. On the other hand, both the silica and titania membranes show excellent stability, as the permeance of supercritical CO
\textsubscript{2} through the two types of membranes, for a given temperature and pressure has remained constant during the whole experimental program.

Regeneration of supercritical carbon dioxide is demonstrated by performing rejection experiments with two oil-like species, i.e. triolein and e-vitamin. Retention factors and the carbon dioxide permeance have been determined simultaneously. Complete retention is possible for both triolein and e-vitamin using a titania membrane at the cost of a considerable reduction in carbon dioxide permeance. For triolein good retention is possible with the silica membrane. The retention factor lies between 0.97 and 0.99, with a reduction in the carbon dioxide permeance of about 20% compared to the pure carbon dioxide permeance.

Although polymer swelling is detrimental for membrane performance, it is an advantageous phenomenon in polymer particle production. For producing polymer particles, e.g. for toner and paint, supercritical CO
\textsubscript{2} is proposed to reduce the viscosity of polymer melts. In order to obtain a processing window for particle production, the solubility of carbon dioxide in two polyester resins and the swelling of the resins have been measured independently. For the two polyester resins, propoxilated bifensol (PPB) and ethoxylated bifensol (PEB), the solubility of CO
\textsubscript{2} increases with an increase in pressure and a decrease in temperature as a result of variations in CO
\textsubscript{2} density. Moreover, the solubility of carbon dioxide in the resins has been described using the Sanchez-Lacombe equation of state.

The research presented in this thesis has lead to an improved insight in employing organic and inorganic membranes for the regeneration of supercritical carbon dioxide. The study of the swelling behavior gives a better understanding of the behavior of polymers in high density CO
\textsubscript{2}, which can be used in the development of polymeric membranes and in particle production methods. Finally, it can be concluded that
different inorganic membranes are available that have a reasonably high flux, are stable, and have a good retention performance at supercritical conditions. The use of these inorganic membranes opens the possibility for continuous and efficient regeneration of supercritical fluids.
Chapter 1

General Introduction

Abstract
Interest in supercritical carbon dioxide (scCO$_2$) as a solvent for various reactions and separations has increased rapidly. Current focus is on minimizing the energy requirement for scCO$_2$ applications. The use of membrane technology to regenerate scCO$_2$ can be an interesting alternative to avoid the depressurization step. The purpose of this chapter is to present an overview of the membrane technology for regeneration of supercritical carbon dioxide. Finally, the outline of the thesis is presented.
1.1. Supercritical fluids

In 1822, Baron Charles Cagniard de la Tour showed experimentally that there is a critical temperature above which a single substance can only exist as a fluid instead of either being a gas or a liquid. A liquid placed in a sealed container is in equilibrium with its vapor. When the liquid is heated and compressed the density of the vapor increases. Above a certain value of the temperature and pressure, which is called the critical point, the density of the vapor becomes equal to the density of the liquid and the interface between liquid and vapor disappears. Since this system is neither a liquid nor a gas, it is called a supercritical fluid (SCF) (see Figure 1.1).

Supercritical carbon dioxide (scCO$_2$) is the most frequently used SCF, because it is environmentally friendly, nontoxic, non-flammable, inexpensive, has relatively easily achievable critical P and T conditions, and the extraction power can be tuned by temperature and pressure. Therefore, scCO$_2$ is used as an alternative green solvent for various reactions, extractions, and separation processes.

![Figure 1.1: Photographs showing the transformation of liquid CO$_2$ to supercritical CO$_2$ upon heating, observed by the disappearance of the meniscus (heating order 1-4).](image)

The main advantages of supercritical fluids are their physical properties resembling those of both liquids and gases, see Table 1.1. The combination of low viscosities and high diffusion coefficients found in supercritical fluids is a major advantage because low viscosity leads to good infiltration of the extraction material, a small pressure drop, good mass transfer, and improved phase separation. High diffusion coefficients will improve mass transport, and mass transfer rates in scCO$_2$ are higher than in...
conventional organic solvents. In general, mass transfer limitations are negligible in SCF [1]. In Table 1.2 the critical conditions of a number of species are given (also see Figure 1.2 for phase diagram).

Figure 1.2: Pressure-Temperature phase diagram with T the triple point and C the critical point.

Table 1.1: Physical properties of gases, compressed gases and liquids.

<table>
<thead>
<tr>
<th>State</th>
<th>Density [kg m$^{-3}$]</th>
<th>Dynamic viscosity [Pa s]</th>
<th>Diffusion coefficient [m$^2$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas at (T$<em>{ambient}$, P$</em>{ambient}$)</td>
<td>0.6-2.0</td>
<td>(1-3) x 10$^{-5}$</td>
<td>(0.1-0.4) x 10$^{-4}$</td>
</tr>
<tr>
<td>Supercritical fluid at (Tc, Pc)</td>
<td>200-500</td>
<td>(1-3) x 10$^{-5}$</td>
<td>0.7 x 10$^{-4}$</td>
</tr>
<tr>
<td>Supercritical fluid at (Tc, 4Pc)</td>
<td>400-900</td>
<td>(3-9) x 10$^{-5}$</td>
<td>0.2 x 10$^{-4}$</td>
</tr>
<tr>
<td>Liquid</td>
<td>600-1600</td>
<td>(0.2-3) x 10$^{-3}$</td>
<td>(0.2-2.0) x 10$^{-9}$</td>
</tr>
</tbody>
</table>

Table 1.2: Critical conditions of various inorganic and organic solvents [2].

<table>
<thead>
<tr>
<th>Name</th>
<th>Critical temperature [K]</th>
<th>Critical pressure [MPa]</th>
<th>Molecular weight [g mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>304</td>
<td>7.38</td>
<td>44.0</td>
</tr>
<tr>
<td>Water</td>
<td>647</td>
<td>22.1</td>
<td>18.0</td>
</tr>
<tr>
<td>Sulfur hexafluoride</td>
<td>319</td>
<td>3.76</td>
<td>146.1</td>
</tr>
<tr>
<td>Argon</td>
<td>151</td>
<td>4.86</td>
<td>40.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>305</td>
<td>4.87</td>
<td>30.1</td>
</tr>
<tr>
<td>Propane</td>
<td>370</td>
<td>4.25</td>
<td>44.1</td>
</tr>
<tr>
<td>Ammonia</td>
<td>405</td>
<td>11.3</td>
<td>17.0</td>
</tr>
</tbody>
</table>

1.2. Membrane technology for regeneration of scCO$_2$

Supercritical fluid technology is a versatile technology, which requires an economical method to recycle the supercritical carbon dioxide. The use of membrane technology to regenerate scCO$_2$ can be an interesting alternative to avoid the depressurization step, which is necessary for the recovery of the extracts. In principle, a small trans-membrane
pressure should be sufficient to regenerate the carbon dioxide while the solutes are retained by the membrane. Membrane stability and selectivity are the main issues in membrane development for use at supercritical conditions. The development of new microporous polymer and inorganic membranes has offered new perspectives for membrane separations at supercritical conditions.

Since the early 1990s, membrane separation of supercritical fluids has been the subject of research. The efforts to understand the fundamentals of membrane materials for use in high pressure carbon dioxide started approximately in the last decade [3]. Initially, the focus has been on the development of polymeric membranes for use in supercritical carbon dioxide [4,5,6]. Working with model compounds and a Nafion composite membrane, it was shown that the new process provides synergistic effects leading to improved performance [7].

One of the main observations on the permeation across the membranes in the early studies was the occurrence of hysteresis for CO\(_2\) permeance. Muller et al. [4] studied supercritical CO\(_2\) permeation through an aluminum oxide ultrafilter. The permeabilities observed for the supercritical state were up to four times higher than for gaseous CO\(_2\). However, the permeability obtained by increasing and decreasing the pressure difference across the membrane between 1 and 18 MPa revealed a hysteresis phenomenon, which was not observed at 353 K. Hysteresis was also observed for composite nanofilters consisting of a macroporous alumina substrate and a mesoporous titanium oxide selective top layer [5].

The hysteresis phenomenon was explained by assuming partially irreversible CO\(_2\) adsorption onto the pore walls, apparently reducing the apparent pore radius. The reduction in pore size could be enhanced by a local increase in the fluid density and thus in the viscosity. This kind of adsorption and diffusion phenomenon was also observed for high pressure carbon dioxide permeation across alumina-silica membranes [8,9,10].

In the case of polyimide membranes, at high temperatures a linear dependence of the permeation activation energy on the kinetic molecular diameter of the penetrants was found. This shows that the diffusion of penetrants and intermolecular interactions are important factors [11,12].

### 1.2.1. Polymeric membranes

Polymeric membranes can be classified as porous, e.g. micro- or ultrafiltration membranes, or as non-porous. One important characteristic of polymers for membrane separation is the state of the polymer, like amorphous, semicrystalline or crystalline. This state is significant for the mechanical, chemical, and thermal stability, and has an
influence on the permeation properties [7]. Amorphous polymers are mostly used for membrane separations because the permeability is an order of magnitude higher than that of crystalline polymers. Amorphous polymers appear in a glassy and a rubbery state. In the glassy state the mobility of the polymer chains is very restricted, because the chains cannot rotate freely around their main chain bonds. The chain mobility and the volume between the polymer chains, which is called the “free volume”, are responsible for the solubility and the diffusion of the molecules penetrating through the membrane. The physical properties are determined to a large extent by the polymer backbone and by adding different side groups to the backbone. The fact that CO$_2$ has a plasticizing effect and can swell many polymers is the main difficulty in membrane separation of scCO$_2$ with polymeric membranes. These effects result in a strong decrease in stability and selectivity, which makes the membrane process unfavorable.

### 1.2.2. Inorganic Membranes

The other important class of membranes is inorganic membranes. Inorganic membranes exhibit physical and chemical properties that are not, or only partially, shown by organic membranes, including a better structural stability without the problems of swelling or compaction. Generally, they can withstand harsh chemical environments and high temperatures [13,14]. The inorganic membranes can be broadly classified into five categories, i.e. glass, metal, carbon, ceramic, and zeolite membranes. These membranes are actually microporous sieves and separation is based on a tortuous path, adsorption-diffusion and size exclusion type of mechanisms [15]. Most of the inorganic membranes consist of $\alpha$-alumina (Al$_2$O$_3$) as the support layer and a selective top layer [3,4,7,8,16,17,18]. Various studies are available on different selective top layers, such as silica [3,7,18], TiO$_2$ [4], ZrO$_2$-TiO$_2$ [14], zeolite [12,17] including silicalite [8], and carbon molecular sieves [19]. A substrate layer of alumina provides a relatively open porous structure having an average pore size of about 200-300 nm [8]. Reported pore sizes for inorganic membranes applied for supercritical carbon dioxide applications are in the range of 0.5 to 3.3 nm [7,12,14,18]. As an example, in the case of caffeine separation using a zeolite membrane with a pore size as low as 1.1 nm, separation occurs by a molecular sieving mechanism [20].

### 1.2.3. Overview of regeneration of CO$_2$ using polymeric membranes

A perfluorinated polymer (Nafion) and Mylar, a polyethylene terephthalate have been investigated for separation of naphthalene and 1,4-naphthoquinone from supercritical carbon dioxide [21]. Nafion shows good CO$_2$ permeability and high rejection for both
components. It was concluded that the CO$_2$ flux through those polymeric membranes depends on temperature and feed fugacity.

Table 1.3: Overview of polymeric membranes for different solute separations from scCO$_2$.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Solutes</th>
<th>P (MPa)</th>
<th>T (K)</th>
<th>ΔP (MPa)</th>
<th>Separation performance/factor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion® (perfluorinated polymer) Mylar (PET)</td>
<td>Naphthalene, 1,4- naphthoquinone</td>
<td>P=6.5–26</td>
<td>T=304–320</td>
<td>ΔP=0.035–0.172</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cellulose tri- and di-acetate</td>
<td>Lemongrass oil, orange oil and nutmeg essential oil</td>
<td>P=12</td>
<td>T=313</td>
<td>90% oil retention</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Kapton®</td>
<td>Hydrocarbons</td>
<td>P=8–12</td>
<td>T=423</td>
<td>Separation factor of 12.8</td>
<td>10,11</td>
<td></td>
</tr>
<tr>
<td>Polyimide/ Polyamide</td>
<td>Ethanol</td>
<td>P=15</td>
<td>T=373</td>
<td>Separation factor of 87</td>
<td>10, 21</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>Caffeine</td>
<td>P=7.95</td>
<td>T=308–313</td>
<td>ΔP=0.3</td>
<td>100% caffeine rejection</td>
<td>14</td>
</tr>
</tbody>
</table>

Ohya et al. [11,12] have developed symmetric and asymmetric polyimide Kapton membranes for the separation of hydrocarbons from carbon dioxide, especially alkanes or alkenes obtained from enhanced oil recovery. For supercritical fluid feed mixtures with a of CO$_2$ and iso-octane with a molar concentration ratio of 25:1, a separation factor of 12.8 was obtained at 423 K between 8 and 12 MPa. A linear relationship between the flux and transmembrane pressure was obtained. A similar relationship between the flux and the transmembrane pressure was also observed by Semenova et al. [21] and Hsu et al. [22] in the case of ethanol separation with polyimide and polyamide membranes, respectively. An overview of different polymeric membranes used for regeneration of scCO$_2$ is given in Table 1.3.

In order to generalize the prediction of the rejection of a specific component using a membrane, model compounds such as polyethylene glycols (PEGs) have been used to describe the molecular weight cut off (MWCO) range of the membranes [3,4,5]. Sarrade et al. [5] also demonstrated that fractionation of low and high molecular weight fatty acids in scCO$_2$ is possible using nanofiltration separation.

Other fields of membrane application at near critical and supercritical conditions are the separation of different phases from each other, and to increase the phase boundary area. These processes are called perstraction and were proposed by Robinson and Sims [23].
Perstraction has been used to extract special compounds from fruit juice concentrate, and the membrane is used to separate the fruit juice concentrate from the scCO$_2$.

1.3. Outline of the thesis
In this thesis the regeneration of supercritical carbon dioxide using different membranes has been explored. The main focus of the research is to develop and study polymeric and inorganic membranes for scCO$_2$ applications.

In chapter 2 permeation of supercritical carbon dioxide through a polyamide composite membrane is discussed. In particular, the polymeric membrane top layer has been developed for use in supercritical carbon dioxide. The CO$_2$ transport through the membrane is described as a function of the ratio of the density and viscosity. In chapter 3 the transport mechanisms of supercritical fluids through an inorganic silica membrane are discussed, by comparing the permeation behavior of CO$_2$ and SF$_6$. A comparison with the polymeric membranes is also given. In chapter 4 the solubility of PEGs (MW= 200, 400 and 600), triolein and e-vitamin in supercritical carbon dioxide is discussed. The phase equilibria determine the processing window for membrane separation. A proper description of the solubility is important to avoid concentration polarization on the top layer of the membrane. In chapter 5 the rejection performance of polyamide, silica and titania membranes is discussed. The rejection studies have been performed using two systems; the first system is a mixture of scCO$_2$ and triolein and the other system consists of scCO$_2$-e-vitamin mixtures. In chapter 6 the swelling of two polyester resins by scCO$_2$ is discussed. This work could open up the possibility to study swelling of different polymers used as membrane materials. In chapter 7 conclusions are drawn, based on the work described in this thesis. Also, a number of SCF applications where membranes are used to integrate reactions and separations are discussed, with the focus on the ‘regeneration’ of the supercritical fluid.

The main purpose of the research described in this thesis is to enlarge the operating window of membranes for regeneration of supercritical carbon dioxide. Therefore, the studies presented in this thesis are relevant in order to make supercritical fluid technology more energy efficient for extractions, reactions and separations.
References


Chapter 2

Permeation of Supercritical CO₂ through Polymeric Hollow Fiber Membranes*

Abstract
Permeation of carbon dioxide has been measured for two types of composite polymeric hollow fiber membranes for feed pressures up to 18 MPa at a temperature of 313 K. The membranes consist of a polyamide copolymer (PA) layer or a polyvinyl alcohol (PVA) layer on top of a polyethersulfone (PES) support membrane. For both membranes the carbon dioxide permeance has a maximum as a function of the feed pressure at about 8 MPa. A good description of the maximum in the carbon dioxide permeance is possible with a model based on the ratio of the density to viscosity. A comparison with permeation results for nitrogen for feed pressures up to 16 MPa, supports the findings that viscous flow is the main mechanism for mass transport across the membranes. Both membranes show an increase in the carbon dioxide permeance as a function of the exposure time to supercritical carbon dioxide. Cross-linking of the PA layer resulted in a stable PA-based membrane at the cost of a small reduction in the carbon dioxide permeance.

2.1. Introduction

Membrane technology offers a suitable option for continuous regeneration of high pressure carbon dioxide. In particular, the use of a membrane can lead to a reduction in pressure losses and recompression costs. Several studies have shown that polymeric membranes tested for carbon dioxide separation can be used successfully for the regeneration of supercritical carbon dioxide (scCO$_2$) [1-6]. Sarrade et al. [4,5] have used a multilayer composite nanofilter, comprising a macroporous $\alpha$-alumina substrate, a mesoporous titanium oxide underlayer, and an organic top layer of Nafion. The stability of these organo-mineral nanofiltration membranes in carbon dioxide has been studied and the governing transport mechanism for different carbon dioxide pressures has been determined. Schell et al. [6] proposed the use of a gas diffusion membrane for intensive hydrocarbon recovery. It was concluded that carbon dioxide transfer across the membrane was predominantly by convection rather than by diffusion.

A limited number of modeling studies have been carried out to describe supercritical carbon dioxide permeation through membranes. Most work focuses on the effect of the pressure difference across the membranes on the permeation, which typically shows a linear dependence between the CO$_2$ permeation and the pressure difference [4,7,8]. Sarrade et al. [4] studied CO$_2$ permeation for pressures up to 28 MPa, and observed a maximum in the CO$_2$ permeance as a function of feed pressure.

The objective of this work is to study the permeation of gaseous and supercritical carbon dioxide across two types of composite polymeric hollow fiber membranes with different top layers. First, the steady state CO$_2$ permeance through the polymeric membranes is studied, and the effect of the feed pressure on the permeation is obtained. Next, because plasticization of carbon dioxide on polymers deteriorates the performance of the membranes, the stability of the membranes is tested when exposed to scCO$_2$ for a longer period of time. This includes studying the effect of cross-linking of the polymeric top layer on the stability of the membrane in the presence of scCO$_2$. In particular, the PA-based membrane has been evaluated using two different degrees of cross-linking.

2.2. Experimental

2.2.1. Setup and methods

The high pressure permeation setup used to measure the steady state flux through the membranes is schematically depicted in Figure 2.1. The experimental setup is designed to test the membranes up to feed pressures of 40 MPa and temperatures up to 473 K.
The membranes were placed in a thermally controlled oven (Heraeus) and the temperature was measured with a Pt100 thermocouple. A thermocouple was placed at the feed side of the carbon dioxide stream in order to measure the temperature of the fluid stream entering the membrane module. Carbon dioxide was filtered by an inline filter to feed pure fluid for smooth operation of the HPLC pump (Jasco). To make sure that the feed to the pump is in the liquid phase, the pump piston heads were cooled to a temperature of 278 K. The fluid was heated to supercritical conditions by a coil, which is placed inside the oven. The amount of fluid flowing in the system was measured by a coriolis type mass flow meter.

To start the permeation experiments, fluid was fed to the feed and permeate side of the membrane by keeping the valve VP open. Both sides of the membrane were pressurized to assure that no excess pressure difference across the membrane could exist, which could damage or break the membrane. When the desired pressure at the feed side was obtained valve VP was closed. The pressure in both compartments of the membrane was controlled by a back pressure regulator (BPR, Tescom). The BPR on the permeate side was fine-tuned to create the desired pressure difference across the membrane. The pressure on both sides of the membrane was measured by two pressure sensors (AE Sensors) with an accuracy of 0.01 MPa. The BPRs were placed in a thermally controlled water bath to ensure steady operation. This was necessary because carbon dioxide expanded during regulation of the pressure and the BPRs were cooled severely due to Joule-Thompson expansion effect [9]. The flow of expanded carbon dioxide was measured using a wet gas meter (Schlumberger). Small flows were measured with a soap bubble flow meter.

Permeation experiments were performed using a pressure difference across the membrane ranging between 0.05 to 0.3 MPa, using a dead end configuration. The amount of fluid going through the membrane at a certain ΔP was measured for different feed pressures, which in turn gives the flux through the membrane in terms of number of moles of carbon dioxide permeating through a fixed surface area of the membrane per unit time. The complete series of experiments was repeated with different feed pressures ranging from 1 to 18 MPa using about the same pressure difference across the membrane.
2.2.2. Materials
Carbon dioxide (grade 5.0) and nitrogen (grade 5.0) were obtained from HoekLoos (Amsterdam, The Netherlands).

2.2.3. Membrane preparation
Two different selective top layers, polyvinyl alcohol (PVA) and polyamide copolymer (PA) were placed on an ultrafiltration polyethersulfone (PES) support membrane. The internal diameter and wall thickness of the PES support membrane was 1.5 mm and 425 μm, respectively. PES was employed due to its low hydrophobicity, as compared to other polymers usually used for membrane preparation. Hydrophilic membranes are generally less accessible to fouling which is an important issue in membrane performance [8]. PES possesses very good chemical and thermal stability, and the glass transition temperature ($T_g$) is 503 K.

A selective top layer of PVA of about 1-2 μm of thickness was developed by a solution coating method, and the polyamide (PA) top layer was prepared by an interfacial polymerization process. The thickness of the PA top layer was about 0.5-1 μm. The reaction scheme of the interfacial polymerization process is shown in Figure 2.2a.

**Figure 2.1:** High pressure membrane setup for steady state permeation measurements.
During the interfacial polymerization process two bi-functional monomers (a di-acid chloride and a diamine) were allowed to react, resulting in a typical network structure at the water/organic solvent interface. Also, two polyamide top layers were obtained with a different degree of cross-linking. The cross-linked layers were obtained by addition of 0.1 wt% and 0.3 wt% 1,5,8,12-tetraazadodecane (N₄) as the cross-linking agent, respectively. The cross-linking agent is denoted as N₄ because the molecule has four amine groups which react to form a network with the polymer chains causing cross-linkage (see Figure 2.2b). The N₄ was added in a water phase and then brought into contact with the organic solvent interface in order to react and obtain cross-linked membrane fibers.

![Isophthaloyl Chloride](image1)

**Figure 2.2a:** Interfacial polymerization reaction scheme for forming the polyimide (PA) selective membrane top layer.

![Crosslinking agent, N₄](image2)

**Figure 2.2b:** Crosslinking agent, 1,5,8,12-tetraazadodecane (N₄)

### 2.2.4. Scanning electron microscopy
Membrane structure and dimensions were determined with a JEOL Scanning Electron Microscope (SEM). Cross sections of the membranes were obtained by freezing-fracturing, i.e. by the immersion of the sample in liquid nitrogen. The membranes were mounted on an aluminum disk with a double surface type. The sample holder was then placed in a sputter-coater and subsequently evacuated. Gold was used as the coating
material. Then the SEM pictures were obtained at certain magnifications to see the details of the membrane.

2.2.5. **Swelling detection with viewing-cell**
An attempt was made to detect the swelling of the membrane fiber in carbon dioxide by using a high pressure viewing-cell. The membrane fiber was inserted into a UV-cuvet as shown in Figure 2.3. The overall thickness of the fiber (base membrane + top layer) was in the range of 1.5 to 1.93 mm depending on the thickness of the top layer. It was measured visually by using a cathetometer, which has an accuracy of 0.01 mm. These visual observations only could show if there was any increase in overall thickness of the membrane mainly due to swelling of the PES support membrane.

![Figure 2.3: High pressure viewing-cell for visual swelling detection.](image)

2.3. **Theory**
Several models are available in the literature to describe the mass transport through membranes. The transport depends on the experimental conditions and the type of membrane. Inside a porous membrane with a distribution of pore sizes, several mechanisms like molecular sieving, capillary condensation, Knudsen flow, and Hagen-Poiseuille (viscous flow) are possible. For example, at moderate conditions the observed gas fluxes through mesoporous membranes, i.e. membranes with pore diameter smaller than 50 nm, are much higher than the flux expected by Knudsen diffusion [10,11]. This increase is attributed to so-called “surface flow”. Way and Roberts [12] suggested that this phenomenon is a result of interactions between the pore wall and the gas molecules. Hence a layer of adsorbed molecules builds up on the pore wall. In membrane
technology, however, the term surface diffusion has also been used to describe transport phenomena through materials such as Vycor glass [12] and silane modified γ-alumina membranes [13].

Most of the models [10,11,12] are used to describe the transport of gases and have only been tested for subcritical pressures. With respect to the permeance of carbon dioxide through polymeric membranes two mechanisms for mass transport are considered here. Viscous flow occurs when molecules collide exclusively with each other. However, if the pores are smaller and/or when the pressure of the gas is reduced, the mean free path of the diffusing molecules becomes comparable or larger than the pore size of the membrane. Collisions between the gas molecules are now less frequent than collisions with the pore wall and this kind of transport is known as Knudsen diffusion.

To describe the molar flux, $J$, through a membrane in the case of viscous flow, the Hagen-Poiseuille model [14] can be used

$$J = \frac{\varepsilon}{\tau} \frac{r^2}{8LM} \frac{\rho_f \Delta P}{\eta_f}$$  \hspace{1cm} (2.1)

with

$$\beta = \frac{\varepsilon}{\tau} \frac{r^2}{8LM}$$  \hspace{1cm} (2.2)

In the case of Knudsen diffusion the flux is given by [14]

$$J = D_k \frac{\varepsilon}{\tau} \frac{\pi r^2}{RTL} \Delta P$$  \hspace{1cm} (2.3)

where $D_k$ is the Knudsen diffusion coefficient, which is given by

$$D_k = 0.66 \frac{8RT}{\sqrt{\pi M}}$$  \hspace{1cm} (2.4)

In the following the permeance, $Q$, will be used to describe the mass transport through the membrane, which is given by

$$Q = \frac{J}{\Delta P}$$  \hspace{1cm} (2.5)

From Eq. (2.3) and Eq. (2.5) it follows that in the case of Kundsen diffusion the permeance is independent of the pressure. In the case of the Hagen-Poisseuille model, Eq. (2.1), the density and viscosity of the fluid are a function of the pressure, and as a result the permeance, Eq. (2.5), can be a strong function of the pressure.
2.4. Results and Discussion

2.4.1. Steady state permeation

To evaluate the performance of the two polymeric membranes the steady state CO$_2$ flux for feed pressures up to 18 MPa has been obtained for different pressure differences across the membrane.

First, a comparison is made between the permeation of CO$_2$ through the PES base membrane and the membrane with a selective PA top layer. The CO$_2$ flux as a function of the pressure difference, for a feed pressure of 10 MPa, through the PES membrane and the PA membrane are given in Figure 2.4. For both membranes the flux increases linearly with the pressure difference, and the CO$_2$ flux through the PES base membrane is about 15 times higher than the flux through the PA membrane.

![Graph](image)

**Figure 2.4:** Flux of carbon dioxide through the PES base membrane and the PA membrane as a function of the pressure difference across the membrane, for a feed pressure P= 10 MPa and T = 313 K.

Next, the CO$_2$ flux has been obtained as a function of the feed pressure for the PA and the PVA membrane. The results for the CO$_2$ permeance through the two membranes are given in Figure 2.5a for the PA membrane and in Figure 2.5b for the PVA membrane. From Figure 2.5 it follows, for both membranes, that the permeance first monotonically increases with the feed pressure up to about the pressure where carbon dioxide becomes supercritical. The CO$_2$ permeance through the two membranes has a maximum at about 8 MPa. This is somewhat higher than the pressure of 7.38 MPa, which indicates the CO$_2$ critical pressure. With a further increase in pressure the permeance decreases to some
extent, to reach a more or less constant value for pressures above 10 MPa. The CO\textsubscript{2} permeance through the PA membrane is about three times higher than the CO\textsubscript{2} permeance obtained with the PVA membrane.

![Graph](image)

**Figure 2.5:** Permeance of carbon dioxide through (a) PA membrane and (b) PVA membrane as a function of the feed pressure with $\Delta P=0.3$ MPa and $T = 313$ K.

These findings for the permeance of CO\textsubscript{2} are consistent with results reported in literature [4,15,16]. Muller et al. [15] and Nakamura et al. [16] observed a maximum in the permeance of CO\textsubscript{2} for inorganic ultrafiltration membranes. Also, Sarrade et al. [4] have observed a maximum in the permeance of CO\textsubscript{2} for organomineral membranes; these are composite organic/inorganic membranes and are referred to as TN membranes. These membranes comprise a tubular macroporous $\alpha$-alumina substrate, which is lined with a mesoporous titanium oxide underlayer and a microporous Nafion polymer top layer with a mean pore diameter of about 1 nm. The results for the permeance of CO\textsubscript{2} across the PA membrane are in same order as the results reported for the permeance of CO\textsubscript{2} across the TN membranes [4]. On the other hand, the CO\textsubscript{2} permeance (at 15 MPa) through the PA membrane is about 25 times higher than the permeance of scCO\textsubscript{2} through microporous silica membranes [17], and about 10 times higher than the CO\textsubscript{2} permeation through MFI zeolite membranes at about 300 K [7].

### 2.4.2. Viscous flow

From Eq. (2.1) it is clear that the ratio of the density to the viscosity will have a dominant effect on the permeation behaviour. Gaseous as well as supercritical carbon dioxide is well known for its plasticizing effect on polymers; therefore, it will be difficult to establish the transport properties in a polymer. To elucidate the transport
mechanism across the two polymeric membranes also some permeation experiments with nitrogen have been carried out. It is expected that nitrogen acts as an inert fluid, and that it does not have any detrimental effect on the membranes.

In Figure 2.6, the density and viscosity of carbon dioxide and nitrogen are given up to a pressure of 18 MPa. For CO\textsubscript{2} it is seen that for pressures below the critical pressure (7.38 MPa), the viscosity varies only slightly with pressure, while the density increases considerably. Around the critical point both the viscosity and density show a rapid increase. Above the critical point the change in the viscosity is somewhat larger than the change in density (Figure 2.6a). On the other hand, for nitrogen the viscosity and density both increase in a linear manner with an increase in pressure, over the whole pressure range (Figure 2.6b). For both fluids, the results for the density and viscosity as a function of the pressure have been calculated with the Modified-Benedict-Webb-Rubin (MWBR) model [9].

![Viscosity and density of (a) carbon dioxide and (b) nitrogen as a function of pressure at 313 K.](image)

**Figure 2.6:** Viscosity and density of (a) carbon dioxide and (b) nitrogen as a function of pressure at 313 K.

In Figure 2.7 a comparison is made between the experimentally obtained permeance for CO\textsubscript{2} and N\textsubscript{2} across the PA membrane and a fit with Eq. (2.1). It is seen that a good description of both permeances is possible, using the results for the density and viscosity as given in Figure 2.6. Below the critical point the CO\textsubscript{2} permeance increases because of the increase in density. Around the critical pressure, the viscosity and density of CO\textsubscript{2} change in such a way that a maximum is observed in the permeance. Above the critical point both the density and viscosity change with pressure, and as a result a slowly decreasing CO\textsubscript{2} permeance is obtained. The nitrogen permeance through the PA
membrane has also been measured, and the experimentally obtained results and a fit with Eq. (2.1) are given in Figure 2.7b. It can be seen that the nitrogen permeance increases almost linearly with pressure, indicating that also in this case the permeance is proportional to the density to viscosity ratio.

Furthermore, the $\beta$ parameter, Eq. (2.2) consists of the membrane properties and varies only with the molecular weight of the fluid. The pore diameter of the PA top layer is calculated from the carbon dioxide and nitrogen permeance for a feed pressure of about 9 MPa. Using the data of Table 2.1 a value for the pore diameter of 1.9 and 1.7 nm is obtained for CO$_2$ and N$_2$, respectively. From the fact that the values for the pore diameters are approximately the same it follows that there is not a significant difference in the membrane properties for the two fluids. The values for the porosity and tortuosity are average values taken from literature [7,14]. So small difference arising from swelling of the polymer in the case of CO$_2$ permeation are not accounted for. This might explain the small difference in pore size, obtained from modeling for the two fluids. This means that (gaseous) nitrogen can be used to determine the membrane pores size, giving the similar result as obtained from scCO$_2$ permeation.

Figure 2.7: Comparison between experimental results and results obtained with Eq. (2.1) and Eq. (2.5) for the permeance of (a) carbon dioxide and (b) nitrogen as a function of the feed pressure at 313 K. Results are for the PA membrane with $\Delta P=0.3$ MPa and $T = 313$ K.

A description of the permeance based on Knudsen diffusion is not appropriate, because in that case the mass transport across the membrane is independent of the pressure. Clearly, this is not observed experimentally for both membranes investigated.
**Table 2.1**: Overview of PA membrane and fluids properties.

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pressure [MPa]</td>
<td>9.0</td>
<td>8.95</td>
</tr>
<tr>
<td>Permeance $10^{-6}$ [mol m⁻² sec⁻¹ Pa⁻¹]</td>
<td>2.13</td>
<td>0.93</td>
</tr>
<tr>
<td>Viscosity $10^{-5}$ [Pa sec]</td>
<td>3.48</td>
<td>2.01</td>
</tr>
<tr>
<td>Density [kg m⁻³]</td>
<td>485.5</td>
<td>91.8</td>
</tr>
<tr>
<td>Layer thickness L [μm]</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Porosity $\varepsilon$ [-]</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Tortuosity $\tau$ [-]</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pore diameter [nm]</td>
<td>1.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Values for porosity and tortuosity are taken from literature [7, 14].

**2.4.3. Effect of cross-linking the top layer on the stability**

For polymers employed for regeneration of supercritical carbon dioxide a good plasticization and swelling resistance is required. Plasticization occurs because carbon dioxide diffuses through the polymer matrix and increases the mobility of the polymeric chains. As a result the polymer will swell upon sorption of carbon dioxide and the diffusion of carbon dioxide through the polymer will increase. Plasticization is undesirable for most “gas separation” membranes since the polymers used in these applications depend largely on diffusivity selectivity to achieve high overall permselectivity [18, 19].

During the measurements, it has been observed that both the PA and PVA membranes were showing some flux increment of about 30 - 50% during long term experiments. In these experiments the membranes have been exposed to scCO₂ (15 MPa, 313 K) for about 6 to 8 h. This indicates that the polymeric structure is changing, which most likely is a result of swelling and plasticization effects. An attempt has been made to detect the swelling by a visual technique, however, no visual change in overall thickness of the membranes is observed. It can be noted that a typical experiment to obtain the CO₂ permeance as a function of the feed pressure (Figures 2.5a and 2.7a) lasted about 2 h, where the membranes have been exposed to scCO₂ for about 1 h. Furthermore, the results presented in Figure 2.5a and 2.7a have been obtained with two different PA membranes, considering the small difference in CO₂ permeance the membrane manufacturing process showed reasonable reproducibility.

An option to improve the stability of the membranes is by cross-linking the polymer network in the active layer. The permeance measurements showed that the PA membrane with the highest degree of cross-linking (0.3 wt% N4) was not permeable to
carbon dioxide, indicating that the pores are too small to let carbon dioxide pass. The cross-linked PA membrane with the lowest degree of cross-linking (0.1 wt% N\textsubscript{4}) is permeable to CO\textsubscript{2}. In Figure 2.8 the result for a long term experiment with scCO\textsubscript{2} (15 MPa, 313 K) is shown. The CO\textsubscript{2} permeance obtained for a constant pressure difference of about 0.3 MPa remains constant during the experiment of about 6 h, indicating a high degree of stability. The value obtained for the CO\textsubscript{2} permeance across the cross-linked PA membrane is about 10 % lower than the value obtained for the PA membrane. This is a result of a reduction in the polymer chain flexibility caused by cross-linking the porous polymer network.

![Graph showing CO$_2$ permeance over time](image)

**Figure 2.8:** Carbon dioxide permeance through a cross-linked PA membrane (0.1 wt\%) as a function of time. Results are for a feed pressure of 15 MPa, ΔP=0.3 MPa and T = 313 K.

Microscope pictures of the cross-linked PA membrane were taken with SEM before and after they have been exposed to supercritical carbon dioxide to see changes in the structure (Figure 2.9). From the microscope pictures it is clear that there are not many changes, implying that the structure in the membrane is stable enough, even after being exposed to high pressure carbon dioxide for a long time.
2.5. Conclusion

Composite polymeric hollow fiber membranes with PA and PVA top layers have been tested for carbon dioxide permeance at a wide range of pressures. For the two types of membranes the same behavior for the CO$_2$ permeance has been observed. Initially, the permeance increases with an increase in feed pressure, and a maximum in the permeance is observed around the pressure where CO$_2$ becomes supercritical. In the supercritical state the CO$_2$ permeance slowly decreases. The transport mechanism through the membranes can be described by the Hagen-Poiseuille law for viscous flow. The stability of the PA membrane has been improved by cross-linking of the selective layer. Using 0.1 wt% of cross-linker resulted in an improved stability of the membrane against plasticization and swelling by carbon dioxide. The CO$_2$ permeance is reduced by about 10% as compared to the non-cross-linked membrane. These results open the possibility of regenerating supercritical carbon dioxide by using polymeric membranes, which have relatively high fluxes.

List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔP</td>
<td>Pressure difference</td>
<td>[Pa]</td>
</tr>
<tr>
<td>J</td>
<td>Flux</td>
<td>[mol m$^{-1}$ sec$^{-1}$]</td>
</tr>
<tr>
<td>L</td>
<td>Selective layer thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>M</td>
<td>Molecular weight of fluid</td>
<td>[g mol$^{-1}$]</td>
</tr>
<tr>
<td>Q</td>
<td>Permeance</td>
<td>[mol m$^{-2}$ sec$^{-1}$ Pa$^{-1}$]</td>
</tr>
<tr>
<td>r</td>
<td>Pore radius</td>
<td>[m]</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>[J K$^{-1}$ mol$^{-1}$]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>D$_k$</td>
<td>Knudsen diffusion coefficient</td>
<td>[m$^2$ sec$^{-1}$]</td>
</tr>
</tbody>
</table>
Greek

- \( \beta \): Membrane structural parameter \([\text{m mol g}^{-1}]\)
- \( \varepsilon \): Porosity \([-]\)
- \( \tau \): Tortuosity \([-]\)
- \( \eta_f \): Fluid viscosity \([\text{Pa sec}]\)
- \( \rho_f \): Fluid density \([\text{kg m}^3]\)

References


Chapter 3

Permeation of Supercritical Fluids across Polymeric and Inorganic Membranes*

Abstract

The permeation of supercritical CO₂ and SF₆ across two different types of microporous membranes has been studied as a function of temperature and feed pressure. A general picture appears where for both species the permeance as a function of the feed pressure has a maximum. For both the polymeric and the silica membranes close to the temperature where the different species become supercritical the maximum in the permeance is observed at the critical pressure. In the supercritical regime the main mechanism for the mass transport is viscous flow, and there is almost no contribution from surface diffusion through the micropores. The permeance of the fluids obtained for different condition can be described by a single mobility constant, which is independent of temperature and pressure.

3.1. Introduction

Membrane technology offers a suitable option for continuous regeneration of supercritical fluids. One of the main issues in high pressure applications is the regeneration of the supercritical fluid (SCF), which makes up the major part of the operational costs [1]. In particular, the use of a membrane can lead to a reduction in pressure losses and recompression costs.

Thermal and chemical stability of inorganic microporous membranes, i.e. membranes with a pore size smaller than 2 nm, makes this type of membranes suited for high temperature and high pressure applications, ranging from membrane reactors, gas separation, to the regeneration of supercritical fluids [2,3]. A number of inorganic microporous membranes are available, including zeolite membranes [4], carbon molecular sieve membranes [5,6], silica membranes [7,8], and activated alumina membranes [9,10]. At the moment, inorganic membranes have to compete with polymeric microporous nanofiltration membranes, because of the availability of polymeric membranes with different properties. However, polymeric membranes suffer from some drawbacks, in particular lack of stability, when used for regeneration of SCFs. This is mainly a result of plasticization of the polymer [11,12].

The permeation of supercritical fluids across membranes is interesting from both a fundamental and practical point of view [13,14,15,16]. In practice, both polymeric and inorganic membranes are being used to regenerate SCFs, like the separation of small species [17,18,19], oil-like components [20,21,22], and homogeneous catalysts [23], from the fluid while maintaining supercritical conditions. Transport phenomena in microporous materials have extensively been studied for the diffusion of gaseous species. For a textbook on the diffusion in inorganic materials, including zeolites and carbon molecular sieves, see Kärger and Ruthven (1992) [24]. However, only a limited number of studies are available dealing with the mass transport in microporous membranes, both inorganic and polymeric, at supercritical conditions [5,25,26].

Katsaros et al. [5] studied the permeation of pure helium and pure carbon dioxide through carbon membranes with a pore size of 0.7 nm, up to pressures of 6 MPa. As a function of the pressure a clear maximum in the carbon dioxide permeance was observed between 3 and 4 MPa. Recently, it was demonstrated that microporous silica membranes have a reasonable flux of supercritical CO$_2$ [26].

The objective of this work is to describe the permeation of supercritical CO$_2$ and supercritical SF$_6$ across two different types of membranes at different operating
conditions. The permeation of the two SCFs has been obtained for composite polymeric membranes and for a microporous alumina supported silica membrane.

3.2. Experimental

3.2.1. Membrane setup and methods
The high pressure permeation setup used to measure the steady state flux through the membranes is schematically depicted in Figure 3.1. The experimental setup is designed to test the membranes up to feed pressures and temperatures of 40 MPa and 473 K, respectively. The membranes were placed in a temperature controlled oven (Heraeus) and the temperature was measured with a Pt100 thermocouple. A thermocouple was placed at the feed side of the gas stream in order to measure the temperature of the fluid stream entering the membrane module. The inlet stream was filtered by an inline filter to feed pure liquid CO$_2$ and SF$_6$ for smooth operation of the HPLC pump (Jasco). To make sure that the feed to the pump is in the liquid phase, the pump piston heads were cooled to a temperature of 278 K. The gas stream was heated to supercritical conditions by a coil, which was placed inside the oven. The amount of fluid flowing in the system was measured by a Coriolis type mass flow meter.

To start the permeation experiments, a fluid stream was fed to the feed and permeate side of the membrane by keeping the valve VP open. Both sides of the membrane were pressurized to ensure that no excess pressure difference across the membrane could exist, which could damage or break the membrane. When the desired pressure at the feed side was obtained valve VP was closed. The pressure in both compartments of the membrane was controlled by a back pressure regulator (BPR, Tescom). The BPR on the permeate side was fine-tuned to create the desired pressure difference across the membrane. The pressure on both sides of the membrane was measured by two pressure sensors (AE Sensors) with an accuracy of 0.01 MPa.

The BPRs were placed in a temperature controlled water bath to ensure steady operation. This was necessary because in case of carbon dioxide it was expanded during regulation of the pressure and the BPRs were cooled severely due to the Joule-Thompson expansion effect. The flow of the expanded gas stream was measured using a wet gas meter (Schlumberger). Small flows were measured with a soap bubble flow meter.
Permeation experiments were performed using a pressure difference across the polymeric membrane between 0.05 to 0.3 MPa and across the silica membrane between 0.1 to 1.5 MPa, using a dead end configuration. The amount of CO$_2$ or SF$_6$ going through the membrane at a certain $\Delta P$ was measured for different feed pressures, which in turn gives the flux through the membrane in terms of number of moles of CO$_2$ or SF$_6$ permeating through a fixed surface area of the membrane per unit time. The complete series of experiments was repeated with different feed pressures ranging from 1 to 18 MPa for CO$_2$ and ranging from 1 to 6 MPa for SF$_6$, using about the same pressure difference across the membrane.

3.2.2. **Equilibrium adsorption isotherms**

Equilibrium isotherms of CO$_2$ on silica powders were obtained for four different temperatures and for pressures up to 0.8 MPa. The isotherms were measured gravimetrically using an Igasorp (Hiden Analytical).
3.2.3. **Density and viscosity**
The values for the CO\(_2\) density and viscosity as a function of the pressure have been calculated with the Modified-Benedict-Webb-Rubin (MWBR) model (Reid and Prausnitz, 1987). The values for the SF\(_6\) density and viscosity as a function of the pressure have been obtained from literature [27].

3.2.4. **Gases**
Carbon dioxide (grade 5.0), sulfur hexafluoride (grade 2.8) were obtained from HoekLoos (Amsterdam, The Netherlands).

3.2.5. **Silica membrane**
Microporous alumina supported silica membranes were obtained from ECN (Petten, The Netherlands). The supported silica membranes consist of the alumina support plus the selective top layer, at the outer wall of the tube, which is made of amorphous silica. The alumina support consists of four layers, three layers of \(\alpha\)-alumina and one of \(\gamma\)-alumina [8].

3.2.6. **Polymeric membranes**
Two different selective top layers, polyvinyl alcohol (PVA) and a polyamide copolymer (IPC), were deposited on an ultrafiltration polyethersulfone (PES) support membrane. The internal diameter and wall thickness of the PES support membrane was 1.5 mm and 425 \(\mu\)m, respectively. A selective top layer of PVA of about 1-2 \(\mu\)m thickness was developed by a solution coating method, and the polyamide (IPC) top layer was prepared by an interfacial polymerization process. The thickness of the IPC top layer was about 0.5-1 \(\mu\)m. During the interfacial polymerization process two bi-functional monomers (a di-acid chloride and a diamine) were allowed to react, resulting in a typical network structure at the water/organic solvent interface [28].

3.3. **Theory**

3.3.1. **Mass transport mechanisms**
The mass transport through different types of membranes is mainly determined by the pore size of the selective (top) layer of the membrane [24]. In Figure 3.2 the main transport mechanisms are indicated for membranes with pores diameters in the
microporous (d [nm]<2) and mesoporous (2<d [nm]<50) range. In general, intra-particle transport through the micropores is governed by surface diffusion and viscous flow, while inter-particle flow through the mesopores is governed by viscous and Knudsen flow [4]. It is noted that for the different regimes, i.e. inter-particle and intra-particle, the porosity, $\varepsilon$, will be different. Furthermore, it is assumed that for polymer membranes, in general, mass transport takes place through the "pores" formed by the polymer network by one prevailing mechanism.

![Diagram of mass transport through membranes with pores of different sizes.](image)

**Figure 3.2:** Main mechanisms for mass transport through (inorganic) membranes with pores of different sizes. Surface diffusion (I) and viscous flow (II) are the main intra-particle mechanisms, and viscous flow (II) and Knudsen diffusion (III) are the main mechanism for inter-particle transport.

The flux through a membrane as a result of Knudsen diffusion is given by:

$$J = D_k \frac{\varepsilon_{\text{inter}} \pi r^2}{\tau RT L} \Delta P$$  \hspace{1cm} (3.1)

with the Knudsen diffusivity given by:

$$D_k = 0.66 r \frac{8RT}{\pi M}$$  \hspace{1cm} (3.2)

For viscous flow the flux through a membrane is given by:

$$J = \left( \frac{\varepsilon_i}{\tau} \frac{r^2}{8LM} \right) \frac{\rho_f}{\eta_f} \Delta P$$  \hspace{1cm} (3.3)

where $i$ refers to interparticle (inter) or intraparticle (intra), and with the mobility parameter $\beta$ equal to:

$$\beta = \left( \frac{\varepsilon_i}{\tau} \frac{r^2}{8LM} \right)$$  \hspace{1cm} (3.4)
Surface diffusion through the micropores can be envisaged as the diffusion of molecules in an adsorbed layer. This means that for this kind of transport also an adsorption isotherm is required to describe the diffusion [29,30]. In general, equilibrium adsorption in microporous materials is given by a type I isotherm, often denoted by a Langmuir isotherm, and this type of adsorption is characterized by a plateau at high pressures [9]. The flux for surface diffusion is given by:

\[ J = e_{\text{intra}} \rho_{\text{mem}} q_{\text{sat}} D_x(\theta) \frac{d\theta}{dx} \quad (3.5) \]

In this equation the driving force for surface diffusion is given by the difference in surface occupancy between the feed side and the permeate side of the membrane:

\[ \frac{\Delta \theta}{\Delta x} = \frac{1}{\Delta x} (\theta_F - \theta_P) \quad (3.6) \]

In general, the amount adsorbed in a microporous material is described by the Langmuir isotherm:

\[ q = q_{\text{sat}} \frac{bP}{1 + bP} \quad (3.7) \]

with the fractional surface occupancy \( \theta = q/q_{\text{sat}} \).

Using the Langmuir isotherm the concentration dependent surface diffusion can be rewritten, with as a result for the flux:

\[ J = e_{\text{intra}} \rho_{\text{mem}} q_{\text{sat}} \frac{D_x(0)}{1 - \theta} \frac{d\theta}{dx} \quad (3.8) \]

In the following the results for the permeation across the different membranes will be expressed in terms of the permeance:

\[ Q = J / \Delta P \quad (3.9) \]

### 3.4. Results and Discussion

In order to establish the relative contributions of the different diffusion mechanisms to the total mass transport of SCFs, the permeation of different species across two different types of membranes has been studied. First the results for the silica membrane are presented and then results obtained with different polymeric membranes are used to confirm the observed permeation behavior. Some relevant properties of the supercritical fluids used are given in Table 3.1.
<table>
<thead>
<tr>
<th>Critical temperature</th>
<th>Critical pressure</th>
<th>Mass [g mol(^{-1})]</th>
<th>Kinetic diameter [nm]</th>
</tr>
</thead>
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<tr>
<td>CO(_2)</td>
<td>304 [K]</td>
<td>7.38 [MPa]</td>
<td>44</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>319 [K]</td>
<td>3.76 [MPa]</td>
<td>146</td>
</tr>
</tbody>
</table>

3.4.1. Silica membranes

The silica membrane is a microporous membrane with intra-particle pores in the order of 0.6 nm [8]. However, it is known that as a result of the sol-gel synthesis procedure also some inter-particle pores exist in silica membranes [31]. It is therefore anticipated that transport though the silica membrane can take place by surface diffusion and viscous flow, as shown in Figure 3.2. To quantify the contribution from the mass transport through the micropores, adsorption isotherms of CO\(_2\) on silica powders have been measured.

The CO\(_2\) equilibrium isotherms up to a pressure of about 0.8 MPa are given in Figure 3.3a, together with the fits of the Langmuir isotherm model. It is seen that a reasonable description is possible with the Langmuir model. For the two lowest temperatures, 293 K and 313 K, there is a small difference between the Langmuir fit and the experimental data. The results of the optimization procedure to determine the Langmuir isotherm parameters \(q_{sat}\) and \(b\) are given in Table 3.2. One of the main characteristics of the Langmuir isotherm is the plateau at elevated pressures. At high pressures, in the supercritical regime, the amount adsorbed is given by the plateau value of the isotherm. So, at high pressure there is almost no difference in the amount adsorbed at the feed and the permeate side. For low pressures, gaseous carbon dioxide, the amount adsorbed is given by the initial (linear) part of the isotherm. This means that, according to Eqs (3.5) and (3.6) the driving force, \(\Delta \theta/\Delta x\), diminishes for high pressures. Using the values given in Table 3.2, the CO\(_2\) isotherms have been extrapolated to 10 MPa. The driving force in terms of \(\Delta \theta=\theta_1-\theta_P\) (=\(d\theta\) in Eq. (3.8)), for a pressure difference of 0.5 MPa across the silica membrane as a function of the feed pressure is given in Figure 3.3b. It is clearly seen that for feed pressures above about 5 MPa there is almost no driving force for CO\(_2\) to permeate through the membrane. This is more or less independent of the temperature. This means that there will be no contribution of surface diffusion to the mass transport of CO\(_2\) through the micropores at supercritical conditions, and viscous flow becomes the governing mechanism. It is noted that for viscous flow the flux across the membrane is a function of the ratio of the viscosity to the density of the SCF, see Eq. (3.3).
Table 3.2: Values for the Langmuir isotherm for the adsorption of CO$_2$ on silica powders. The parameters are obtained from a fit with Eq. (3.7) to the experimental results given in Figure 3.3a.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>$q_{sat}$ [mmol g$^{-1}$]</th>
<th>$b$ [10$^{-5}$ Pa$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>4.01</td>
<td>0.46</td>
</tr>
<tr>
<td>313</td>
<td>3.35</td>
<td>0.34</td>
</tr>
<tr>
<td>333</td>
<td>3.11</td>
<td>0.20</td>
</tr>
<tr>
<td>353</td>
<td>2.85</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Figure 3.3a: Adsorption isotherms of carbon dioxide on silica powder and theoretical results obtained from a fit with the Langmuir isotherm model, Eq. (3.7).

Figure 3.3b: Driving force in terms of difference in occupancy, $\Delta \theta = \theta_f - \theta_p$, for permeation of carbon dioxide across the silica membrane as a function of the feed pressure, for a pressure difference of $\Delta P = 0.5$ MPa.
In Figure 3.4 the permeation of CO$_2$ across the silica membrane is given as a function of the feed pressure, for different temperatures. For all the four temperatures a maximum is observed in the permeance of CO$_2$. The permeation at 323 K is fitted using Eq. (3.3), which resulted in a mobility parameter, $\beta$, equal to $4.2 \cdot 10^{-15}$ [m mol g$^{-1}$]. This mobility constant is then used to predict the permeation of CO$_2$ at the other two temperatures. Furthermore, the same mobility constant is used to predict the permeation of (supercritical) CO$_2$ for a feed pressure of 10 MPa as a function of the temperature. It is seen in Figure 3.4 that also in this case good agreement is obtained between the experimental and theoretical result.

![Figure 3.4: Permeance of carbon dioxide through silica membrane as a function of the feed pressure with a pressure difference of $\Delta P=0.5$ MPa. The result at 323 K is obtained by least square fitting of the experimental data with Eq. (3.3), and the results at 313 K and 333 K are calculated (prediction) using the value for the fit parameter in Eq. (3.3).](image-url)
Figure 3.5: Permeance of supercritical carbon dioxide through silica membrane as a function of temperature, for a feed pressure of $P = 10$ MPa and a pressure difference of $\Delta P = 0.5$ MPa.

To verify the modeling results the permeation of gaseous CO$_2$ as a function of the temperature has also been determined, see Figure 3.5. It is expected that for the diffusion of gases through the silica membrane the main contribution will be from mass transport through the micropores. For low pressures, gaseous carbon dioxide, the amount adsorbed is given by the initial, linear part of the isotherm. This means that there is a clear difference in the amount adsorbed at the feed and the permeate side, and there is a significant contribution of the driving force, $\Delta \theta = \theta_f - \theta_p$, to the permeation of gaseous carbon dioxide.

There are two theoretical results shown in Figure 3.6. One result is based on taking only viscous flow, Eq. (3.3) with $\beta = 4.2 \cdot 10^{-15}$ [m mol g$^{-1}$], into account, and the second result takes both viscous flow and surface diffusion, Eqs (3.3) and (3.8), into account. The result for only viscous flow gives clearly a too low value for the permeance, and also in this case the permeance shows a decreasing behavior. A reasonable description is possible with the combined model of surface diffusion and viscous flow. The parameters used to describe the permeance with the combined model are given in Table 3.3. It is noted that the data in Table 3.3 are based on the permeation of carbon dioxide across a silicalite-1 membrane. It is assumed that the diffusion and adsorption parameters for the silica and silicalite-1 membrane are about the same, because both membranes have a pore diameter of about 0.5 nm.
The results in Figure 3.6 indicate that for the permeation of gases through the silica membranes surface diffusion should be taken into account. The maximum in the permeance for gaseous CO\textsubscript{2} is a result of a decrease in the amount adsorbed and an increase in the surface diffusivity, with increasing temperature [30].

**Table 3.3:** Parameters for surface diffusion [31] and viscous flow of CO\textsubscript{2} permeation through the silica membrane as a function of temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface diffusion coefficient [m\textsuperscript{2} sec\textsuperscript{-1}]</td>
<td>5 \times 10\textsuperscript{-9}</td>
</tr>
<tr>
<td>Activation energy for diffusion [kJ mol\textsuperscript{-1}]</td>
<td>9.5</td>
</tr>
<tr>
<td>Saturation amount adsorbed [mmol g\textsuperscript{-1}]</td>
<td>3</td>
</tr>
<tr>
<td>Porosity intra-particle [-]</td>
<td>0.3</td>
</tr>
<tr>
<td>Porosity inter-particle [-]</td>
<td>0.01</td>
</tr>
<tr>
<td>Tortuosity [-]</td>
<td>2</td>
</tr>
<tr>
<td>Density membrane [kg m\textsuperscript{3}]</td>
<td>1.8 \times 10\textsuperscript{3}</td>
</tr>
<tr>
<td>Layer thickness L [m]</td>
<td>200 \times 10\textsuperscript{-9}</td>
</tr>
<tr>
<td>Mobility parameter [m mol g\textsuperscript{-1}]</td>
<td>4.2 \times 10\textsuperscript{-15}</td>
</tr>
</tbody>
</table>

**Figure 3.6:** Permeation of gaseous carbon dioxide as a function of the temperature, for a feed pressure of P = 0.5 MPa and a pressure difference of ΔP = 0.4 MPa. Comparison between viscous flow Eq. (3.3) and combined viscous flow and surface diffusion Eqs (3.3) and (3.8) model predictions, using the data of Table 3.3.

The results for the permeation of scCO\textsubscript{2} across the silica membrane suggest that the permeation of SCF can be described by a relative simple description based on Eq. (3.3) for viscous flow. To verify if indeed viscous flow gives a "unified" model for
permeation of SCFs through microporous membranes two additional series of experiments have been carried out. First, the permeation of supercritical SF$_6$ as a function of the feed pressure across the silica membrane has been determined. Second, the permeation of seCO$_2$ across two polymeric membranes has been determined as well. The results for the permeation of SF$_6$ across the silica membrane are given in Figure 3.7. Also for SF$_6$ the permeance shows a clear maximum as a function of the feed pressure. SF$_6$ becomes supercritical at 319 K and 3.76 MPa (Table 3.1). The maximum in the permeance obtained at 321 K is just below 4 MPa, close to the supercritical pressure of SF$_6$. Again, Eq. (3.3) is used to fit and predict the experimental result for the permeance showing reasonable agreement.

![Figure 3.7: Permeance of sulfur hexafluoride as a function of feed pressure across the silica membrane with a pressure difference of ΔP=0.5 MPa. The result at 333 K is obtained by least square fitting of the experimental data with Eq. (3.3), and the result at 321 is calculated (prediction) using the value for the fit parameter in Eq. (3.3)](image)

3.4.2. Polymeric membranes
Finally, the permeation of CO$_2$ across two different polymeric membranes, IPC and PVA, has been determined as a function of the feed pressure. The results for the permeance are given in Figure 3.8. Again, a clear maximum in the permeance is observed for each of the two membranes, and a good description of the CO$_2$ permeance is given with Eq. (3.3). For both membranes the maximum in the permeance occurs at a pressure of about 8 MPA. This is somewhat higher than the pressure of 7.38 MPa, which indicates the CO$_2$ critical pressure.
Figure 3.8a: Permeance of carbon dioxide through the IPC membrane as a function of the feed pressure with a pressure difference of $\Delta P = 0.3$ MPa and $T = 313$ K. Theoretical result is obtained from a fit with Eq. (3.3).

Figure 3.8b: Permeance of carbon dioxide through the PVA membrane as a function of the feed pressure with a pressure difference of $\Delta P = 0.3$ MPa and $T = 313$ K. Theoretical result is obtained from a fit with Eq. (3.3).

### 3.4.3. Evaluation
To clarify the origin of the maximum in the permeance, the viscosity and density for SF$_6$ are shown in Figure 3.9 as a function of the pressure. As expected for a SCF around the supercritical pressure both the density and the viscosity show a strong increase.
However, the density and viscosity do not change in the same way, and when the ratio of the viscosity to the density is considered this shows a maximum.

It is noted that Knudsen diffusion is not the main mechanism of transport in the supercritical regime, because for Knudsen diffusion the permeance, Eqs (3.1), (3.2), and (3.9), is independent of the pressure difference across the membranes.

Figure 3.9: Density and viscosity of SF₆ as a function of the pressure, at a temperature of 321 K [27].

One of the main issues related to the description of the diffusion in microporous materials is the fact that both the pore size (distribution) and the mass transport mechanism are, in general, not known in advance. This means that first a number of mass transport mechanisms have to be compared in order to establish which mechanism describes the diffusion best. From the permeation results for supercritical CO₂ and supercritical SF₆ it can be concluded that viscous flow is the main mechanism for mass transport in microporous membranes. When the mechanism for mass transport is known, the pore size can be calculated. The results for the pore size of the silica and the IPC membrane are given in Table 3.4. The results are obtained using the CO₂ permeance at a feed pressure of 9 MPa, and it is noted that the values for the tortuosity and porosity are assumed values. For the silica membrane it is assumed that the main transport is through inter-particle pores, which are present in the silica layer for about 1% of the surface area. With the assumed values for the tortuosity and in particular for the porosity a reasonable estimation for the pore diameters can be given. It seems that the higher permeance through the IPC membrane is a result of a larger pore diameter and a higher porosity of the selective layer, see Table 3.4.
Finally, the fact that carbon dioxide and sulfur hexafluoride have a high permeance through microporous membranes opens the way to economically viable regeneration of supercritical fluids.

**Table 3.4:** Overview of the IPC and silica membrane properties for carbon dioxide permeation at 313 K. The values for the porosity and the tortuosity are assumed values.

<table>
<thead>
<tr>
<th></th>
<th>IPC</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pressure [MPa]</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Permeance [mol m⁻² sec⁻¹ Pa⁻¹]</td>
<td>2.1·10⁻⁶</td>
<td>5.8·10⁻⁸</td>
</tr>
<tr>
<td>Viscosity 10⁻⁵ [Pa sec]</td>
<td>3.48</td>
<td>3.48</td>
</tr>
<tr>
<td>Density [kg m⁻³]</td>
<td>485.5</td>
<td>485.5</td>
</tr>
<tr>
<td>Layer thickness L [m]</td>
<td>1·10⁻⁶</td>
<td>200·10⁻⁹</td>
</tr>
<tr>
<td>Porosity ε [-]</td>
<td>0.3</td>
<td>0.01</td>
</tr>
<tr>
<td>Tortuosity τ [-]</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Mobility parameter [m mol g⁻¹]</td>
<td>1.5·10⁻¹³</td>
<td>4.2·10⁻¹⁵</td>
</tr>
<tr>
<td>Pore diameter [nm]</td>
<td>1.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### 3.5. Conclusions

The permeation of CO₂ and SF₆ through two different types of microporous membranes has been studied for supercritical conditions. It can be concluded that the permeation through the two microporous membranes can be described by taking only viscous flow into account. The different membranes have a reasonably high flux, which opens the possibility for efficient regeneration of supercritical fluids. In addition, the fact that a relatively simple model gives a good description of the permeation behavior at supercritical conditions might be useful in the characterization of microporous membranes. Permeation of SCFs provides a means to establish the amount of intra-particle pores present in inorganic membranes. When the contribution of viscous flow through the inter-particle pores is known from supercritical permeation measurements, then gaseous permeation experiments can be corrected for the viscous contribution.
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>Langmuir parameter</td>
<td>[Pa⁻¹]</td>
</tr>
<tr>
<td>Dₚ</td>
<td>Surface diffusion coefficient</td>
<td>[m² sec⁻¹]</td>
</tr>
<tr>
<td>Dᴷ</td>
<td>Knudsen diffusion coefficient</td>
<td>[m² sec⁻¹]</td>
</tr>
<tr>
<td>J</td>
<td>Flux</td>
<td>[mol m⁻¹ sec⁻¹]</td>
</tr>
<tr>
<td>L</td>
<td>Selective layer thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>M</td>
<td>Molecular weight of fluid</td>
<td>[g mol⁻¹]</td>
</tr>
<tr>
<td>ΔP</td>
<td>Pressure difference</td>
<td>[Pa]</td>
</tr>
<tr>
<td>q</td>
<td>Amount adsorbed</td>
<td>[mmol g⁻¹]</td>
</tr>
<tr>
<td>qₘₐₜ</td>
<td>Saturation amount adsorbed</td>
<td>[mmol g⁻¹]</td>
</tr>
<tr>
<td>Q</td>
<td>Permeance</td>
<td>[mol m⁻² sec⁻¹ Pa⁻¹]</td>
</tr>
<tr>
<td>r</td>
<td>Pore radius</td>
<td>[m]</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>[J K⁻¹ mol⁻¹]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>x</td>
<td>Space coordinate</td>
<td>[m]</td>
</tr>
</tbody>
</table>

### Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>β</td>
<td>Mobility parameter</td>
<td>[m mol g⁻¹]</td>
</tr>
<tr>
<td>εₒₜₑₜ</td>
<td>Interparticle porosity</td>
<td>[-]</td>
</tr>
<tr>
<td>εᵢₜᵣₜ</td>
<td>Intraparticle porosity</td>
<td>[-]</td>
</tr>
<tr>
<td>τ</td>
<td>Tortuosity</td>
<td>[-]</td>
</tr>
<tr>
<td>ηₒₙ</td>
<td>Fluid viscosity</td>
<td>[Pa sec]</td>
</tr>
<tr>
<td>ρₒₙ</td>
<td>Fluid density</td>
<td>[kg m⁻³]</td>
</tr>
<tr>
<td>ρₘₑₙ</td>
<td>Membrane density</td>
<td>[kg m⁻³]</td>
</tr>
<tr>
<td>θ</td>
<td>Surface occupancy</td>
<td>[-]</td>
</tr>
</tbody>
</table>

### References

8. M.K. Koukou, N. Papayannakos, N.C. Markatos, M. Bracht, H.M. van Veen, A. Roskam, Performance of ceramic membranes at elevated pressure and temperature:


Chapter 4

Solubility of Polymers and Oil-like Components in Supercritical CO$_2$

Abstract
The solubility of poly ethylene glycols with molecular weights of 200, 400 and 600, triolein and e-vitamin in supercritical carbon dioxide has been determined by cloud point measurements. The solubility experiments have been conducted for pressures up to 30 MPa and at a temperature of 313 and 333 K. In general, the solubility of all components increases with an increase in pressure at a constant temperature. The data obtained using the cloud point measurements show good agreement with literature data obtained using an analytical method. Solubility isotherms for the triolein – CO$_2$ systems have been predicted successfully using the Sanchez-Lacombe equation of state. It can be concluded that the cloud point measurements provide a fast and accurate way to obtain solubility data of various solutes in supercritical fluids.
4.1. Introduction

Low molecular weight lipophilic components are important solutes in the food and pharmaceutical industry. Extraction of these components with supercritical carbon dioxide offers the advantage of working at moderate temperatures to avoid degradation problems [1]. Knowledge of phase equilibria is the most important factor for the optimal design of extraction processes and for the design of separation processes controlled by phase equilibrium in general. However, high pressure phase equilibria involving oil-like components and carbon dioxide have not yet been thoroughly investigated.

The solubility limits of one-component systems in a supercritical fluid can be evaluated on the basis of the cloud points. The cloud point is defined as the pressure and temperature point at which the chemical potential of each component in the homogeneous phase becomes equal. In practice, this translates for a supercritical fluid system to the pressure at which phase separation commences at a given temperature [2]. Bharath et al. [1] have used a static apparatus to obtain VLE data for single-component systems and mixtures of oleic acid and triolein in carbon dioxide. The main purpose was to separate the fatty acid from triglyceride, and also to perform fractionation of mixtures of triglycerides. Bamberger et al. [3] investigated the solubility of fatty acids and triglycerides in carbon dioxide. Brunetti et al. [4] measured the solubility of several components of olive oil in carbon dioxide in the temperature range of 313 to 333 K and at pressures up to 30 MPa. Pereira et al. [5] investigated the VLE and VLLE of mixtures of carbon dioxide and e-vitamin. Meier et al. [6] used a recirculation type cell coupled to supercritical fluid chromatography (SFC). An oscillation tube was used to measure the composition and density of the e-vitamin - carbon dioxide system. Gourgouillon et al. [7] have reported the solubility of polyethylene glycols (PEG) with a molecular weight of 200, 400 and 600, in scCO$_2$, and described the solubility of the PEGs with the Sanchez Lacombe equation of state (EOS).

Polyethylene glycols are available in various molecular weights and can be used as model compounds to characterize membranes in terms of rejection performance. In particular, to study the regeneration of supercritical carbon dioxide using membranes a proper description of the phase equilibria of the solutes is important, because phase separation of the solutes should be avoided.

In this work, the solubility data for PEGs, triolein and e-vitamin in carbon dioxide obtained from cloud point measurements is presented. The main advantage of the cloud point method is that the phase behavior is determined directly from visual observation.
With the cloud point method difficulties associated with sampling are avoided. The results have been compared to the results available in literature to verify the accuracy of the experimental setup. The other objective of the study is to predict the solubility data of triolein using the Sanchez-Lacombe EOS.

4.2. Experimental

4.2.1. Materials
The PEGs (MW of 200, 400 and 600), triolein (purity = 95.0%), and e-vitamin (purity ≥ 98%) were obtained from Sigma-Aldrich and were used as received, i.e. without any further purification. Carbon dioxide (grade 5.0) was obtained from HoekLoos (Amsterdam, The Netherlands). In Table 4.1 some physical properties of triolein and e-vitamin are given.

<table>
<thead>
<tr>
<th>Component</th>
<th>Common name</th>
<th>Molecular formula</th>
<th>Mw (g)</th>
<th>Density (g cm$^{-3}$)</th>
<th>BP (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyceryl Trioleate</td>
<td>Triolein</td>
<td>C$<em>{57}$H$</em>{104}$O$_6$</td>
<td>885.4</td>
<td>0.913</td>
<td>508</td>
</tr>
<tr>
<td>α-Tocopherol acetate</td>
<td>E-vitamin</td>
<td>C$<em>{31}$H$</em>{52}$O$_3$</td>
<td>472.8</td>
<td>0.96</td>
<td>478</td>
</tr>
</tbody>
</table>

4.2.2. Setup
The apparatus used for the cloud point measurements is shown schematically in Figure 4.1. The apparatus was designed to measure cloud points up to a temperature of 573 K and pressures up to 30 MPa. The apparatus consisted of a viewing cell with variable internal volume, which allowed for changes in the cell volume and the pressure by moving the piston. The volume of the viewing cell could be varied between 25 and 45 mL. The high pressure viewing cell was equipped with two quartz windows, a magnetic stirrer bar, and a Pt-100 resistance thermometer. An oil thermostat was used to control the temperature within ± 0.1 K. The pressure in the reactor was measured within ± 0.1 MPa using a pressure transducer (AE sensors). The amount of fluid flowing in the system was measured by a Coriolis type mass flow meter with an accuracy of ± 0.01 g.
4.2.3. Experimental procedure
First, the viewing cell was evacuated, and a certain amount of solute was loaded into the cell. The amount of the solute loaded into the cell was determined using a balance with an accuracy of \( \pm 0.1 \) mg. To remove any trapped air, the cell was then purged a few times with gaseous carbon dioxide at a very low flow rate. In this way, the solute inside the cell did not leave the cell with the gas stream. Subsequently, a known amount of carbon dioxide was fed to the viewing cell. The solution mixture was compressed by moving the piston inside the cell. The pressure in the cell was increased continuously until the solution became optically transparent as a single phase. The solution in the cell was stirred by a magnetic stirrer.

After the system had reached thermal equilibrium and maintained a single phase, the pressure was slowly reduced until the solution became cloudy. By pressing the piston, the pressure was increased and the mixture became clear again. To obtain consistent measurements, the process was repeated three times at each temperature and composition. The reproducibility of the cloud point pressures was within \( \pm 0.1 \) MPa.

4.3. Theory

4.3.1. Sanchez-Lacombe equation of state
The generalization of the classical lattice theory to describe the distribution of molecules in a three dimensional cubic lattice is called the lattice-fluid model. To
predict the solubility at equilibrium conditions, the Sanchez-Lacombe EOS based on the lattice theory was used. In this theory the polymer molecules are ordered according to a lattice structure. The theory accounts for the change in volume due to the presence of “holes” in the lattice and hence, does not require separate parameters to account for the flexibility of the molecule. The experimentally measured solubilities of subcritical and supercritical CO\textsubscript{2} in various polymers have successfully been correlated to the Sanchez Lacombe EOS [7,8,9].

The Sanchez-Lacombe EOS is given by:

\begin{align}
\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[ \ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho} \right] &= 0 \\
\tilde{\nu} &= 1/\tilde{\rho}
\end{align}

where \(\tilde{\rho}, \tilde{\nu}, \tilde{P}, \tilde{T}\) and \(r\) are the reduced density, specific volume, pressure, temperature, and the number of the lattice sites occupied by a molecule, respectively. The reduced parameters are defined as:

\begin{align}
\tilde{\rho} &= \rho / \rho^* \\
\tilde{\nu} &= \nu / \nu^* \\
\tilde{P} &= P / P^* \\
\tilde{T} &= T / T^* \\
r &= MP^*/RT^* \rho^*
\end{align}

where \(\rho^*\) (the corresponding mass density in the close-packed state), \(\nu^*\) (the corresponding specific volume in the close-packed state), \(P^*\) (the hypothetical cohesive energy density in the close-packed state) and \(T^*\) (related to the depth of the potential energy well) are the characteristic parameters of components. The reduced parameters are obtained by fitting PVT data of pure components using Eqs. 4.1 to 4.3.

The EOS used for a mixture is similar to Eq. 4.1. The characteristic parameters used in the EOS for a mixture are obtained using the following mixing rules:

\begin{align}
P^* &= \sum_i \sum_j \phi_i \phi_j P^*_{ij} \\
P^*_{ij} &= \left(1 - k_{ij} \right) \left( P^*_i P^*_j \right)^{0.5}
\end{align}
where $k_{ij}$ is an adjustable interaction parameter, which is a measure for the deviation of $P_{ij}$ from the geometric mean of $P_i$ and $P_j$.

The reduced parameters for the mixture are defined as:

$$T^* = P^* \sum_i (\phi_i^0 T_i^*) / P_i^*$$  \hspace{1cm} (4.6)

$$r_i^0 \nu_i^* = r_i \nu^*$$  \hspace{1cm} (4.7)

$$\nu^* = \sum_i \phi_i^0 \nu_i^*$$  \hspace{1cm} (4.8)

$$1/r = \sum_j \phi_j / r_j$$  \hspace{1cm} (4.9)

$$\phi_i^0 = (\phi_i P_i^* / T_i^*) / \sum_j (\phi_j P_j^* / T_j^*)$$  \hspace{1cm} (4.10)

$$\phi_i = (w_i / \rho_i^*) / \sum_j (w_j / \rho_j^*)$$  \hspace{1cm} (4.11)

where $\phi$ and $w$ represent the volume and weight fraction of components in two phases, respectively. Superscript ‘0’ denotes the pure state of a component. Along with the Eqs. 4.1 to 4.12, the chemical potential, $\mu$, of a component in the available phases are used to predict the solubility of CO$_2$ in a polymer.

At equilibrium:

$$\mu_{i}^{\text{gas}} = \mu_{i}^{\text{polymer}}$$  \hspace{1cm} (4.12)

Here, CO$_2$ is referred to as component ‘1’, while a polymer is referred to as component ‘2’. The chemical potential of 1 in the polymer phase is given by:

$$\mu_{i}^{\text{polymer}} = RT \left[ \ln \phi_i + (1 - r_i / r_2) \phi_2 + r_i^0 \tilde{\rho} \phi_2 \right] + r_i^0 RT \left[ - \tilde{\rho} / T_i + \tilde{T_i} \tilde{\nu} / \tilde{\nu} + \tilde{\nu} (1 - \tilde{\rho}) \ln (1 - \tilde{\rho}) + \tilde{\rho} / r_i^0 \ln \tilde{\rho} \right]$$  \hspace{1cm} (4.13)

Equation 4.13 is also used to calculate the chemical potential $\mu_{i}^{\text{gas}}$ by considering only the gas phase. For polymers of high molecular weight, it is assumed that there is no polymer present in the gas phase. Therefore, the experimental solubility data are regressed with the adjustable interaction parameter, $k_{ij}$, (in Eq. 4.5) solving Eqs. 4.1 to
4.13 simultaneously. Finally, in the following the results will be presented in terms of weight fractions, given by:

\[
\text{wt fraction} = \frac{W_i}{W_{\text{solute}} + W_{\text{CO}_2}} \tag{4.14}
\]

where \(W_i\) is the amount of solute or \(\text{CO}_2\).

4.4. Results and Discussion

4.4.1. Solubility of PEGs, triolein and e-vitamin

The solubility of PEG 200, 400 and 600, triolein and e-vitamin in carbon dioxide has been experimentally determined by cloud point measurement at 313 K and 333 K. From the cloud point measurements only the solubility of the solute in the carbon dioxide phase (P-Y data) can be obtained, and it is not possible to determine the solubility of the \(\text{CO}_2\) in the solute rich phase (P-X data).

In order to verify the accuracy of the experimental method, the measured P-Y values have been compared with values obtained from literature [7,10]. The results for the PEGs are compared in Tables 4.2 to 4.4, where both the P-X and P-Y data from literature are given. The results for triolein and e-vitamin are given in Tables 4.5 and 4.6, respectively.

The experimentally measured solubilities of PEGs are in fair accordance with the results obtained by Gourgouillon et al. [7] and the difference is the range of 4 to 10%. Furthermore, also the solubility data of triolein and e-vitamin are in accordance with solubility data measured by Chen et al. [10]. Again, for both components the difference is in the range of 4 to 10%. The difference (last column in the Tables) is based on the amount of solute in the \(\text{CO}_2\) rich phase (Y values). The difference is given by Y value from literature minus the Y value obtained in this work, divided by the Y value obtained in this work.
### Table 4.2: Phase equilibrium data for the system PEG 200-CO\textsubscript{2} at 313 and 333 K.

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>$X_{\text{PEG200}}$\textsuperscript{(a)}</th>
<th>$Y_{\text{PEG200}}$\textsuperscript{(a)}</th>
<th>$Y_{\text{PEG200}}$\textsuperscript{(b)}</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[wt fr]</td>
<td>[wt fr]</td>
<td>[wt fr]</td>
<td></td>
</tr>
<tr>
<td>3.87</td>
<td>0.9808</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>7.75</td>
<td>0.9610</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>9.72</td>
<td>0.9526</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>12.05</td>
<td>0.9484</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>15.83</td>
<td>0.9476</td>
<td>0.0157</td>
<td>0.0174</td>
<td>10.62</td>
</tr>
<tr>
<td>18.41</td>
<td>0.9420</td>
<td>0.0713</td>
<td>0.0792</td>
<td>11.14</td>
</tr>
<tr>
<td>24.55</td>
<td>0.9384</td>
<td>0.1009</td>
<td>0.1086</td>
<td>7.64</td>
</tr>
<tr>
<td>3.13 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.26</td>
<td>0.9906</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>7.38</td>
<td>0.9725</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>10.90</td>
<td>0.9630</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>14.37</td>
<td>0.9554</td>
<td>0.0170</td>
<td>0.0186</td>
<td>9.08</td>
</tr>
<tr>
<td>18.70</td>
<td>0.9488</td>
<td>0.0460</td>
<td>0.0508</td>
<td>10.38</td>
</tr>
<tr>
<td>20.96</td>
<td>0.9443</td>
<td>0.0773</td>
<td>0.0829</td>
<td>7.18</td>
</tr>
<tr>
<td>24.45</td>
<td>0.9418</td>
<td>0.0729</td>
<td>0.0770</td>
<td>5.60</td>
</tr>
</tbody>
</table>

(a) Data of Gourgoiuillon [7].
(b) This work.

### Table 4.3: Phase equilibrium data for the system PEG 400-CO\textsubscript{2} at 313 and 333 K.

<table>
<thead>
<tr>
<th>P (MPa)</th>
<th>$X_{\text{PEG400}}$\textsuperscript{(a)}</th>
<th>$Y_{\text{PEG400}}$\textsuperscript{(a)}</th>
<th>$Y_{\text{PEG400}}$\textsuperscript{(b)}</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[wt fr]</td>
<td>[wt fr]</td>
<td>[wt fr]</td>
<td></td>
</tr>
<tr>
<td>313 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.23</td>
<td>0.9648</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>10.62</td>
<td>0.9324</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>16.11</td>
<td>0.9254</td>
<td>0.0297</td>
<td>0.0313</td>
<td>5.11</td>
</tr>
<tr>
<td>19.74</td>
<td>0.9189</td>
<td>0.0319</td>
<td>0.0333</td>
<td>4.38</td>
</tr>
<tr>
<td>24.01</td>
<td>0.9136</td>
<td>0.0452</td>
<td>0.0490</td>
<td>8.46</td>
</tr>
<tr>
<td>333 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.28</td>
<td>0.9775</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>10.37</td>
<td>0.9539</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>14.98</td>
<td>0.9407</td>
<td>0.0045</td>
<td>0.0048</td>
<td>6.16</td>
</tr>
<tr>
<td>20.63</td>
<td>0.9305</td>
<td>0.0175</td>
<td>0.0182</td>
<td>4.28</td>
</tr>
<tr>
<td>24.62</td>
<td>0.9277</td>
<td>0.0323</td>
<td>0.0351</td>
<td>8.58</td>
</tr>
</tbody>
</table>

(a) Data of Gourgoiuillon [7].
(b) This work.
Table 4.4: Phase equilibrium data for the system PEG 600-CO$_2$ at 313 and 333 K.

<table>
<thead>
<tr>
<th>P(MPa)</th>
<th>$X_{\text{PEG600}}$ $^{(a)}$ [wt fr]</th>
<th>$Y_{\text{PEG600}}$ $^{(a)}$ [wt fr]</th>
<th>$Y_{\text{PEG600}}$ $^{(b)}$ [wt fr]</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>313 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.70</td>
<td>0.9772</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>10.16</td>
<td>0.9382</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>15.41</td>
<td>0.9328</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>21.34</td>
<td>0.9234</td>
<td>0.0023</td>
<td>0.0025</td>
<td>8.33</td>
</tr>
<tr>
<td>26.34</td>
<td>0.9185</td>
<td>0.0241</td>
<td>0.0258</td>
<td>7.18</td>
</tr>
<tr>
<td>333 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.63</td>
<td>0.9782</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>10.07</td>
<td>0.9543</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>16.37</td>
<td>0.9434</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>21.24</td>
<td>0.9348</td>
<td>0.0041</td>
<td>0.0045</td>
<td>10.38</td>
</tr>
<tr>
<td>26.50</td>
<td>0.9258</td>
<td>0.0095</td>
<td>0.0100</td>
<td>5.60</td>
</tr>
</tbody>
</table>

(a) Data of Gourgoiuillon [7].
(b) This work.

Table 4.5: Phase equilibrium data for the system triolein-CO$_2$ at 313 and 333 K.

<table>
<thead>
<tr>
<th>P(MPa)</th>
<th>$X_{\text{triolein}}$ $^{(a)}$ [wt fr]</th>
<th>$Y_{\text{triolein}}$ $^{(a)}$ [wt fr]</th>
<th>$Y_{\text{triolein}}$ $^{(b)}$ [wt fr]</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>313 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.24</td>
<td>0.6919</td>
<td>0.4009</td>
<td>0.4217</td>
<td>5.19</td>
</tr>
<tr>
<td>12.37</td>
<td>0.6805</td>
<td>0.4009</td>
<td>0.4325</td>
<td>7.88</td>
</tr>
<tr>
<td>14.16</td>
<td>0.6792</td>
<td>0.6002</td>
<td>0.6374</td>
<td>6.20</td>
</tr>
<tr>
<td>16.05</td>
<td>0.6672</td>
<td>0.6002</td>
<td>0.6548</td>
<td>9.10</td>
</tr>
<tr>
<td>17.74</td>
<td>0.6570</td>
<td>0.7988</td>
<td>0.8379</td>
<td>4.89</td>
</tr>
<tr>
<td>19.40</td>
<td>0.6441</td>
<td>0.7988</td>
<td>0.8563</td>
<td>7.20</td>
</tr>
<tr>
<td>20.83</td>
<td>0.6407</td>
<td>0.7988</td>
<td>0.8411</td>
<td>5.30</td>
</tr>
<tr>
<td>21.88</td>
<td>0.6290</td>
<td>0.9966</td>
<td>1.0653</td>
<td>6.89</td>
</tr>
<tr>
<td>23.14</td>
<td>0.6220</td>
<td>1.1937</td>
<td>1.2772</td>
<td>7.00</td>
</tr>
<tr>
<td>23.99</td>
<td>0.6148</td>
<td>1.1937</td>
<td>1.2999</td>
<td>8.90</td>
</tr>
<tr>
<td>333 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.12</td>
<td>0.7410</td>
<td>0.2008</td>
<td>0.2153</td>
<td>7.22</td>
</tr>
<tr>
<td>12.36</td>
<td>0.7358</td>
<td>0.4009</td>
<td>0.4374</td>
<td>9.10</td>
</tr>
<tr>
<td>14.10</td>
<td>0.7218</td>
<td>0.4009</td>
<td>0.4206</td>
<td>4.91</td>
</tr>
<tr>
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<td>0.7029</td>
<td>0.4009</td>
<td>0.4374</td>
<td>9.10</td>
</tr>
<tr>
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<td>0.6857</td>
<td>0.6002</td>
<td>0.6477</td>
<td>7.91</td>
</tr>
<tr>
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<td>0.6002</td>
<td>0.6375</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>7.09</td>
</tr>
<tr>
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<td>0.7988</td>
<td>0.8631</td>
<td>8.05</td>
</tr>
</tbody>
</table>

(a) Data of Chen [10].
(b) This work.
Table 4.6: Phase equilibrium data for the system e-vitamin at 313 and 333 K.

<table>
<thead>
<tr>
<th>P(MPa)</th>
<th>$X_{\text{e-vita min e}}$ (a) [wt fr]</th>
<th>$Y_{\text{e-vita min e}}$ (a) [wt fr]</th>
<th>$Y_{\text{e-vita min e}}$ (b) [wt fr]</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td>9.88</td>
<td>0.8936</td>
<td>0.6002</td>
<td>0.6284</td>
<td>4.70</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.8896</td>
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<td>1.7454</td>
<td>10.08</td>
</tr>
<tr>
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<td>1.5856</td>
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</tr>
<tr>
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<td>1.9745</td>
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<td>4.89</td>
</tr>
<tr>
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<td>8.65</td>
</tr>
<tr>
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<td>0.8772</td>
<td>2.1679</td>
<td>2.2980</td>
<td>6.00</td>
</tr>
<tr>
<td>21.95</td>
<td>0.8762</td>
<td>2.9342</td>
<td>3.1308</td>
<td>6.70</td>
</tr>
<tr>
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<td>0.8766</td>
<td>2.7437</td>
<td>2.9632</td>
<td>8.00</td>
</tr>
<tr>
<td>24.09</td>
<td>0.8714</td>
<td>3.3132</td>
<td>3.6147</td>
<td>9.10</td>
</tr>
<tr>
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</tr>
<tr>
<td>10.33</td>
<td>0.8838</td>
<td>0.2008</td>
<td>0.2135</td>
<td>6.32</td>
</tr>
<tr>
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<td>0.8819</td>
<td>0.4009</td>
<td>0.4246</td>
<td>5.91</td>
</tr>
<tr>
<td>14.07</td>
<td>0.8819</td>
<td>0.6002</td>
<td>0.6537</td>
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</tr>
<tr>
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</tr>
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<td>6.95</td>
</tr>
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<td>6.09</td>
</tr>
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<td>0.7652</td>
<td>2.9342</td>
<td>3.0777</td>
<td>4.89</td>
</tr>
</tbody>
</table>

(a) Data of Chen [10].
(b) This work.

Gourgouillon et al. [7] and Chen et al. [10] have also experimentally determined VLE equilibrium data, i.e. PXY data for the CO$_2$ and PEG system and the CO$_2$ and triolein system, respectively. However, with cloud point measurements it is only possible to determine VLE in the CO$_2$ rich phase. The data of triolein solubility (P-Y data) in carbon dioxide from this work is in fair accordance with the data of Chen et al. [10]. Therefore, the VLE data of Chen et al. [10] for both the triolein rich phase and the CO$_2$ rich phase have been used to correlate with the Sanchez-Lacombe EOS.

From the results in the Tables 4.2 to 4.6 it follows that the solubility of the different components in supercritical carbon dioxide increases with an increase in pressure, whereas it decreases with an increase in temperature. This is a result of the fact that the CO$_2$ density increases with an increase in pressure and increases with a decrease in temperature. On the other hand, the solubility in CO$_2$ decreases with an increase in the molar mass.
4.4.2. Prediction of solubility in CO\textsubscript{2} with Sanchez Lacombe EOS

Gourgouillon et al. [7] already showed that the solubility of polyethylene glycol polymers (MW of 200, 400 and 600) can be successfully described by the Sanchez Lacombe EOS. In this work, the Sanchez Lacombe EOS is used to model the solubility of an oil-like component, like triolein.

In order to describe the solubility data, first the PVT data of triolein, obtained from literature [11], has been fitted with the Sanchez Lacombe EOS to obtain the characteristic parameters of the pure components. The values for the characteristic parameters of the pure components are given in Table 4.7. Subsequently, the characteristic parameters have been used to calculate the solubility. A non-linear regression optimization procedure (Levenberg-Marquardt, MATLAB 7) has been used to minimize the difference between the chemical potential of CO\textsubscript{2} in the gas phase and the liquid phase, and also to minimize the difference between the experimental and predicted solubilities using the interaction parameter, $k_{12}$.

<table>
<thead>
<tr>
<th>Component</th>
<th>$P^*$ (MPa)</th>
<th>$T^*$ (K)</th>
<th>$\rho^*$ (kg/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>427.70</td>
<td>338.7</td>
<td>1405.5</td>
</tr>
<tr>
<td>Triolein</td>
<td>391.63</td>
<td>591.2</td>
<td>979.5</td>
</tr>
</tbody>
</table>

The results for the weight fraction CO\textsubscript{2} in the CO\textsubscript{2} rich and the triolein rich phase are shown in Figure 4.2. In Figure 4.2a the CO\textsubscript{2} weight fraction in the CO\textsubscript{2} rich phase is given as a function of the total pressure. For the two temperatures the fraction CO\textsubscript{2} decreases with an increase in total pressure. In Figure 4.2b the weight fraction of CO\textsubscript{2} in the triolein rich phase is given. In this case, the fraction of CO\textsubscript{2} increases with an increase in the total pressure.

From the predictions given in Figure 4.2, it can be concluded that the Sanchez Lacombe EOS can be used to model the solubility for the triolein – CO\textsubscript{2} systems for a range of temperatures, pressures and densities.
Figure 4.2: Results for the CO$_2$ solubility isotherms for the triolein – CO$_2$ system. Modeling results obtained using Eqs (4.1) to (4.13). The experimental results at 313 K and 333 K are from Chen [10]. (a) CO$_2$ rich phase, (b) triolein rich phase.

4.5. Conclusions

The solubilities of PEGs (MW of 200, 400 and 600), triolein and e-vitamin in carbon dioxide have been measured by cloud point measurements using a high pressure optical cell. The experimental results have been compared with the values available in literature. The maximum difference between the results presented in this work and literature values is about 10%. For all the components, the solubility in carbon dioxide increases with an increase in pressure and decreases with an increase in temperature. This variation in solubility is well explained by changes in the density with pressure and temperature.
The experimental solubility data of triolein has been successfully correlated with the Sanchez-Lacombe EOS by using the pure component parameters and an adjustable interaction parameter. From this it can be concluded that the Sanchez-Lacombe EOS can be used to describe the solubility isotherms for different type of species in scCO$_2$, including polymers and oil-like components.

References

Chapter 5

Regeneration of Supercritical Carbon Dioxide using Polymeric and Inorganic Membranes

Abstract

Three types of microporous membranes have been used to separate triolein (glyceryl trioleate) and e-vitamin (α-tocopherol acetate) from supercritical carbon dioxide. Retention factors and the carbon dioxide permeance have been determined simultaneously for a polyamide membrane, a silica membrane, and three titania membranes with different molecular weight cut-off. Complete retention is possible for both triolein and e-vitamin using a titania membrane at the cost of a considerable reduction in carbon dioxide permeance. For triolein good retention is possible with the silica membrane. The retention factor lies between 0.97 and 0.99, with a reduction in the carbon dioxide permeance of about 20 %, as compared to the pure carbon dioxide permeance.
5.1. Introduction

The extraction of various components from natural products with supercritical fluids is a promising technology. Supercritical carbon dioxide (scCO₂) is considered to be a green solvent, which has high potential to replace the conventional organic solvents used in chemical industry. Supercritical CO₂ is nontoxic, non-flammable, inexpensive and the extraction power can be tuned by temperature and pressure. Mass transfer rates in scCO₂ are higher than in conventional organic solvents. One of the disadvantages of scCO₂ is the low solubility of high-molecular weight species. The solubility of solutes in scCO₂ generally increases with pressure. Therefore, most applications are operated at higher pressures, which results in a large quantity of carbon dioxide being used. This makes it necessary to regenerate and recycle scCO₂ for improving the economics of the process. Several regeneration techniques including adsorption, absorption, and membrane technology have been investigated [1-3]. An isobaric and/or isothermal operation to remove solutes from a scCO₂ mixture may be possible with adsorption or absorption. The combination of a membrane with the supercritical fluid extraction process could be a suitable option to reduce the recompression costs [4-10]. In principle, a small trans-membrane pressure should be sufficient to regenerate the carbon dioxide while the solutes are retained by a membrane.

Regeneration of scCO₂ using polymeric membranes has been studied to some extent. However, the use of polymeric membranes can suffer from some drawbacks, like a lack of stability when used in scCO₂. Spricigo et al. [4] applied a cellulose acetate reverse osmosis membrane to perform the separation of nutmeg essential oil and dense carbon dioxide. They investigated the effects of feed stream essential oil concentration, temperature and trans-membrane pressure on the retention of essential oil and CO₂ permeability. The membrane showed good CO₂ permeability and stability at supercritical conditions. Semenova et al. [5] studied the separation of scCO₂ and ethanol mixtures with an asymmetric polyimide membrane. A separation factor (α_{ethanol/CO₂}) of 8.7 was obtained. For the separation of scCO₂ and iso-octane mixtures, a separation factor (α_{iso-octane/CO₂}) of 12.8 was obtained [6]. Sarrade et al. [7, 8] characterized the behavior of organomineral nano-filtration membranes in supercritical CO₂. The permeability of scCO₂ and fractionation of triglycerides as a function of the temperature and pressure were investigated.

Microporous inorganic membranes, like silica and titania membranes, exhibit a reasonable permeability for supercritical CO₂, with very good resistance under severe
operating conditions. Typically, microporous membranes have pore diameters smaller than 2 nm. Sartorelli and Brunner [9] used two different types of membranes, an inorganic and a hybrid one, for the separation of low volatility compounds from supercritical CO$_2$. The retention factors obtained were between 0.8 and 0.9. Goetheer et al. [10] successfully applied silica membrane to retain the homogeneous catalyst of 2-4 nm size while carrying out hydrogenation of 1-butene in a membrane reactor. Tan et al. [11] studied the regeneration of supercritical CO$_2$ from mixtures containing caffeine using a commercial nanofiltration membrane, denoted as MD5, having a thin layer of ZrO$_2$-TiO$_2$ with an average pore size of 3 nm on a carbon support layer. The experimental data showed that a rejection factor of caffeine as high as 1.0 in the first 6 hours could be obtained, and that the scCO$_2$ permeation flux was equal to 0.024 mol m$^{-2}$ s$^{-1}$ at 308 K and for a feed pressure of 7.95 MPa.

The objective of this work is to study three different types of membranes to separate triolein and e-vitamin from scCO$_2$. In particular, the performance in terms of retaining the solutes dissolved in supercritical carbon dioxide by a membrane is studied.

5.2. Experimental

5.2.1. Materials
Carbon dioxide (grade 5.0) was obtained from HoekLoos (Amsterdam, The Netherlands). Glyceryl trioleate (triolein, 95.5 purity) and α-tocopherol acetate (e-vitamin) were obtained from Sigma-Aldrich. In Table 5.1 some physical properties of triolein and e-vitamin are given. The structural formulas of triolein and e-vitamin are given in Figure 5.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Common name</th>
<th>Molecular formula</th>
<th>Mw (g)</th>
<th>Density (g cm$^{-3}$)</th>
<th>BP (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyceryl Trioleate</td>
<td>Triolein</td>
<td>C$<em>{57}$H$</em>{104}$O$_6$</td>
<td>885.4</td>
<td>0.913</td>
<td>508</td>
</tr>
<tr>
<td>α-Tocopherol acetate</td>
<td>E-vitamin</td>
<td>C$<em>{31}$H$</em>{52}$O$_3$</td>
<td>472.8</td>
<td>0.96</td>
<td>478</td>
</tr>
</tbody>
</table>
5.2.2. Membranes
The rejection experiments were performed with three different types of membranes. Tubular microporous silica and titania membranes were provided by ECN (Petten, The Netherlands) and VITO (Mol, Belgium), respectively. Polyamide/polyethersulfone composite hollow fiber membranes were obtained from TNO (Eindhoven, The Netherlands).

The silica membrane consisted of several support layers of $\alpha$- and $\gamma$-alumina and the selective top layer at the outer wall of the tube consisted of amorphous silica. The silica layer had a thickness of 200 nm. The silica top layer had a small pore size distribution with pores between 0.5 and 0.8 nm, with an average pore diameter of 0.6 nm. The membrane tube used was 30 cm long and has a diameter of 14 mm.

The titania membranes consisted of an $\alpha$-alumina support with a selective top layer of titania located at the inner wall of the tube. The titania layer had a thickness of about 100 nm. The titania top layer has a small pore size distribution. The titania membranes were available with different MWCOs. In particular, the titania membrane with a MWCO of approximately 200, 700 and 1200 were used in the retention experiments.

A polyamide polymer (PA) was placed on an ultrafiltration polyethersulfone (PES) support membrane [12]. The internal diameter and wall thickness of the PES support membrane was 1.5 mm and 425 $\mu$m, respectively. PES was employed due to its low hydrophobicity, as compared to other polymers commonly used for membrane preparation. Hydrophilic membranes are generally less sensitive to fouling which is an important issue in membrane performance. PES possesses very good chemical and
thermal stability, and the glass transition temperature (Tg) is 503 K. The selective PA top layer was prepared by an interfacial polymerization process. The thickness of the PA top layer was about 0.5 to 1 µm (see also Chapter 2).

5.2.3. Experimental setup and procedures
The experimental high pressure setup which was used to measure the steady state membrane fluxes and membrane rejection performance is schematically depicted in Figure 5.2. The experimental setup was designed to study the membrane permeation and retention up to feed pressures of 40 MPa and temperatures up to 473 K.

The membranes were placed in a thermally controlled oven (Heraeus) and the temperature was measured with a Pt100 thermocouple. A thermocouple was placed at the feed side of the carbon dioxide stream in order to measure the temperature of the fluid stream entering the membrane module. The pressure on the feed and permeate side of the membrane was measured by two pressure sensors (AE Sensors) with a precision of 0.01 MPa. Carbon dioxide was filtered by an online filter to feed pure liquid CO\textsubscript{2} for smooth operation of the HPLC pump (Jasco). In order to feed the liquid phase to the pump, the pump piston heads were cooled by a thermostat. Carbon dioxide was heated to supercritical conditions by a coil, which is placed inside the oven.

The pressure on the retentate and the permeate side was controlled by back pressure regulators (BPR, Tescom). The solute (triolein or e-vitamin) was pumped into the CO\textsubscript{2} at high pressure by means of another HPLC pump with a desired flow rate.

The amount of carbon dioxide flowing in the system was measured by a Coriolis type of mass flow meter. During the rejection experiments the permeate stream of the membrane was expanded in a glass separator to separate the solute from the carbon dioxide. The retention of the solutes by the membrane was measured at different time intervals by evaluation of the mass deposited in the separator. The carbon dioxide permeating through the membrane was measured by a wet gas flow meter (Schlumberger).

To conduct permeation and retention experiments, carbon dioxide was fed to the feed and permeate side of the membrane by keeping the valve VP open. Both sides of the membrane were pressurized to ensure that no excess pressure difference across the membrane could exist, which could damage or break the membrane. When the desired pressure at the feed side was obtained, valve VP was closed. The pressure in both compartments of the membrane was controlled by back pressure regulators BPR1 and BPR2. The BPR1 on the permeate side was fine-tuned to create the desired pressure difference across the membrane.
The BPR1 and BPR2 were placed in a thermally controlled water bath to ensure steady operation. This was necessary because carbon dioxide expands during regulation of the pressure and the BPRs were cooled severely because of Joule-Thompson expansion effect [13]. The flow of expanded carbon dioxide was measured using a wet gas meter FI1 and FI2. The amount of CO$_2$ going through the membrane at a certain $\Delta P$ was measured for different feed pressures, which in turn gave the flux through the membrane in terms of number of moles of carbon dioxide permeating through a fixed surface area of the membrane per unit time. When the membrane was stabilized for the CO$_2$ flux, the solute was injected in the fluid stream by HP2 pump with a desired flow rate. The fluid mixture was passed over the membrane, which separates the stream into a retentate and a permeate stream. Both streams were passed through the glass separators RS and PS in which the solutes phased out and deposited. The flow rate of CO$_2$ was measured by wet gas flow meters. The amount of solute collected in a fixed time interval was analyzed gravimetrically.

### 5.2.4. Theoretical background

The retention factor, $\alpha$, is given by:
\[ \alpha = 1 - \left( \frac{W_p}{W_r} \right) \] (5.1)

where \( W_p \) [g] is the amount of solute at the permeate side of the membrane, and \( W_r \) [g] is the amount of the solute at the retentate.

The CO\(_2\) permeance is defined as the ratio of flux to pressure difference across the membrane, according to:

\[ Q = \frac{J}{\Delta P} \] (5.2)

The weight fraction of solute is given by:

\[ \text{wt fraction} = \frac{W_{\text{solute}}}{W_{\text{solute}} + W_{\text{CO}_2}} \] (5.3)

where \( W_{\text{solute}} \) [g] is the amount of solute and \( W_{\text{CO}_2} \) [g] is the amount of carbon dioxide initially present.

### 5.3. Results and Discussion

The retention of triolein and e-vitamin has been measured for the silica membrane and for titania membranes with different molecular weight cut-off (MWCO). For the polyamide (PA) membrane only the retention of triolein has been determined.

#### 5.3.1. Inorganic silica membrane

First, the retention factor and the scCO\(_2\) permeance have been determined for the silica membrane. In Figure 5.3 the retention factors of triolein and e-vitamin and the CO\(_2\) permeance as a function of time obtained with the silica membrane are given. From Figure 5.3a it follows that in the case of triolein the retention factor slightly increases and the CO\(_2\) permeance slightly decreases as a function of time. With the silica membrane a good retention of triolein is possible. The retention factor depends slightly on the amount of triolein in the feed, and at steady state the retention is always higher than 0.95. For the different weight fractions of triolein, the CO\(_2\) permeance decreases between 10\% and 20\%, as compared to the pure CO\(_2\) permeance.

In the case of e-vitamin, the smaller solute, a considerably lower retention is observed. Typically, for the silica membrane the retention factor is between 0.4 and 0.45. Furthermore, there is no effect of the e-vitamin on the CO\(_2\) permeance. As a function of time a constant CO\(_2\) permeance is observed. From the results shown in Figure 5.3 it can be concluded that the silica membrane has a MWCO in the order of 800 to 900. In the following only triolein retention with the silica membrane will be studied.
In Figure 5.4 the steady state values of the retention factor for different fractions of triolein are compared. There is a slight increase in retention when the amount of triolein in the CO\textsubscript{2} is increased. An increase in the fraction triolein from 0.2 to 0.4 results in an increase in retention factor from about 0.97 to about 0.99. Apparently, with an increase in the amount of triolein in the feed a larger fraction of the membrane surface is covered with triolein. This is confirmed by the behavior observed for the CO\textsubscript{2} permeance shown in Figure 5.3a. The largest decrease in CO\textsubscript{2} permeance is observed for the highest fraction of triolein in the CO\textsubscript{2} feed.

**Figure 5.3a:** Retention factor for triolein and CO\textsubscript{2} permeance obtained for the silica membrane as a function of time, for different triolein fractions. Results are for a feed pressure of 12 MPa, a trans-membrane pressure of 0.5 MPa and at a temperature of 313 K.
Figure 5.3b: Retention factor for E-vitamin and CO$_2$ permeance obtained for the silica membrane as a function of time, for different e-vitamin fractions. Results are for a feed pressure of 12 MPa, a trans-membrane pressure of 0.5 MPa and at a temperature of 313 K.

Figure 5.4: Retention factor for triolein as a function of the weight fraction triolein in the CO$_2$. Results are for a feed pressure of 12 MPa, a trans-membrane pressure of 0.5 MPa and at a temperature of 313 K.

In Figure 5.5 the retention of triolein as a function of time for two temperatures is given. The retention factor slightly increases with time. Furthermore, the two retention factors coincide, indicating that the retention is more or less independent of the temperature. In Figure 5.6 the effect of the CO$_2$ feed pressure on the retention of the triolein is given. The retention factor decreases from about 0.98 to about 0.93 when the CO$_2$ feed pressure is increased from 12 to 17 MPa.
Finally, the reversibility of the retention process is studied using a cycle where triolein in CO\(_2\) and pure CO\(_2\) are fed alternatingly to the membrane. For the first 30 minutes a scCO\(_2\) stream with triolein is fed to the membrane, then for about 40 minutes pure scCO\(_2\) is fed. After 70 minutes, again a scCO\(_2\) stream with triolein is fed to the membrane for about 20 min. During the last cycle, between 90 and 120 min, again pure scCO\(_2\) is fed to the membrane. The retention factor and CO\(_2\) permeance as a function of time for this cycle are given in Figure 5.7.

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**Figure 5.5:** Retention factor for triolein, 0.3 weight fraction, as a function of time obtained for two temperatures. Results are for a feed pressure of 12 MPa and a trans-membrane pressure of 0.5 MPa.

**Figure 5.6:** Retention factor for triolein, 0.3 weight fraction, as a function of the feed pressure of CO\(_2\), for a trans-membrane pressure of 0.5 MPa and at a temperature of 313 K.
It is clearly seen that for a CO₂ feed that contains a weight fraction of triolein of 0.3, the CO₂ permeance decreases in time. In the case of the pure CO₂ feed, the CO₂ permeance increases and reaches about the same value as obtained at the start of the experiment. During the third step, again triolein in CO₂ is fed to the membrane. The same results for the retention factor and CO₂ permeance are observed as during the first period. The CO₂ permeance decreases and the retention of triolein increases slightly. During the last period, again pure CO₂ is fed and the CO₂ permeance starts to increase again. The final value for the permeance at 120 minutes is slightly lower than the initial value for the permeance at the beginning of the experiment.

From Figure 5.7 it follows that when triolein is fed to the silica membrane the CO₂ permeance decreases. This is in agreement with the results shown in Figure 5.3a. During the second and fourth cycle there is no triolein fed to the membrane, and the CO₂ permeance regains its original permeance value. Apparently, during the second and fourth cycle the triolein is removed from the membrane surface and the amount of triolein present at the feed side does not affect the permeation of CO₂.

![Figure 5.7](image_url)

**Figure 5.7**: Results for the triolein retention factor and the CO₂ permeance as a function of time. The feed is cycled with CO₂ + 0.3 weight fraction triolein and pure CO₂, at a temperature of 313 K, a feed pressure of 12 MPa, and a trans-membrane pressure of 0.5 MPa.

### 5.3.2. Inorganic titania membrane

In Figure 5.8 results are given for the retention factor for triolein and the CO₂ flux as a function of time for the titania membranes with a MWCO of 700 and 1200. For the titania-700 membrane, Figure 5.8a, almost complete retention of triolein is obtained.
However, the CO$_2$ flux decreases by more than a factor of two as compared to the pure CO$_2$ flux. It is seen that for the highest fraction of triolein in the feed the CO$_2$ permeance decreases somewhat faster than the lower fraction of triolein, 0.2, in the feed. It is noted that for both weight fractions the retention factor and the CO$_2$ permeance have the same values at equilibrium, which is reached after about 80 min. So, the amount of triolein in the CO$_2$ has an effect on the ‘dynamics’ of the mass transport, but does not have an effect on the equilibrium situation.

In Figure 5.8b the results obtained with the titania membrane with a MWCO value of about 1200 are shown. In this case the retention factor of triolein is between 0.70 and 0.75. The retention factor slightly increases as a function of time, and the retention factor for a weight fraction of triolein of 0.4 is somewhat higher than the retention factor for a weight fraction triolein of 0.2. At equilibrium the retention factor for a weight fraction of 0.2 and 0.4 are 0.72 and 0.73, respectively. With respect to the CO$_2$ permeance, the permeance slightly decreases as a function of time, and depends somewhat on the amount of triolein in the CO$_2$ feed.

**Figure 5.8a:** Retention factor for triolein and CO$_2$ permeance obtained for the titania-700 membrane as a function of time, for two different triolein fractions. Results are for a feed pressure of 12 MPa, a trans-membrane pressure of 0.5 MPa and at a temperature of 313 K.
Figure 5.8b: Retention factor for triolein and CO\(_2\) permeance obtained for the titania-1200 membrane as a function of time, for two different triolein fractions. Results are for a feed pressure of 12 MPa, a trans-membrane pressure of 0.5 MPa and at a temperature of 313 K.

In Figure 5.9 the results are given for the retention of e-vitamin and the CO\(_2\) permeance obtained for the titania-200 membrane. Again, almost complete retention is possible because the MWCO of the membrane is considerably lower than the molecular weight of e-vitamin of 472. However, in this case the CO\(_2\) permeance almost completely vanishes after 1 hour. Apparently, in this case the e-vitamin blocks the pores of the membrane completely.
From the various results obtained for the titania membranes it can be concluded that there is a clear effect of the MWCO of the membranes on the retention. The MWCO of the membranes should ideally be close to the values of the molecular weight of the solutes in order to have a high retention and a high CO$_2$ permeance. In the case that the MWCO of the membrane is much smaller than the mass of the solute the CO$_2$ permeance vanishes, because the solute blocks the membrane pores.

5.3.3. Polymeric polyamide membrane
Finally, the performance of the polyamide membranes with respect to the retention of triolein has been studied. These polymeric membranes have the highest CO$_2$ permeance of the three types of membranes studied. Therefore, it is to be expected that only for triolein there will a reasonable retention. In Figure 5.10 the retention of triolein by the IPC membrane is shown as a function of time.

![Figure 5.10: Retention factor for triolein and CO$_2$ permeance obtained for the IPC membrane as a function of time. Results are for a feed pressure of 12 MPa, a transmembrane pressure of 0.5 MPa and a temperature of 313 K.](image)

It is noted that both the retention factor and the CO$_2$ permeance are constant in time. This differs somewhat from the behavior observed for the retention of triolein by the titania-1200 membrane; see Figure 5.8b, where both the rejection and the permeance are a weak function of time. The retention factor of triolein for the IPC membrane is about 0.83, which is slightly higher than the retention factor obtained with the titania-1200 membrane. This suggests that the ‘pore size’ of the IPC membrane is somewhat smaller than the pore size of the titania-1200 membrane. Also, the affinity of triolein for the
polymeric membrane could be somewhat higher, which might be a result of swelling of the polymer on a microscopic scale.

In Figure 5.11 the effect of the CO$_2$ feed pressure on the retention of the triolein is given. For the IPC membrane the retention factor is more or less independent of the feed pressure. Again, this is different from the behaviour observed for the retention of triolein by the inorganic membranes, e.g. for the silica membrane, Figure 5.6, the rejection factor decreases with an increase in the feed pressure.

![Figure 5.11: Retention factor for triolein, 0.3 weight fraction, as a function of the feed pressure of CO$_2$. Results are for a feed trans-membrane pressure of 0.3 MPa and a temperature of 313 K.](image)

5.4. Conclusions

Retention experiments have been conducted with two different solutes and three different types of membranes. The effect of the amount of solute in the feed and the effect of the feed pressure on the rejection factor and the CO$_2$ permeance has been studied in detail. There is a small difference in the time dependency of the retention factor and the CO$_2$ permeance observed for the inorganic membrane and the polymeric membrane.

The fact that different membranes are available with a high CO$_2$ permeance offers possibilities for efficient regeneration of carbon dioxide while maintaining supercritical conditions.
References

Chapter 6

Solubilities of Sub- and Supercritical CO₂ in Molten Polyester Resins: Measurements and Predictions*

Abstract
Solubilities of carbon dioxide (CO₂) in polyester resins based on propoxilated bisfenol (PPB) and ethoxylated bisfenol (PEB) have been measured using a magnetic suspension balance at temperatures ranging from 333 to 420 K and pressures up to 30 MPa. An optical cell has been used to independently determine the swelling of the polymers, which has been incorporated in the buoyancy correction. In both polyester resins, the solubility of CO₂ increases with increasing pressure and decreasing temperature as a result of variations in CO₂ density. Moreover, the experimental solubility has been described using the Sanchez-Lacombe equation of state. A linear relationship between the adjustable interaction parameter of the Sanchez-Lacombe equation of state and temperature exists for both polymers.

6.1. Introduction

Polyester resins in powder form are frequently used in the paint and toner industry. Milling, grinding and spray drying are the particle formation processes commonly used in the industry. Narrow particle size distribution, solvent recovery and the prevention of volatile organic components (VOC) emission are the major challenges associated with these processes. Moreover, the classical processes have clear disadvantages in terms of energy requirement due to expensive cryogenic cooling, and problems with product quality due to heat dissipation during milling which causes clogging by molten polymer particles. This has motivated chemists as well as chemical engineers to adopt supercritical technologies in which the problems described above can be eliminated. Unusual solvent properties above the critical point like gas-like diffusivities and liquid-like densities make supercritical technology attractive. PGSS (Particles from gas saturated solution) is one of the particle production processes using a supercritical fluid. Supercritical CO\(_2\) has a high solubility in many polymers. In PGSS, the viscosity of the polymer, particle size and morphology of the particles are mainly determined by the amount of CO\(_2\) dissolved in the polymer. Therefore, it is important to determine the solubilities of CO\(_2\) in a polymer at different conditions in order to define the processing window.

Various methods exist to determine the solubility of CO\(_2\) in solid and in molten polymers. Phase separation [2], volumetric [3] and gravimetric [4] methods are commonly used. In the first two methods, the amount of polymer required is large compared to gravimetric methods and hence, the time required to reach equilibrium is substantially longer. Moreover, high accuracy in pressure sensors and volume measurements are required in the first two methods for solubility calculations. These disadvantages are overcome by a gravimetric method, which uses a microbalance [4]. The principle behind the gravimetric method is the weight difference between a CO\(_2\)-free and a CO\(_2\)-sorbed polymer sample. With a microbalance of high accuracy, even a small change in the weight of the polymer sample due to dissolved gas can be measured. Recently, a magnetic suspension balance (MSB), developed by Kleinrahm and Wagner [5], has been used to measure the solubility of CO\(_2\) in various polymers [6,7,8]. A major advantage of using the MSB is that measurements can be carried out at elevated temperatures and pressures without having direct contact between the sample and the balance.
The main objective of this work is to determine the solubilities of CO\(_2\) in polyester resins using a MSB. An important parameter in such gravimetric measurements is the swelling of polymer due to dissolved CO\(_2\). A buoyancy correction due to swelling has to be taken into account while calculating the dissolved quantity of CO\(_2\) in a polymer [6,7,8]. Therefore, an optical cell has been used in separate experiments to observe the swelling of polymers in the presence of CO\(_2\) at similar conditions. The other objective of the study is to describe the solubility data using a thermodynamic model, for which the Sanchez-Lacombe (S-L) equation of state (EOS) has been used [9,10].

6.2. Experimental

6.2.1. Materials
Polyester resins based on propoxilated bisfenol (PPB, CAS: 177834-94-5), and ethoxylated bisfenol (PEB, CAS: 170831-75-1) were obtained from Akzo Nobel, The Netherlands. The physical properties of the polymers are provided in Table 6.1. Both polymers were amorphous which was confirmed by DSC measurements. The dry grade (> 99.5 %) carbon dioxide was used for the measurements. All chemicals were used as received without further purification.

Table 6.1: Physical properties of the polymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Tg (K)</th>
<th>(\eta_0) at 363 K (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPB</td>
<td>2700</td>
<td>7000</td>
<td>325-329</td>
<td>2965</td>
</tr>
<tr>
<td>PEB</td>
<td>8500</td>
<td>20000</td>
<td>328-332</td>
<td>47540</td>
</tr>
</tbody>
</table>

6.2.2. Apparatus and method

Magnetic suspension balance

A magnetic suspension balance (MSB), Figure 6.1, was used for measuring the solubility of CO\(_2\) in both polymers. The MSB can be used at temperatures up to 473 K and pressures up to 50 MPa. A polymer sample was kept in a basket which was not directly connected to the weighing balance (microbalance), but was kept in place using a so-called suspension magnet. The suspension consists of a measuring load, a sensor core and a permanent magnet. The measured weight of the basket containing the polymer was transmitted by a magnetic suspension coupling to an external microbalance and thus, leak-proof measurements can be performed. In the MSB apparatus, the
microbalance can be tared and calibrated during measurements as the sorption times are generally sufficiently long.

![Diagram of the magnetic suspension balance apparatus](image)

**Figure 6.1:** The magnetic suspension balance apparatus used for the solubility measurements.

Using the MSB, the amount of CO$_2$ dissolved in a polymer was determined from the following relationship:

$$W_{CO_2} = \Delta W + \rho_{CO_2} \cdot V_P \cdot (P, T, S) + V_B$$  \hspace{1cm} (6.1)

where $\Delta W$ is the weight difference between a CO$_2$ equilibrated polymer sample and the polymer sample without CO$_2$ at similar temperature T and pressure P. $\rho_{CO_2}$, $V_P$ (P, T, S) and $V_B$ are the density of CO$_2$, the volume of the polymer after contacting CO$_2$ with a solubility in the polymer S and the volume of the basket, respectively. The second term in Eq. (6.1) is a buoyancy correction term, which is required as polymers swell considerably when exposed to high CO$_2$ pressures. As it was not possible to observe the polymer swelling simultaneously during the solubility measurements, an optical cell was used separately for the swelling measurements.

CO$_2$ solubility measurements were carried out above the glass transition temperature (Tg) of both polyesters. Temperature and pressure were varied from 333-420 K and 5-30 MPa, respectively. The polymer sample was first exposed to a vacuum for
approximately 6 hours at the measurement temperature and an initial level was recorded. This was followed by addition of CO\textsubscript{2} in the chamber until the desired pressure was attained. The sample was allowed to attain sorption equilibrium (approximately 6 hours) before the final level was recorded. Subsequently, more CO\textsubscript{2} was introduced to attain a higher pressure and the new reading was recorded after equilibrium. Thus, solubility isotherms as a function of pressure were obtained.

**Optical cell**

A high-pressure optical cell used for swelling measurements is shown in Figure 6.2. The cell can be used at temperatures up to 473 K and pressures up to 35 MPa. The inner volume of the cell was 20 mL. The temperature of the cell was controlled within 0.1 K using an oil bath. CO\textsubscript{2} was pumped to the cell at elevated pressures using an HPLC pump. A 10 mL glass cuvette having a square cross section was used for holding a polymer sample. In the cuvette, the swelling of the polymer occurred only in one direction as the other directions were confined by the walls of the cuvette as shown in Figure 6.2. The swelling of the polymer was viewed through a quartz window of the optical cell. A cathetometer having a precision of 0.01 mm was used to measure the difference in the height of the sample from which a fractional change in the volume of the polymer was calculated.

![Figure 6.2](image_url)

**Figure 6.2:** (a). The optical cell used for measuring the swelling of a polymer (b) the one-dimensional swelling of a polymer.
Here, the change in the volume of the polymer sample is termed as fractional swelling, $\Delta V/V_o$, $\Delta V$ and $V_o$ are the increment in the volume of the polymer sample due to swelling and the volume of the polymer sample in the absence of dissolved CO$_2$, respectively.

It can be seen from Eq. (6.1) that the data obtained using a MSB are not sufficient to calculate the solubility. Therefore, swelling measurements were carried out separately at the same temperatures. For these measurements, a sample was prepared by pouring a molten polymer into a mould having a shape similar to the cuvette. After weighing the molded sample, it was fitted into the cuvette. The sample was again heated slightly above its Tg and pressed against the cuvette walls by a metal rod. The cylinder was then kept inside the cell and was heated to the desired temperature for about 4 hours. Subsequently, the polymer surface was marked with a cathetometer followed by the addition of CO$_2$ to the desired pressure. Due to a rapid initial swelling, it was difficult to mark the surface immediately after the addition of CO$_2$ with the cathetometer. Pressure-volume-temperature (PVT) data of the polymer (i.e. specific volume of the polymer) were used to correct the initial cathetometer reading. The sample was then allowed to attain equilibrium. As the sorption equilibrium was reached, no further swelling of the polymer occurred. Then, the new surface was marked with the cathetometer. The difference in the sample volume was used to calculate the swelling of the polymer. For subsequent measurements at higher pressures an additional amount of CO$_2$ was introduced stepwise and a similar procedure was adopted.

The PVT data of the polymers were obtained using a high-pressure Gnomix PVT apparatus (DatapointLabs, USA) for a temperature range from 317 K to 473 K and pressures up to 40 MPa. The PVT data of CO$_2$ were obtained from the Span and Wagner EOS [11].

6.3. Theory

6.3.1. Sanchez-Lacombe equation of state

The generalization of the classical lattice theory to describe the distribution of molecules in a three dimensional cubic lattice is called the lattice-fluid model. This model is able to predict vapor-liquid equilibrium in a fundamental manner. To predict the solubility at equilibrium conditions, the Sanchez-Lacombe EOS based on the lattice theory was used. In this theory the polymer molecules are ordered according to a lattice structure. The theory accounts for the change in volume due to the presence of “holes”
in the lattice and hence, does not require separate parameters to account for the flexibility of the molecule. An assumption used in the Sanchez-Lacombe EOS is that the polymer is monodisperse. The experimentally measured solubilities of subcritical and supercritical CO\(_2\) in various polymers have successfully been correlated to the Sanchez Lacombe EOS [6,7,8].

The Sanchez-Lacombe EOS is given by:

\[
\tilde{\rho}^2 + \tilde{P} + \tilde{T} \ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho} = 0 \quad (6.2)
\]
\[
\tilde{\nu} = 1/\tilde{\rho} \quad (6.3)
\]

where \(\tilde{\rho}, \tilde{\nu}, \tilde{P}, \tilde{T}\) and \(r\) are the reduced density, specific volume, pressure, temperature, and the number of the lattice sites occupied by a molecule, respectively.

The reduced parameters are defined as:

\[
\tilde{\rho} = \rho / \rho^*, \quad \tilde{\nu} = \nu / \nu^*, \quad \tilde{P} = P / P^*, \quad \tilde{T} = T / T^*, \quad r = MP^*/RT^*\rho^* \quad (6.4)
\]

where \(\rho^*\) (the corresponding mass density in the close-packed state), \(\nu^*\) (the corresponding specific volume in the close-packed state), \(P^*\) (the hypothetical cohesive energy density in the close-packed state) and \(T^*\) (related to the depth of the potential energy well) are the characteristic parameters of components. The reduced parameters are obtained by fitting PVT data of pure components using Eqs. 6.2 to 6.4.

The EOS used for a mixture is similar to Eq. 6.2. The characteristic parameters used in the EOS for a mixture are obtained using the following mixing rules:

\[
P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \quad (6.5)
\]
\[
P_{ij}^* = (1 - k_{ij} (P_i^* P_j^*)^{0.5}) \quad (6.6)
\]

where \(k_{ij}\) is an adjustable interaction parameter, which is a measure for the deviation of \(P_{ij}\) from the geometric mean of \(P_i^*\) and \(P_j^*\).
The reduced parameters for the mixture are defined as:

\[
T^* = P^* \sum_i (\phi_i^0 T_i^*) / P_i^* \\
\]

\[
r_i^0 \nu_i^* = r_i \nu^* \\
\]

\[
\nu^* = \sum_i \phi_i^0 \nu_i^* \\
\]

\[
1/r = \sum_i \phi_i / r_i \\
\]

\[
\phi_i^0 = (\phi_i P_i^* / T_i^*) / \sum_j (\phi_j P_j^* / T_j^*) \\
\]

\[
\phi_i = (w_i / \rho_i^*) / \sum_j (w_j / \rho_j^*) \\
\]

where \(\phi\) and \(w\) represent the volume and weight fraction of components in two phases, respectively. Superscript ‘0’ denotes the pure state of a component. Along with the Eqs. 6.1 to 6.12, the chemical potential, \(\mu\), of a component in the available phases are used to predict the solubility of CO\(_2\) in a polymer.

At equilibrium:

\[
\mu_i^{\text{gas}} = \mu_i^{\text{polymer}} \\
\]

Here, CO\(_2\) is referred to as component ‘1’, while a polymer is referred to as component ‘2’. The chemical potential of 1 in the polymer phase is given by:

\[
\mu_i^{\text{polymer}} = RT \left[ \ln \phi_i + (1 - r_1 / r_2) \phi_2 + r_i^0 \tilde{\rho} \phi_2^2 \right] + \\
\]

\[
r_i^0 RT \left[ - \tilde{\rho} / T_1 + \tilde{\rho} \tilde{i} / T_i + \tilde{i} (1 - \tilde{\rho}) \ln (1 - \tilde{\rho}) + \tilde{\rho} / r_i^0 \ln \tilde{\rho} \right] \\
\]

Equation 6.14 is also used to calculate the chemical potential \(\mu_i^{\text{gas}}\) by considering only the gas phase. For polymers of high molecular weight, it is assumed that there is no polymer present in the gas phase. Therefore, the experimental solubility data are regressed with the adjustable interaction parameter, \(k_{ij}\), (in Eq. 6.6) solving Eqs. 6.2 to 6.14 simultaneously.
6.4. Results and Discussion

The PVT data of the polymers and CO$_2$ are essential for the interpretation of the swelling measurements and in the S-L EOS as discussed above. Therefore, the PVT and swelling studies are described before the solubility results.

The PVT data have been successfully modeled using the S-L EOS for a wide range of temperatures, pressures and densities. The results for CO$_2$, PPB and PEB are shown in Figures 6.3, 6.4 and 6.5, respectively. The characteristic parameters of the pure components, obtained using the S-L EOS are given in Table 6.2. Subsequently, these parameters have been used to calculate the solubility.

Figure 6.3: The CO$_2$ solubility isotherms of PPB, $k_{12}(333 \text{ K}) = 0.1931$, $k_{12}(368 \text{ K}) = 0.2224$, $k_{12}(420 \text{ K}) = 0.2571$.

Figure 6.4: The CO$_2$ solubility isotherms of PEB, $k_{12}(334 \text{ K}) = 0.1761$, $k_{12}(373 \text{ K}) = 0.1906$, $k_{12}(418 \text{ K}) = 0.2265$. 
When CO₂ is dissolved into a polymer, the mobility of the polymer chains is increased due to disentanglement of the polymeric chains. As a result, the free volume inside the polymer is increased and swelling of the polymer takes place. Experimentally obtained swelling isotherms of PPB and PEB in the presence of CO₂ using the optical cell apparatus are shown in Figures 6.6 and 6.7, respectively. It can be seen from these figures that the fractional swelling is increased with increasing pressure for both PPB and PEB.
In general, the higher the dissolved amount of CO\textsubscript{2} in a polymer the larger is the swelling of the polymer. This effect is the result of an increasing CO\textsubscript{2} density upon an increase in pressure. Since the CO\textsubscript{2} density decreases with temperature, a reduction in the swelling is expected at higher temperatures in both polymers. However, this is observed only for PPB. The swelling of PEB increases with an increasing temperature. This has also been reported for poly (dimethyl siloxane) (PDMS) [12], poly (ethylene-terephtalate) (PET) and bisphenol-A polycarbonate (PC) [13]. It has been suggested that the CO\textsubscript{2} density is not the only parameter, which affects the swelling of the polymer. A positive temperature influence on chain mobility is pronounced compared to
the influence of CO$_2$ density for an inverse swelling behavior [13]. This effect is only present in PEB, which is most probably caused by an easily accessible free volume due to its low MW, even at low temperatures.

Figure 6.8: Fractional swelling isotherms of PPB in the presence of CO$_2$.

Figure 6.9: Fractional swelling isotherms of PEB in the presence of CO$_2$.

CO$_2$ solubilities in both polymers have been measured and have been predicted using the S-L EOS. The results are shown in Figure 6.8 and Figure 6.9. The experimental data from the MSB are corrected for buoyancy effects using the results of the swelling measurements. The CO$_2$ solubility is represented in terms of the weight fraction of CO$_2$. 
dissolved in the polymer. The solubilities of CO$_2$ have been corrected with the experimental swelling data. For both polymers, it is found that the solubility increases with increasing pressure, whereas it decreases with an increasing temperature. This relates to high CO$_2$ densities at high pressures and low temperatures, and vice versa. At a low temperature, 333 K, the solubility behavior is not linear above 15 MPa for both polymers. Probably at elevated pressures, the free volume available in the polymer is reduced due to compression of the polymer. Such effects are more pronounced at a lower temperature due to the relatively small free volume. Moreover, Figure 6.8 and 6.9 also show that this non-linear behavior is absent at high temperatures.

The CO$_2$ solubilities in PPB are higher than in PEB. The importance of minor changes in the groups present in a polymer for the CO$_2$ solubility has already been discussed in the literature [14,15]. The accessible free volume in PPB is smaller due to higher chain entanglements (high MW) compared to PEB, which makes it for CO$_2$ more difficult to access the carboxyl groups in PEB than in PPB. Albeit the swelling increases with an increase in temperature in PEB, the relatively low CO$_2$ densities at high temperatures reduce the solubility.

The solubility results have been correlated with the S-L EOS for both PPB and PEB, see also Figure 6.8 and 6.9, respectively. In order to fit the S-L EOS to the experimental solubility data, Eq. (4.2 - 4.14) have been solved using the characteristic parameters determined from the PVT data (Table 6.2). A non-linear regression optimization procedure (Levenberg-Marquardt, MATLAB 7) has been used for minimizing the difference between the chemical potential of CO$_2$ in the gas phase and the polymer phase, and also between the experimental and predicted solubilities using the interaction parameter, $k_{12}$. It can be seen from Figures 6.8 and 6.9 that the S-L EOS is a versatile tool for predicting the CO$_2$ solubility in PPB and PEB. In the case of both polymers, $k_{12}$ varies linearly with temperature, so that a simple linear relationship between $k_{12}$ and $T$ can be used to interpolate and possibly extrapolate the solubilities at different temperatures and pressures, Figure 6.10. Though the S-L EOS has already been reported for several polymers to predict the swelling due to dissolved CO$_2$, it has not been tested together with the experimental swelling and solubility data for molten polymers. The density of a mixture can be determined using the S-L EOS, which has been used to predict the swelling of both polymers, from which it can be concluded that the swelling is poorly predicted by this EOS for PPB and PEB. Recently, over prediction of swelling using the S-L EOS has also been reported for EVA polymers by Jacobs et al. [16]. The linear mixing rule for the volume of the mixture in the S-L EOS may be responsible for
this poor predictability. To overcome this problem, Royer et al. [12] have successfully introduced a correction parameter in the mixing rule used for the volume in the S-L EOS to predict the swelling of PDMS.

![Graph showing linear relationship between k_{12} and T for PPB and PEB.]

**Figure 6.10:** A linear relationship between \( k_{12} \) and \( T \) for both PPB and PEB.

### 6.5. Conclusions

The solubilities of CO\(_2\) have been measured in PPB and PEB in the molten state using the MSB. It appeared to be necessary to correct the data obtained from the MSB with independent swelling data. The CO\(_2\) solubility in the polymers increases with an increase in pressure and decreases with an increase in temperature. The CO\(_2\) solubility in PEB is lower than in PPB which is mainly due to its smaller accessible free volume as a result of the higher MW. At 333 K, a non linear trend for solubility-pressure has been observed at elevated pressures due to compression. The experimental solubility data have been correlated with the S-L EOS using the pure component parameters and an adjustable interaction parameter. A linear relationship has been obtained between the temperature and the interaction parameter for both PPB and PEB. Although the S-L EOS has often been used to predict the swelling of a polymer in the presence of CO\(_2\), it is not valid for the polymers investigated here.
References

Chapter 7

Conclusions and Future Outlook

Abstract
In this chapter an overview is given of recent developments of membrane technology in combination with supercritical fluids (SCF) applications, focusing on the use of membranes for the regeneration of SCFs and for the integration of reaction and separation using membrane reactors. From the description of the permeation behavior it follows that for the supercritical regime the governing mechanism for mass transport in the inorganic membranes is by viscous flow. The availability of different types of inorganic membranes that are stable in SCF opens the possibility for continuous operation of supercritical processes.
7.1. **Introduction**

The two main areas of membrane applications in combination with supercritical fluids (SCF) are the separation of solutes from the supercritical phase, including the regeneration of relatively pure supercritical fluids, and the integration of reaction and separation using membrane reactors. In these applications the stability of the membranes in terms of the permeation and retention are important factors. In particular, inorganic membranes are suitable for use in SCF applications due to their intrinsic physical and chemical stability. The use of stable inorganic membranes could open the possibility for the continuous operation of supercritical processes, with an energy efficient regeneration of the SCF.

7.2. **Regeneration of SCF using membranes**

In fluid separations the interaction of the components dissolved in the supercritical phase can affect the separation characteristics of the membrane [1]. Most of the applications of membranes in combination with supercritical fluids (SCF) are restricted to species which are soluble in the SCF, which cover components with a molecular weight in the order of 100 to 1500.

7.2.1. **Food processing**

A typical example of the regeneration of relatively pure supercritical fluids applies to food processing, which includes the recovery of aromas and flavors from herbs and spices, extraction of edible oils, and removal of contaminants. Carbon dioxide is particularly advantageous for processing of food materials due to its inertness. Moreover, in certain cases using supercritical fluids is the only way to meet product specifications [2]. However, an economical method to recycle the dense carbon dioxide is not yet available. The use of a reverse osmosis membrane separation process can be an alternative to avoid the intense depressurization step, which is necessary for the recovering of the extracts [3]. Moreover, excellent separation performance of commercially available reverse osmosis membranes has been obtained for separation of D-limonene, which is the main component of citrus peel oil [4].

More recently, caffeine has been used as model solute to explore the possibilities of using inorganic membranes for scCO$_2$ regeneration [3,5,6,7]. Fujii et al. [1] employed a thin porous silica membrane with an average pore size of 3.3 nm synthesized by the sol–gel method to regenerate carbon dioxide. The caffeine rejection and the permeability flux of scCO$_2$ were observed to be 0.65 and 0.023 mol m$^{-2}$ s$^{-1}$, respectively. Chiu et al.
[6] studied the separation of scCO$_2$ and caffeine with a nanofilter having a thin layer of ZrO$_2$-TiO$_2$ with an average pore size of 3 nm on a carbon substrate. The experimental data indicate that a 100% caffeine rejection can be obtained at 308 K and 7.95 MPa, which is near the critical point of carbon dioxide. Tan et al. [7] developed tubular filters coated with mesoporous silica and microporous silicalite. Alumina tubular filters were used as the support layers for the preparation of the mesoporous silica and microporous silicalite membranes. With the mesoporous silica membrane filter caffeine rejection was observed as high as of 0.98 in the first 6 h, which dropped slightly at longer times. It was proposed that the adsorption of the caffeine in the mesoporous silica layer was the major mechanism for the separation. The supercritical carbon dioxide permeation flux was observed to be 0.074 mol m$^{-2}$ s$^{-1}$, which was close to the value of 0.079 mol m$^{-2}$ s$^{-1}$ obtained for the support filter. This indicates that there is a small mass transfer resistance in the mesoporous layer.

### 7.2.2. Dry cleaning

Another area where regeneration of SCF becomes interesting is garment dry cleaning. Van Roosmalen et al. [8] have demonstrated that toxic perchloroethylene (PERC) can be successfully replaced by high pressure carbon dioxide in dry cleaning processes. Furthermore, Photinon et al. [9] has described the recovery of liquid and supercritical carbon dioxide by using microporous stainless steel and ceramic tubular modules, with the main focus on dry cleaning applications.

### 7.3. Membrane reactors

Membrane reactors and catalytic membranes can be used to integrate catalytic conversion, product separation and recovery of the catalyst into one single operation. Integration of reaction and separation has several advantages, including continuous operation, high productivity, easy control and straightforward scaling-up.

Goetheer et al. [10] applied membrane technology to retain an homogeneous Wilkinson’s catalyst in a continuous process that uses supercritical carbon dioxide as solvent. The catalyst is separated from the products by a microporous silica membrane, see Figure 7.1. The size of the catalyst, 2–4 nm, is clearly larger than the pore diameter, 0.5–0.8 nm, of the silica membrane. The membrane, therefore, retained the catalyst, while the substrates and products diffused through the membrane. Stable operation and continuous production of n-butane has been achieved at a temperature of 353 K and a pressure of 20 MPa.
Knez et al [11] described a membrane reactor in which a membrane is used as a separation unit to retain the biocatalyst in the reactor. The hydrolysis of sunflower oil in scCO\textsubscript{2} was performed as a model reaction in the reactor with Lipolase 100T as a catalyst. Hydrolysis reaction is an important industrial reaction, because it is a major route to produce surfactants and detergents from fats and oils.

### 7.3.1. Catalytic membranes

Membranes formed by depositing water-soluble polymers onto a ceramic porous support exhibited excellent properties for continuous processes. The hydrophilicity of the gel layer formed on the membrane surface assures high water permeability, and provides an adequate microenvironment to immobilize enzymes by covalent attachment [12].

An example of a catalytic membrane reactor, where the catalyst is immobilized on the membrane, is presented by Pomier et al. [13]. The membrane reactor concept is validated for a fluidification/filtration/reaction process. In particular, the concept was tested for combining enzyme, membrane and scCO\textsubscript{2} to castor oil modification. In the presence of supercritical CO\textsubscript{2} the viscosity of oils is reduced, which circumvents the use of high temperatures normally applied to reduce the viscosity. Furthermore, the use of moderate temperatures avoids the degradation of the oils. This idea opens interesting prospects for the biotransformation of (biological) products with a high viscosity.

### 7.3.2. Equilibrium reactions

One of the main applications of catalytic membranes is to overcome the equilibrium conversion by selectively removing the byproduct [14]. In particular, because of the
availability of water-selective microporous silica membranes, reactions where water is the byproduct seem interesting, like esterification and carbonylation reactions. Lozano et al. [15] have studied the synthesis of butyl butyrate from butyl vinyl ester and 1-butanol in supercritical carbon dioxide. Candida antarctica lipase B (Calb) immobilized on a macroporous acrylic resin was used as the catalyst for the esterification. It was demonstrated that the selective water removal by a ceramic membrane coated with different hydrophilic polymers to covalently attach the Calb enhances the enzymatic activity and selectivity during the reaction. The membranes were applied for continuous butyl butyrate synthesis in a cross-flow reactor with different organic solvents and supercritical CO₂ as reaction media. Advantages of using scCO₂, over organic solvents, are the improved mass transport and the separation of the reaction products by tuning the solvent power. An example of a carbonylation reaction is the production of dimethyl carbonate (DMC) from carbon dioxide and methanol. DMC is a novel material and has attracted much attention to replace toxic and corrosive materials such as dimethyl sulfate and phosgene [16]. The main reaction scheme using carbon dioxide as one of the reagents is:

\[
2\text{CH}_3\text{OH} + \text{CO}_2 \leftrightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O}
\]

In general, the DMC yield is only in the order of 2 to 5 % because of the limiting equilibrium conditions. It has been demonstrated that the yield can be increased significantly by removing the water from the reaction mixture to drive the equilibrium in the favorable way [17,18].

7.3.3. Inorganic membranes for supercritical fluid applications

For the development of high pressure applications using membrane technology, the stability of the membranes in terms of the permeance and retention are the two most important parameters. From the various results for the permeation and retention behavior of the different membranes it follows that the inorganic silica and titania membranes are stable under supercritical conditions.
The description of the permeation behavior shows that for the supercritical regime the governing mechanism for mass transport in the inorganic membranes is by viscous flow.

The fact that viscous flow is the main transport mechanism means that the inorganic membranes have limited capacity to separate different (supercritical) fluids. Therefore, the main application will be related to the retention of relatively large molecules.
solubilized in supercritical fluids, using the possibility to adjust the permeance and retention by changing the molecular weight cut-off of the titania membranes.

From the results shown in Figure 7.2 it can be seen that a similar permeance is observed for the titania membranes with a different molecular weight cut-off.

From the results for the CO$_2$ permeance an estimate can be made for the relationship between the pore size and the molecular weight cut-off of the titania membranes. It is seen, see Figure 7.3 that the pore size decreases linearly with a decrease in molecular weight cut-off. For low values of the MWCO, below a MWCO of 550, the pore size becomes independent of the MWCO. This indicates that for the titania membranes the smallest pore size that can be obtained is about 0.5 nm.

7.4. Concluding remarks

The availability of different types of inorganic membranes that are stable in SCF opens the possibility for continuous operation of supercritical process. The two main applications anticipated at this moment are the regeneration of SCFs and the integration of reaction and separation. In the latter case, the membrane is used for the recovery or immobilization of the catalyst. The findings described in the thesis can be relevant for to the development of clean and more efficient chemical processes.

References


Samenvatting

Voor veel toepassingen is het gebruik van superkritische vloeistoffen een effectieve methode om organische oplosmiddelen te vervangen. Een van de voornaamste problemen in toepassingen met superkritische oplossingen is echter de regeneratie ervan. Over het algemeen wordt regeneratie bereikt door het verlagen van de oplosbaarheid van de opgeloste component in de superkritische vloeistof. Regeneratie door expansie of koelen gaat gepaard met een hoog energieverbruik, omdat de vloeistof weer op druk en temperatuur gebracht moet worden om superkritische omstandigheden te bereiken. Selectieve membraanscheiding van superkritische vloeistoffen biedt interessante mogelijkheden voor de regeneratiestap.

In dit proefschrift worden drie verschillende composietmembranen getest op het gebruik in superkritische vloeistoffen. Er zijn polymeermembranen gebruikt, bestaande uit een polyethersulfon ultrafiltratie membraan als basismembraan met twee verschillende selectieve polyemere toplagen. Eén toplaag bestaat uit polyvinylalcohol (PVA) en de ander uit een polyamide. Het keramische membraan bestaat uit een support laag van α- en γ− alumina met silica als selectieve laag. Tenslotte zijn membranen met een selectieve titania toplaag met verschillende ‘molecular weight cut-off’ op een α-alumina support getest.

De effectiviteit van de verschillende membranen is geëvalueerd door de flux van verschillende componenten als functie van voedingsdruk, temperatuur en drukverschil over het membraan te meten. Bovendien zijn verschillende membranen getest op het regenereren van superkritisch koolstofdioxide. De oplosbaarheid van olieachtige componenten in superkritisch koolstofdioxide is bepaald doormiddel van de vlokpunt methode. Kennis van de fase-evenwichten is belangrijk om een homogene superkritische fase te behouden gedurende de regeneratie. Fasescheiding van de opgeloste stoffen en CO₂ moet worden voorkomen, omdat dit de effectiviteit van het membraan vermindert. Bij de ontwikkeling van de polymeermembranen zijn het zwellen en weekmakingseffect van CO₂ op de polymeren ook bestudeerd.

Met betrekking tot het permeatiedrag, is gebleken dat onder superkritische omstandigheden het hoofdmechanisme voor massatransport over de verschillende membranen visceuze flow is. Voor de drie typen membranen bestaat een maximum in de permeatie van CO₂ en SF₆ als functie van voedingsdruk. Voor permeatiemetingen uitgevoerd bij een temperatuur net boven de temperatuur waarboven CO₂ en SF₆
superkritisch worden, wordt een maximum gevonden in de permeatie waarbij de druk van component superkritisch wordt. De permeatie van de twee superkritische vloeistoffen verkregen bij verschillende omstandigheden kan worden beschreven door een enkele mobiliteitsconstante, die onafhankelijk is van temperatuur of druk. Bij superkritische condities wordt het massatransport voornamelijk bepaald door het fasegedrag in de vloeistof. Bij hoge druk heeft CO\textsubscript{2} een weekmakend effect op de twee polymeermembranen, wat ten koste gaat van de stabiliteit van de membranen. Door de mate van crosslinking te verhogen wordt de stabiliteit van het membraan aanzienlijk verbeterd. Dit gaat echter ten koste van CO\textsubscript{2} permeatie. Zowel de silica als titania membranen vertonen daarentegen uitstekende stabiliteit, aangezien de permeatie van superkritisch CO\textsubscript{2} door de twee typen membranen bij een gegeven druk en temperatuur constant is gebleven gedurende het gehele experimentele traject.

Regeneratie van superkritisch koolstofdioxide wordt aangetoond door het uitvoeren van rejection experimenten met twee olieachtige componenten, te weten trioleine en vitamine E. Retentiefactoren en koolstofdioxide permeatie zijn gelijktijdig bepaald. Zowel voor trioleine als vitamine E is complete retentie mogelijk met een titania membraan, wat wel een aanzienlijke vermindering van koolstofdioxide permeatie met zich meebrengt. Voor trioleine is een hoge retentie mogelijk met het silica membraan. De retentiefactor ligt tussen 0.97 en 0.99, met een vermindering van de koolstofdioxide permeatie van ongeveer 20 % in vergelijking met zuivere koolstofdioxide permeatie.

Hoewel het zwellen van polymeren een negatieve invloed heeft op de effectiviteit van het membraan, is het voordelig voor de productie van polymeerdeeltjes. Voor het produceren van polymeerdeeltjes voor bijvoorbeeld een toner of verf, kan superkritisch CO\textsubscript{2} gebruikt worden om de viscositeit van de polymere smelt te verminderen. Om een processing window voor de deeltjesproductie vast te stellen, zijn de oplosbaarheid van koolstofdioxide in twee polyester resins en het zwellen van de resins onafhankelijk van elkaar gemeten. Voor de twee polyester resins, gepropoxileerd bisfenol (PPB) en geethoxyleerd bisfenol (PEB), neemt de CO\textsubscript{2} oplosbaarheid toe met toenemende druk en afnemende temperatuur als gevolg van dichtheidvariaties van CO\textsubscript{2}. Bovendien is de oplosbaarheid van koolstofdioxide in de resins beschreven met de Sanchez-Lacombe toestandsvergelijking.

Het onderzoek dat in dit proefschrift gepresenteerd wordt, heeft geleid tot een verbeterd inzicht in het gebruik van organische en anorganische membranen voor de regeneratie van superkritisch koolstofdioxide. Het onderzoek naar het zwelgedrag zorgt voor een beter begrip van het gedrag van polymeren in hoge dichtheid CO\textsubscript{2}, wat gebruikt kan
worden in de ontwikkeling van polymeermembranen en in de productie van deeltjes. Tenslotte kan worden geconcludeerd dat verschillende anorganische membranen beschikbaar zijn die een redelijk hoge flux hebben, stabiel zijn en goede retentie eigenschappen vertonen onder superkritische omstandigheden. Het gebruik van deze anorganische membranen maakt continue en efficiënte regeneratie van superkritische vloeistoffen mogelijk.
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List of Publications


9. V.E. Patil, L.J.P. van den Broeke, J.T.F. Keurentjes, “Permeation of sub and super-critical carbon dioxide through silica and polymeric membranes”, *Proceedings of the 7th Italian symp. on Supercritical Fluids and Their Applications (Trieste, Italy)* June 2004.

Curriculum vitae

Vishal Eknath Patil was born in Thane, India, on 10\textsuperscript{th} June 1977. In 1994 he completed higher secondary education in science branch. He obtained Bachelor of Chemical Engineering degree at University of Bombay, Department of Chemical Technology (UDCT) in June 1998. Later, he worked for as a Process Engineer at Indo German Petrochemical Limited (IGPL) at Bombay till July 1999.

In September 1999, he joined University of Twente in The Netherlands for a Master of Technological Design program specialized in Process Technology. After successfully finishing his masters program, in October 2001, he joined research group, Process Development Group at Technical University of Eindhoven. His PhD research work is described in this thesis, which was performed under the supervision of Prof. Jos Keurentjes. The research results have been published and orally presented in various international conferences and international journals in the field of Chemical Engineering.

During PhD he followed various courses to master Dutch language and in November 2004, he also obtained a National Diploma of Dutch language (NT2, Nederlands als tweede Taal - Dutch as a second language).
