

A Systematic Investigation of Transport Phenomena in Organic Solvent Nanofiltration

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Life is what happens while you're busy making other plans
(John Lennon)

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Abstract

In several industries organic solvent nanofiltration (OSN) offers a high potential as energy-, product- and waste-saving alternative compared with commonly used unit operations. Thus, organic solvent nanofiltration gained importance in recent decades. This technology separates complex organic mixtures under mild conditions.

To use the full potential of OSN, a thorough understanding of the separation mechanism is essential. This work systematically investigates solvent as well as solute transport through a dense PDMS-based polymeric OSN membrane. Experiments with four different solute classes, namely polyethylene glycol (194 - 820 Da), linear carboxylic acid (228 - 340 Da), polystyrene (162 - 2000 Da) and n alkanes with different chain length (142 - 339 Da) were performed. These solutes are dissolved in n-hexane, toluene, isopropanol or in methanol.

Furthermore the transport of n alkanes with different chain length (142 - 339 Da) is comprehensively quantified not only in pure solvents but also in binary mixtures of isopropanol/toluene, methanol/toluene and methanol/isopropanol.

Negative retentions were observed using isopropanol or methanol as pure solvent and n alkanes or linear carboxylic acids as solutes, whereas positive retentions were measured with polyethylene glycol as solute. In contrast, using toluene or n-hexane as solvent, all observed retentions were positive. A significant minimum in retentions was found for all n alkanes with different chain length in the binary mixture of toluene and methanol.

Furthermore salt permeation and retention in water/methanol mixtures were investigated. Membrane performance varied depending on the composition ranging from aqueous to methanol solutions. Ion pair formation or ion dissociation correlates with a different salt retention

So, depending on the solvent or solvent mixtures and the solute, there exist considerable differences in the retention behaviour due to different membrane-solvent-solute interactions. This significantly changes flux and retention. Also negative retentions were observed, opening up new possibilities for further applications of organic solvent nanofiltration.

Zusammenfassung

Durch das große Einsparpotential hinsichtlich Energie, Produkt- und Abfallströme hat die organophile Nanofiltration in den letzten Jahrzehnten immer mehr an Bedeutung gewonnen. Diese Technologie bietet die Möglichkeiten unter milden Bedingungen auch komplexe organische Gemische zu trennen.

Durch nicht vollständiges Grundlageverständnis wird das Potential dieser Technologie bisher nicht vollständig genutzt. In der vorliegenden Arbeit wird eine systematische Studie vorgestellt die einen Betrag leisten soll Transportvorgänge in einen Nanofiltrationsprozess mit organischen Lösemitteln besser verstehen und gegebenenfalls vorhersagen zu könne. Hierzu wurde der Einfluss verschiedener Faktoren auf den Transport einer silikonbasierten organophilen Nanofiltrationsmembran untersucht. Hierbei wurde insbesondere die sogenannte ‚*Negative Retention*‘ vorgestellt und untersucht.

Zunächst wurde der Einfluss vier verschiedener Lösemittel und vier verschiedener gelöste Komponentenklassen untersucht. Hierbei wurde zunächst die Trennleistung der Membran unter Verwendung einer Komponentenklasse in einem Lösemittel charakterisiert. Das Phänomen des negativen Rückhalts konnte beobachtet werden und wurde des Weiteren systematisch untersucht. Einen Zusammenhang zwischen der Affinität und der negativen Retention konnte hergestellt werden. Des Weiteren wurde die Membranleistung durch zwei unterschiedliche Komponentenklassen, welche in jeweils reinem Lösemittel gelöst wurden charakterisiert. Im Anschluss wurde dann der Einfluss von binären Lösemittelmischungen auf den Membran-Rückhalt von zwei unterschiedlichen Komponentenklasse aufgezeigt.

Für ein tiefergehendes Verständnis bezüglich unterschiedlicher Retention durch die Verwendung von unterschiedlichen Lösemitteln zu generieren wurden Sorptionsmessungen durchgeführt. Ein deutlicher Zusammenhang zwischen der Sorption und der Trennleistung konnte hierdurch hergestellt werden.

Die Verbindung zur klassischen, wässrigen Nanofiltration wurde im Anschluss durchgeführt. Hierzu wurde der Rückhalt von ein- und mehrwertigen Salzen in wässrigen Methanol-Lösungen untersucht. Der Zusammenhang zwischen der Dissoziation und des unterschiedlichen Rückhaltes wurde hierbei deutlich.

Die mathematische Beschreibung dieser Transportvorgänge wurde dann durchgeführt. Erfolgreiche Simulationen aber auch Grenzen dieser konnten hier beobachtet werden.

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CHAPTER 1

INTRODUCTION

1.1 Organic solvent nanofiltration - Current application and potential

Nanofiltration, according to the IUPAC definition, is a "pressure-driven membrane-based separation process in which particles and dissolved macromolecules smaller than 2 nm are rejected" [1]. In the presence of organic solvents, these separation processes are referred to as *Organic Solvent Nanofiltration* (OSN) or *Solvent Resistant Nanofiltration* (SRNF).

One of the first paper, mentioned this pressure-driven solvent separations was publish in 1965 [2]. However further membrane development was required to achieve a breakthrough of OSN only in the beginning of the century. Since then, organic solvent nanofiltration has received considerable attention, due to the promising energy- and waste-saving using this membrane process as an innovative separation unit. Applications have been proposed for several industries such as food industry, homogeneous catalysts recycling, solvent replacement, recovery of organic solvents, painting and pharmaceutical industries [3-7].

As one of the first large scale OSN application the MAX-DEWAX process was realized by ExxonMobil as solvent recovery unit [8-11]. This solvent lube oil dewaxing process used a polyimide membrane and improved the oil yield by 3-5 vol.-%, while reducing the energy consumption by nearly 20 % [12]. The potential of OSN as an energy saving process could be clearly shown by using the MAX-DEWAX process.

Solvent recovery in food industry is also often proposed as potential application of OSN. For instance, the process of vegetable oil preparation contains a solvent extraction step with solvent/oil mixture, which is usually separated by distillation with high energy amount. This energy consumption as well as processing costs can be reduced by implementing organic solvent nanofiltration [13-15]. However, still further membrane development is demanded in order to provide high separation efficiencies and long-term stability [16-18].

OSN offers also potential application in pharmaceutical industries [19, 20]. Pharmaceuticals are produced in highly complex multi-step synthesis using different solvents. Organic solvent nanofiltration can be applied for instance as an alternative to distillation or extraction in downstream processing or between reaction steps in order to realize the necessary solvent exchange. Solvent consumption is highly reduced by implementing OSN-based solvent exchange [21, 22]. Furthermore, using OSN the solvent exchange can be performed at room or operation temperature with respect to thermolabile compounds [23, 24]. Also process costs can be reduced using OSN for instance in downstream processing as an active pharmaceutical ingredient (API) purification step [25, 26].

With respect to catalysts recycling OSN offers new application in order to recover and reuse expensive homogeneous catalysts from reaction mixtures [27-29]. Possible applications using continuous reaction-separation processes were investigated reducing catalyst deactivation and losses as well as energy costs [30, 31]. However, recycling efficient is

important and has to further increase in order to reduce catalyst consumption and accordingly production costs [32, 33].

As it is described above organic solvent nanofiltration offers in general high potential as energy-, product- and waste-saving alternative to commonly used unit operation in several industries. However, further development is required with respect to thorough understanding of transport phenomena in organic solvent nanofiltration in order to allow simple and fast implementation of OSN.

1.2 Theoretical background: Transport models for OSN

The mathematical description of solvent and solute transport through OSN membranes is highly complex and requires a thorough understanding of transport phenomena. Due to the complexity of this transport process no universally accepted model is currently available. The various reported approaches can be grouped in three different kinds of mathematical models [4, 34-36]: First of all the pore flow model assuming size exclusion mechanisms to determine the transport. Secondly, models originate from irreversible thermodynamics, treating the membrane as black-box. Thirdly, models based on solution-diffusion mechanism.

The *Pore-Flow Model* assumes that the transport occurs due to pressure driven convective flow through pores in the membrane. Accordingly, separation is based on size exclusion. Considering the assumption of constant concentration of solvent over the membrane, the solvent flux can be described by the Hagen-Poiseuille equation:

$$J_i = \frac{\varepsilon r_p}{8\eta\tau} \cdot \frac{(\Delta p - \Delta\pi)}{l} = K_{HP}(\Delta p - \Delta\pi) \quad (1)$$

In order to simplify this model the structural factors surface porosity ε , pore size r_p , tortuosity τ , membrane thickness l and the only one solvent parameter (viscosity η) are grouped into the Hagen-Poiseuille coefficient K_{HP} .

The mathematical description of solute flux is usually based on Nernst-Planck equation. Both, diffusive and convective terms are used to calculate solute flux. The extension to the '*Donnan Steric Pore-flow Model*' by Bowen and Mukthar [37] for instance uses diffusive and convective steric hindrance and Donnan exclusion effects in order to describe the solute transport through a porous membrane [38].

Further development of the basic pore-flow theory leads to the '*Surface Force Pore Flow Model*' developed by Matsuura and Sourirajan [39]. This approach describes solute and solvent transport through a porous membrane influenced by surface forces. This model and extensions of them depends consequently on solvent and solute properties and takes solvent-solute-membrane interaction into account [40, 41].

Additionally to pore-flow approaches, *models based on irreversible thermodynamics*, are used to describe transport phenomena in organic solvent nanofiltration processes. The Kedem-Katchalsky [42] or the Spiegler-Kedem [43] models are the most commonly known models based on this theory. Considering the membrane as a black box, the transport of solvent i and solute j through a nanofiltration membrane can be described by the following phenomenological equations according to the Kedem-Katchalsky model [42]:

$$J_i = P(\Delta p - \sigma \Delta \pi) \quad (2)$$

$$J_j = B \Delta \pi + (1 - \sigma) J_i \Delta c_i \quad (3)$$

Both solute and solvent fluxes J are described using the reflection coefficient σ and the osmotic pressure difference Δp . The pure solvent permeability coefficient P is described as function of solubility and diffusivity of the solvent while another permeability coefficient of the solute B and the average solute concentration across the membrane Δc is used in order to calculate solute flux.

These equations were adapted and enhanced by Spiegler and Kedem [43]. The differential and due to that more correct form of these equations were used. Consequently the solute flux is calculated according the following equation:

$$J_j = B \Delta x \left(\frac{dc_i}{dx} \right) + (1 - \sigma) J_i \Delta c_i \quad (4)$$

Combining, both diffusion and convection, the transport equations of Spiegler and Kedem are commonly used in order to describe retentions of uncharged molecules [44-47].

The *Solution-Diffusion Model* (SD) developed by Lonsdale et al. [48] is the most widely accepted explanation describing the transport in dense membrane processes. As driving force only a concentration gradient exists while the pressure is assumed to be constant over the membrane. Using this assumption but also additionally ones reported for instance by Wijmans and Baker [36] the following equation was developed:

$$J_i = \frac{D_i K_i}{l} \left[c_{iF} - c_{iP} \exp\left(\frac{-v_i \Delta p}{RT}\right) \right] \quad (5)$$

According to this equation the flux J of component i is a function of diffusion coefficient D_i , partition coefficient K_i , membrane thickness l , feed or permeate concentration c_{iF} , c_{iP} , molar volume v_i , transmembrane pressure Δp , temperature T and gas constant R .

The term $\frac{D_i K_i}{l}$ is often summed up to permeability constant P_i . This permeability depends on solvent or solute properties but also on membrane material properties.

However, this model describes solvent and solute flux as independent of each other. Due to this assumption the model is often extended or modify, since coupled transport is found to be important in order to describe retention in organic solvent nanofiltration.

Sherwood et al. [49] extended the solution diffusion model, developing a concept of imperfection in the polymer matrix where convective transport occurs. The so called '*Solution-Diffusion with Imperfection Model*' (SDI) combines diffusive and convective flow like it is described in the following equation formulated by Yarushchuk [50]:

$$J_i = J_{i,SD} + J_{i,SDI} \quad (6)$$

$$J_i = J_{i,SD} + \frac{c_{iM} B_0}{\eta l} \Delta p \quad (7)$$

Using this extension of the solution-diffusion model, the flux is additionally a function of a specific permeability B_0 , concentration c_{iM} , viscosity η , membrane thickness l and transmembrane pressure Δp .

Further development using the classical solution diffusion approach and assuming that diffusion of solvent and solute in the membrane are not independent, leads to a combination of Solution-Diffusion model with Maxwell-Stefan multicomponent diffusion theory [51-54]. The Maxwell-Stefan theory does not neglect friction forces and takes mutual diffusion into account. Effects due to interactions between membrane and component as well as interaction between each component are considered. Using this approach, the following equation was developed in order to describe the flux of one component through a nanofiltration membrane [55]:

$$-\frac{d\mu_i}{dz} = \frac{RT}{c_{tot}x_i} \sum_{j=1, j \neq i}^n \left[\frac{1}{D_{ij,MS}} (J_i x_j - J_j x_i) \right] + \frac{J_i}{D_{iM,MS}} \quad (8)$$

Here, the Maxwell-Stefan diffusion coefficients $D_{ij,MS}$, $D_{iM,MS}$ are introduced. The chemical potential $d\mu$ can be replaced using further assumption to reduce the complexity of this model. Due to the consideration of solvent-solute-membrane interaction this approach gains more and more attention in the last decade [56-58].

1.3 Negative retention - A transport phenomenon in organic solvent nanofiltration processes

Although OSN processes have been studied for several years and much knowledge has been gained, they are not yet completely understood. For instance the phenomenon called '*negative retention*' is little understood and requires systematic evaluation. So far a limited number of publications describing negative retention of organic solutes in organic solvent nanofiltration processes with both polymeric and inorganic membranes are available [45, 46, 59-64]. Negative retention occurs, if a molecule which is dissolved in organic solvent is preferential transported through the membrane and enriched in the permeate. So, the solvent is retained by the membrane while the solute passes through.

Using the basic equation calculating the membrane retention

$$R_i = 1 - \frac{c_{i,p}}{c_{i,F}} \quad (9)$$

the retention R gets negative if a higher permeate concentration of the component $c_{i,p}$, is reach compared to the feed concentration of this component $c_{i,F}$.

It is supposed that greater affinity of solute molecules to membrane material compared to the affinity of the solvent to the membrane material leads to negative retention. This affinity can be influenced by changing the components or by using solvent or solute mixtures. Since solute-solvent-membrane interactions also determines this process, the thoroughly understanding of organic solvent nanofiltration including negative retention is not yet achieved and further research is required.

1.4 Scope and outline of this thesis

Scope of this thesis is to increase the understanding of transport phenomena in dense OSN-membranes focusing especially on negative retentions. A systematic investigation was carried out to understand these transport phenomena using a defined workspace illustrated in Fig. 1.1. A 3-dimensional relationship between solubility-parameter of solute, of solvent and of membrane is presented. Since only one membrane is used in this work this solubility parameter is kept constant. So a workspace is formed where the described systematically investigation of permeation and retention behavior depending on the relation of solubility parameter is carried out in this thesis.

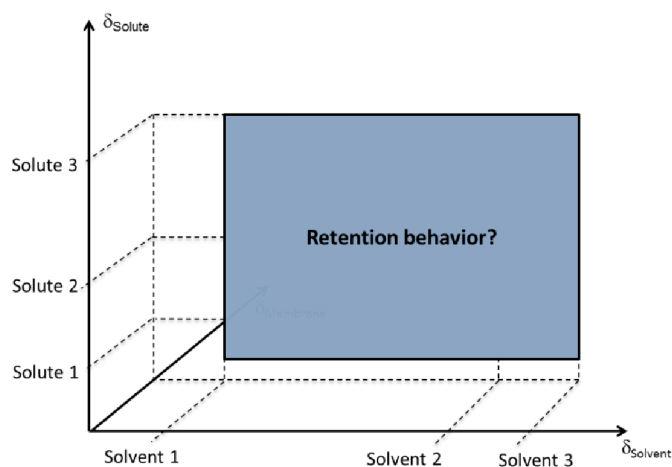


Fig. 1.1: Defined workspace of this thesis due to 3-Dimensional relationship between solubility parameter of solute, solvent and membrane

Fig. 1.2 summarizes the outline of this thesis. First of all chapter 2 introduces the systematic investigations of solute transport through a dense PDMS-based polymeric OSN membrane. Changing the solvent or the solute, considerable differences in retentive behavior are shown. Even negative retentions are observed. This systematic investigation proofs the dependence of solute-solvent-membrane interactions on the transport of the investigated components.

The transport of these solutes is comprehensively quantified not only in pure solvents but also in binary solvent mixtures. Chapter 3 systematically investigates the retention behavior in organic solvent nanofiltration in solvent mixtures using the dense PDMS-based composite membrane. Depending on the solvent and on the ratio of these solvents in case of binary mixtures, considerable differences in retentions of these solutes are discovered. Chapter 4 revises the influence of solvent mixtures and extends the investigation to solute mixtures of different solute classes in pure solvents but also in solvent mixtures in order to improve the understanding of transport phenomena in dense polymeric nanofiltration membranes. Influences of solute-group mixtures on the retentions are verified.

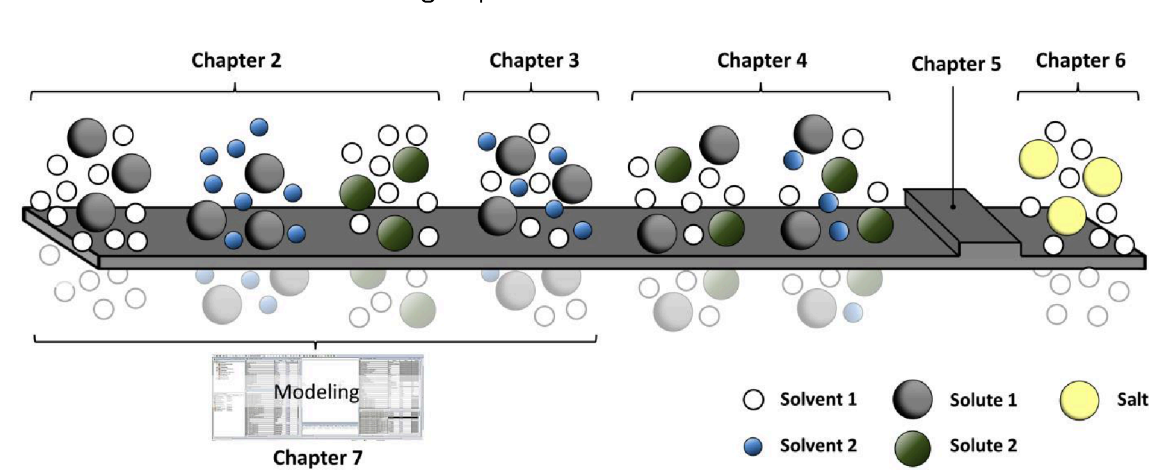


Fig. 1.2: Outline of this thesis

Chapter 5 introduces the influence of different solvent, solvent mixtures as well as solution of different solutes in the investigated solvent on the swelling degree. This swelling degree is correlated to retentions in order to increase the understanding of negative retentions due to higher solubility of solutes compared to solvents.

Since very little is known about the transport of aqueous ionic solutions through hydrophobic non-porous silicone-based nanofiltration membranes, Chapter 6 addresses this topic as the last part of the experimental investigation. The retention behavior of the silicone-based membrane is analyzed using three different salts in different MeOH/H₂O solutions. These results are for some aspects compared with a well-established hydrophilic, polyamide-based membrane.

A systematic investigation of transport phenomena in organic solvent nanofiltration requires also a mathematical description. Chapter 7 introduces a transport model, in order to describe the before discussed experimental results. A Maxwell-Stefan model based on

the assumption of a solution-diffusion transport mechanism is used to simulate the solvent as well as the solute fluxes in pure solvents but also in multi-component mixtures.

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CHAPTER 2

ON NEGATIVE RETENTIONS IN ORGANIC SOLVENT NANOFILTRATION

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2.1 Introduction

Organic solvent nanofiltration (OSN) has received more and more importance as an innovative energy-efficient separation process over the past decade. This also increases the interest in understanding the separation mechanism in more detail [1, 2]. Several authors investigated the retention behavior of polymeric solvent resistant membranes [3-8]. Generally, positive retentions of the dissolved solutes are observed. Much of the research focuses on (a) reducing the molecular weight cut-off or (b) unraveling the transport mechanism [9-15].

Only very few papers report negative solute retention in organic solvent nanofiltration: negative retention indicate that the solute is enriched in the permeate stream as compared to the bulk feed concentration. While negative retentions are frequently encountered in aqueous nanofiltration due to differences in ion permeability and the electro-neutrality constraint, only few experimental observations can be found in literature for non-aqueous systems. Systematic explorations of the parameter space affecting such negative retentions are yet missing.

Lonsdale et al. [16] as well as Matsuura and Sourirajan [17] observed negative retention with phenols and cellulose acetate RO membranes in aqueous solutions. Burghoff et al. [18] confirmed these findings and compared various transport models. The retention of linear carboxylic acids in ethanol and hexane was investigated by Koops et al. [19]. They observed negative retention using hexane as solvent and cellulose acetate as membrane material. These researchers interpreted their observations as strong interactions of solutes with the acetate groups in the membrane.

Bhanushali et al. [20] investigated the retention of different dyes with PDMS-based nanofiltration membranes and found also negative retention when using Sudan IV as solute dissolved in methanol. As an explanation they reported a high convective contribution of the solute flux while the methanol flux is low. Recently, PDMS has also been used as membrane material in the investigation of Zeidler et al. [21]. They studied the retention behavior of 14 different molecules in THF, n-heptane and ethanol and measured negative retention when using ethanol as solvent.

Negative retentions were also observed using glassy polymers having high free volume. Tsarkov et al. [22] investigated the performance of different membranes using glassy polymers (PTMSP, PMP, PIM-1) as membrane material and dyes as solutes. The retention of Solvent Blue 35 dissolved in ethanol was negative with three different membranes.

Darvishmanesh [5] reports negative retentions for asymmetric glassy P84-based polyimide membranes for three dyes dissolved in hexane. In toluene though, the same dyes show strong positive retentions. The authors interpret these data as being related to specific molecular interactions in the membrane/solvent/solute mixture. They substantiate their interpretation with cohesive energy density calculations for the particular mixtures. We follow this line of arguments, however quantify such affinities through solubility parameters.

The Hildebrand parameter can be deduced from the cohesive energy density and quantifies the degree of interaction as an indicator of solubility. It can be numerically estimated with group contribution methods. Alternatively, the three dimensional Hansen solubility parameter can be used to predict a tendency relating to the solubility of solvents in polymeric materials. This parameter is generated by using dispersion forces, dipole-dipole forces and hydrogen-bonding forces. Essentially, if the solubility parameters of two components are similar, they are mutually soluble [23].

Even though negative retentions have been reported in literature before, systematic evaluation of the parameter space solvent/solute in a membrane material is yet not established. The work presented here extends current knowledge in a systematic manner: we use a silicon-based elastic polymer that reacts reversibly on solvent swelling as opposed to the behavior of previously reported transport behavior of a glassy asymmetric membrane that suffer from swelling history and aging [24]. Furthermore, we have developed analytical procedures that allow analysis of membrane retention for oligomeric solute molecules that differ by a monomer unit only. This subtle tuning of the solute for a range of solvent and a membrane reacting elastically upon swelling gives us confidence to report thorough mass transport data and explore the origin of negative retentions in organic solvent nanofiltration.

2.2 Experimental

2.2.1 Materials

Toluene, isopropanol, methanol and n-hexane were used as solvent in this work. The most important properties of the above mentioned solvents are summarized in Table 2.1.

Table 2.1: Physicochemical properties of the used solvents [25, 26]

Solvent	Formula	Molecular weight (kg kmol ⁻¹)	Viscosity (mPa·s)	Surface Tension (mN m ⁻¹)	molar Volume (m ³ mol ⁻¹)	Dielectric constant (-)	Solubility Parameter (MPa ^{0.5})
Isopropanol	C ₃ H ₇ OH	60.10	2.0	21.7	76.92	18.3	23.7
Methanol	CH ₃ OH	32.04	0.6	22.6	40.4	32.60	29.7
Toluene	C ₇ H ₈	92.14	0.59	28.5	106.85	2.38	18.3
n-Hexane	C ₆ H ₁₄	86.18	0.31	18.4	130.5	1.9	14.9

Polyethylene glycol with different molecular weights, n-alkanes with different chain length, polystyrene with a wide molar mass distribution, and myristic acid, behenic acid and stearic acid as linear carboxylic acids were used as solutes. The structures are shown in Fig. 2.1. and the most important properties of these solutes are summarized in Table 2.2.

Table 2.2: Solutes properties [19, 23, 27, 28]

Name	Formula	Molecular weight (kg kmol ⁻¹)	Solubility Parameter (MPa ^{0.5})
n-Alkanes			
Decane	C ₁₀ H ₂₂	142.3	15.8
Dodecane	C ₁₂ H ₂₆	170.3	16.1
Tetradecane	C ₁₄ H ₃₀	198.4	16.3
Hexadecane	C ₁₆ H ₃₄	226.4	16.5
Octadecane	C ₁₈ H ₃₈	254.5	16.6
Docosane	C ₂₂ H ₄₆	310.6	16.7
Tetracosane	C ₂₄ H ₅₀	338.7	16.7
Octacosane	C ₂₈ H ₅₈	339.7	16.7
Polystyrene			
PS	[C ₈ H ₈] _n	162-2000	18.7
Polyethylen glycol			
PEG	[C ₂ H ₆ O ₂] _n	194-590	23.7-20.5
Carboxylic acids			
Myristic acid	C ₁₃ H ₂₇ COOH	228.4	17.5
Stearic acid	C ₁₇ H ₃₅ COOH	284.5	16.6
Docosanic acid	C ₂₁ H ₄₃ COOH	340.6	15.9

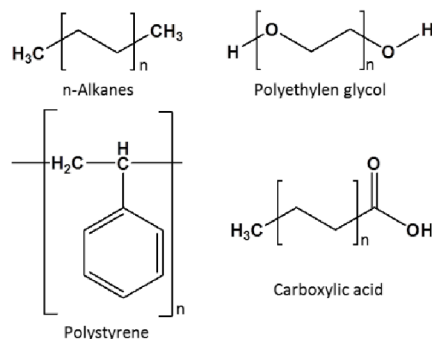


Fig. 2.1: Chemical structures of the used solutes

The membrane used in this study is a composite membrane development product of Evonik Industries. For the support layer polymeric ultrafiltration membranes were used made of polyimide. These were coated with a thin film of silicone acrylates as active layer with defined properties. The used membrane is similar to the membrane described in the patent of Evonik industries [29]. The solubility parameter of the membrane is $\delta_{\text{Membrane}} = 15.5 \text{ MPa}^{0.5}$ [13].

2.2.2 Experimental Procedure

The experiments were performed with a cross-flow set-up shown in Fig. 2.2. Two test cells are connected in parallel having a membrane area of 100 cm² each. The feed is pressurized with a piston pump and circulate with a gear pump through the test cells. The feed flow is

between 250 and 400 kg h⁻¹, in order to avoid concentration polarization. Since, no spacers were used in this work, the cross-flow velocities are around 1 m s⁻¹. With a hydraulic diameter of 9.8 mm the Reynolds numbers are in the range between 5000 and 33000 depending on the viscosity of the solvent used.

The temperature is controlled with a LAUDA cooling thermostat to around 25 °C. This temperature, the applied pressure, the feed fluxes and the permeate fluxes are automatically recorded.

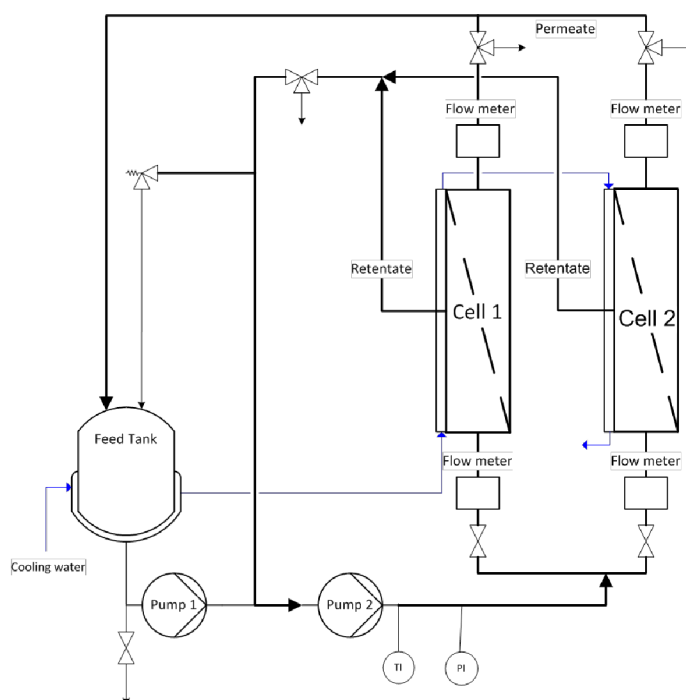


Fig. 2.2 Schematic of the cross-flow filtration set-up

Before starting the experiments the membrane was submerged in toluene for 24 h and for 2 h in the solvent used. After placing the membrane in the test cells, the membrane was pressurized for 4 h to reach the steady state. Compaction was not observed with the used membrane. To determine the retention, two permeate samples per test cell and one retentate sample was taken simultaneously. The values for the retention shown in this work are averages of four measured retention.

First of all, the fluxes of pure toluene were measured at 10, 20, 30 and 40 bar transmembrane pressure (TMP). Afterwards, polystyrene was added with a total amount of 1 wt-% and the retention in toluene was measured. Subsequently, the system was cleaned with pure toluene and a mixture of toluene and polyethylene glycol was added. Thereafter, the retention of carboxylic acid and n-alkanes was successively measured.

The same procedure was used for isopropanol, methanol and n-hexane. Hence, a new membrane was used for every experimental series with one solvent. The retention experiments were performed with a total amount of 1 wt-% of the solute and with the same ratio of every single component.

However, not all solvent/ solute - mixtures could be measured, since some solutes were insoluble in the used solvents. Table 2.3 shows a summary of the performed experiments.

Table 2.3: Summary of the performed experiments

Solute	Solvent	TMP
-	Toluene	10,20,30,40 bar
	n-Hexane	
	Isopropanol	
	Methanol	
n-Alkanes	Toluene	20,30 bar
	n-Hexane	
	Isopropanol	
	Methanol	
PEG	Toluene	20,30 bar
	Isopropanol	
	Methanol	
Carboxylic acids	Toluene	20,30 bar
	n-Hexane	
PS	Toluene	20,30 bar
	n-Hexane	

2.3 Analytics

In order to calculate the retention, concentrations of solutes in the permeate and retentate have to be determined. So the retention can be calculated with the following equation:

$$R_i = 1 - \frac{c_i(\text{Permeate})}{c_i(\text{Retentate})}$$

According to this formula, a higher concentration of the solute in the permeate than in the retentate results in negative retention.

2.3.1 Determination of carboxylic acid concentration by gas chromatography

The gas chromatography (GC) system used in the work was a GC 6890 system (Agilent, CA, USA) with liquid auto sampler, split / splitless injection and flame ionization detector (FID). An Agilent 19091J-413 HP-5 column was used coated with 5 % phenyl methyl siloxane, 30 m length, 0.32 mm inner diameter and 0.25 µm thickness. However many compounds cannot be gas chromatographed unmodified but must be converted into stable and volatile derivatives to achieve successful elution and separation. Myristic, stearic- and behenic acid are nonvolatile compounds and can be converted into volatile esters by methylation. For this derivatization 1 ml N,N-dimethylformamide - dimethylacetal (DMF/DMA) is added to 0.5 ml

sample. The sample is heated up to 90 °C on a sand bath for 60 min, then cooled down to room temperature before analyzed. The injector temperature was 250 °C and helium (2.4 ml min^{-1}) was used as carrier gas and split injection of 2 μl each sample (split ratio 40:1). Injector temperature was 250 °C. Temperature program: initial temperature was 200°C, hold for 2 minutes, followed by a temperature ramp of 10 K min^{-1} until 260 °C. Hold time 1 min. Total run time was 9 minutes. Every sample was measured at least twice. Substances were identified by retention times of the particular derivatized compounds.

Calibration curves for all three acids were established as a four point calibration curve with pure acid standards in the range from 0 to 8 g l^{-1} free acid in hexane, toluene and isopropanol. Calibration range in methanol was up to 5 g l^{-1} with myristic- and stearic acid but without behenic acid because of insufficient solubility. The data points were fitted by a linear regression. The correlation coefficient of the calibration curves for all compounds was at least 0.9995 or higher. All procedures were carried out in at least three replications. The concentration of the particular acid was calculated based on the calibration curves with external standards. The standard deviation of all measurements was usually $< 1 \%$.

2.3.2 Determination of alkane concentration by gas chromatography

The gas chromatography (GC) system used in the work was the same as described before. The injector temperature was 250 °C. 2 μl of each sample were injected splitless. Injector temperature was 280 °C. Temperature program: initial temperature was 80 °C, hold for 3 minutes, followed by a temperature ramp of 20 K min^{-1} until 300 °C. Hold time 2 min. Total run time was 16 minutes.

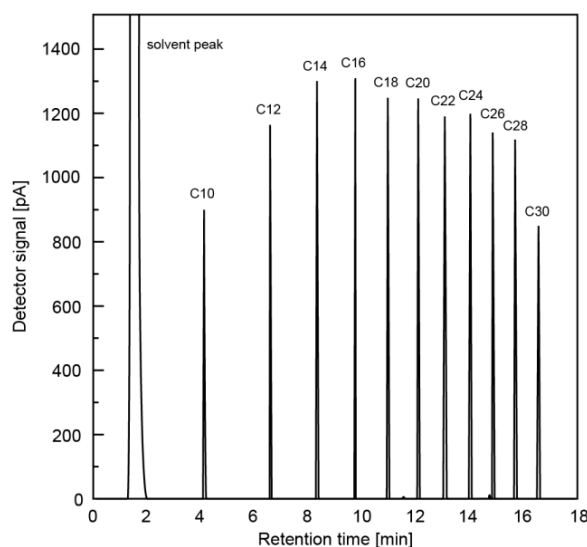


Fig. 2.3: Typical chromatogram of the GC analyses of an aliphatic alkane mixture dissolved in hexane

The samples for analyses were dissolved in hexane, toluene, isopropanol or methanol. The maximum concentration of a particular alkane was ca. 2000 mg l^{-1} . Samples were diluted

1:50 with hexane prior to GC analyses. Each sample was measured at least twice. Substances were identified by retention times of the particular alkane. Calibration curves were established in the range from 0 to 80 mg l⁻¹ for all 11 alkane as a five point calibration curve with external standards from Neochema, Germany, n-Alkane-Mix 11 (C10-C30 linear), 200 µg ml⁻¹ each alkane, dissolved in n-hexane. The data points were fitted by a linear regression. The correlation coefficient of the calibration curves for all compounds was at least 0.9995 or higher. All procedures were carried out in at least three replications. The standard deviation of all measurements was usually < 1 %. Fig. 2.3 shows a typical example of a chromatogram of the GC analyses of an aliphatic alkane mixture dissolved in hexane.

2.3.3 Determination of MWCO of polystyrene and PEG oligomers by GPC

The concentration of the oligomers as a function of MW was determined by Gel Permeation Chromatography (GPC). Molecules are separated due to their different hydrodynamic volumes. The system used was an Agilent-HPLC (series 1100) with a solvent degasser, binary pump, UV- and refractive index (RI) detectors, auto sampler, column thermostat and Chemstation-software. GPC- software PSSWinGPC Unity, GPC columns, PEG- and polystyrene oligomer standards were from PSS, Mainz, Germany. All samples were filtrated through 0.45 µm membrane filter prior to analysis.

PEG analysis: Column set used was a pre column Suprema, 10 µm particles, 8.0 mm x 50 mm (ID x length) and 2 columns Suprema, 30 Å pore size, 10 µm particles, 8.0 mm x 300 mm (ID x length). The mobile phase was water, isocratic flow 0.5 ml min⁻¹ at 30 °C, 50 µl sample injection, RI-detector and 62 min total run time. Calibration curves were created with PEG oligomer standards in the range from 106 to 3200 Da dissolved in methanol, fitted with a 5th order regression.

Sample preparation for PEG-samples in toluene: A sample volume of 1000 µl was pipetted into a 1.5 ml glass vial and carefully heated up to 80 °C in order to evaporate the solvent carefully. Finally 1000 µl methanol was added to resolve the PEG. The sample was homogenized and analyzed. The height of the detector signal is proportional to the concentration.

Polystyrene analysis: The column set used was a pre column SDV, 5 µm particles, 8.0 mm x 50 mm (ID x length) and 2 columns SDV, 50 Å pore size, 5 µm particles, 8.0 mm x 300 mm (ID x length). The mobile phase was tetrahydrofuran, isocratic flow 0.5 ml min⁻¹ at 30 °C, 40 µl sample injection, UV-detector (262 nm/ref 360 nm), 55 min total run time. Calibration curve was created with 8 polystyrene oligomers from 162 - 1920 Da dissolved in hexane and 10 standards from 162 - 6100 Da in toluene, fitted with a 5th order regression. Fig. 2.4 shows a typical chromatogram overlay of polystyrene oligomer samples.

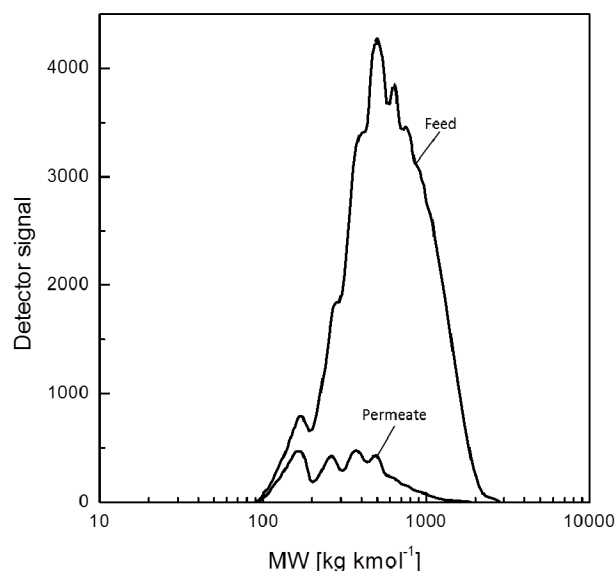


Fig. 2.4: Typical chromatogram overlay of feed and permeate concentrations of polystyrene oligomer samples showing a clear reduction of large MW oligomers

2.4 Results and discussion

2.4.1 Pure solvent fluxes

First, all fluxes of pure toluene, isopropanol, n-hexane and methanol were measured as a function of applied transmembrane pressures (TMP). The results are shown in Fig. 2.5.

It is obvious that n-hexane has the highest flux. The fluxes of isopropanol and methanol are much lower than the fluxes of toluene and n-hexane but the difference between isopropanol and methanol is not that high.

The permeability of the solvents follows the order n-hexane > toluene > methanol > isopropanol. Generally, this mass transport behavior can be described by the solution diffusion model [30]. Hence, the kinetic parameter “diffusion coefficient” as well as the thermodynamic parameter “solubility” influences the permeation rates. The distinct difference between the alcohols and the hydrocarbons however is likely to be strongly influenced by the solubility contribution to the permeability. The high polarity of alcohols in contrast to the hydrophobic membrane material reduces solubility as compared to the hydrocarbons and reduces fluxes.

This can be correlated to differences of the solubility parameters between membrane and solvent ($|\delta_{\text{Membrane}} - \delta_{\text{Solvent}}|$): The smaller the difference between the solubility parameter of the solvent and the membrane, the higher the solubility of the solvent in the membrane.

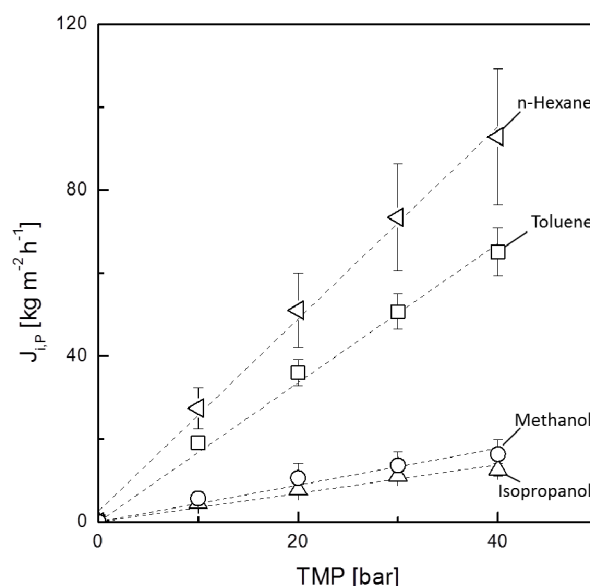


Fig. 2.5: Pure solvent fluxes of n-hexane (∇), toluene ($\square$), methanol (O) or isopropanol (Δ) at different transmembrane pressures and room temperature

Table 2.4 presents the permeability of each solvent and the values for these differences ($|\delta_{\text{Membrane}} - \delta_{\text{Solvent}}|$). It is shown, that the permeability decreases with increasing difference between the solubility parameters of solvent and membrane. However, the permeability of methanol is slightly higher than the permeability of isopropanol even though the value of $|\delta_{\text{Membrane}} - \delta_{\text{Solvent}}|$ is also higher. We attribute this to the influence of the diffusion coefficient on the permeability. In a forthcoming manuscript we will present a comprehensive Maxwell-Stefan based model describing the transport of solvent as well as multi-component mixtures.

Table 2.4: Permeability and $|\delta_{\text{Membrane}} - \delta_{\text{Solvent}}|$ values for pure solvents

Solvent	Permeability ($\text{kg m}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	$ \sigma_{\text{Solvent}} - \sigma_{\text{Membrane}} $ ($\text{MPa}^{0.5}$)
n-Hexane	2.52	0.63
Toluene	1.75	2.73
Methanol	0.49	14.2
Isopropanol	0.38	8.0

2.4.2 Retention measurement in different solvent

2.4.2.1 Toluene

Fig. 2.6 compare the retention of polystyrene, polyethylene glycol, carboxylic acids and n-alkanes with different chain lengths dissolved in pure toluene at 20 and 30 bar transmembrane pressure. It is shown that polystyrene has the highest retention of up to 95 % (640 kg kmol^{-1}). The retention of the three carboxylic acids is slightly lower. The retention value for myristic acid with a molecular weight of 228 kg kmol^{-1} is around 62 % and for behenic acid (350 kg kmol^{-1}) 75 %. The retention is lower for polyethylene glycol as solute dissolved in toluene. Here, a retention of 43 % to 85 % ($194 - 540 \text{ kg kmol}^{-1}$) is observed. However, these retentions are not significantly influenced by the feed pressure, in contrast to the retention of n-alkanes with different chain lengths. Here, the applied pressure shows a stronger influence on the retention. The retention of n-alkanes dissolved in toluene spans from only 4 to 70 % with a transmembrane pressure of 20 bar and up to 75 % with 30 bar.

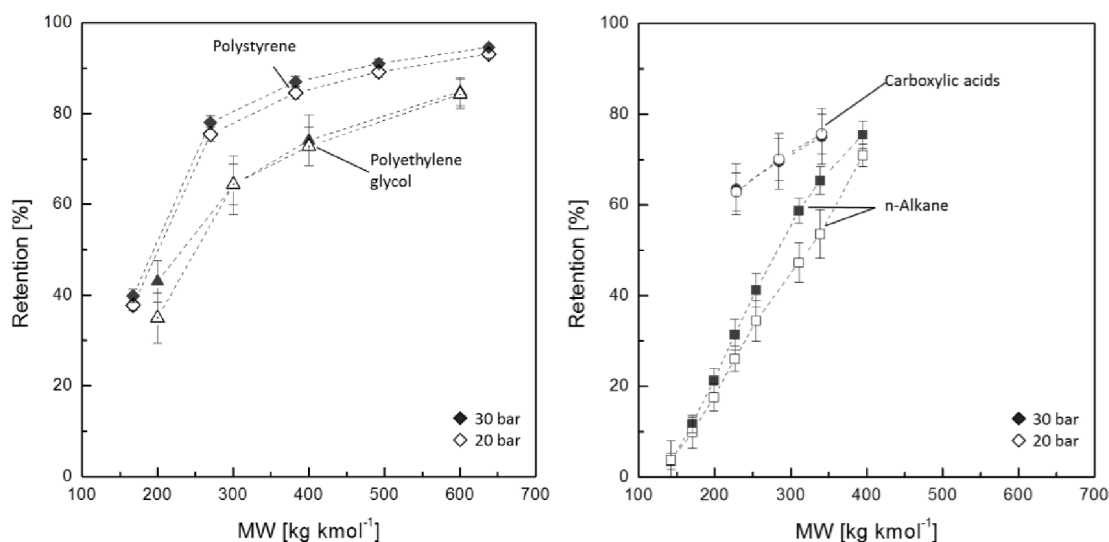


Fig. 2.6: Retention of polystyrene (◇), polyethylene glycol (Δ), carboxylic acids (O) and n-alkanes (□) dissolved in pure toluene at 20 and 30 bar transmembrane pressure

We suggest that the difference in the retention is related to the different solubility of the solute in the membrane material. The retention values for solutes of comparable MW of around 270 kg kmol^{-1} and the values for the difference of $|\delta_{\text{Membrane}} - \delta_{\text{Solute}}|$ are shown in Table 2.5. It can be seen that the solvent as well as the solutes (octadecane ($\text{C}_{18}\text{H}_{38}$), stearic acid, polystyrene) in fact have a high affinity for the membrane. Nonetheless, the affinity of the solvent toluene to the membrane is predominant, hence the retention is positive and high. The maximum difference between the solubility parameter of solutes and membrane, but also between solute and toluene is reached with polyethylene glycol. Accordingly, the retention is not as high as with polystyrene, but still reaches 64 %.

Table 2.5: Dependence of the retention at 30 bar transmembrane pressure for different solutes of comparable size dissolved in toluene and values for $|\delta_{\text{Membrane}} - \delta_{\text{Solute}}|$

Solute	MW (kg kmol ⁻¹)	Retention (30bar) (%)	$ \delta_{\text{Membrane}} - \delta_{\text{Solute}} $ (MPa ^{0.5})	$ \delta_{\text{Solute}} - \delta_{\text{Toluene}} $ (MPa ^{0.5})	$ \delta_{\text{Membrane}} - \delta_{\text{Toluene}} $ (MPa ^{0.5})
Octadecane	256	41.25	1.0	1.73	
Stearic acid	284	69.55	1.1	1.63	
Polystyrene	269	78.06	3.2	0.47	2.73
PEG	282	64.27	8.0	5.27	

Nevertheless, the retention of octadecane is the lowest, because of the high solubility of this molecule in the membrane. Also a low difference of $|\delta_{\text{Membrane}} - \delta_{\text{Solute}}|$ can be observed for stearic acid, however its retention is higher. Since the transport in a dense membrane can be describe with a solution-diffusion mechanism, the high and positive retention of these molecules can also be due to a low diffusivity. Deconvoluting the effect of solubility and diffusion coefficient remains a challenge when differences in retentions are not dramatically different, as we will show later for the negative retentions.

2.4.2.2 Hexane

Since polyethylene glycol is not soluble in n-hexane, Fig. 2.7 only shows the retention of carboxylic acids, polystyrene and n-alkanes with different chain lengths at 20 and 30 bar transmembrane pressure.

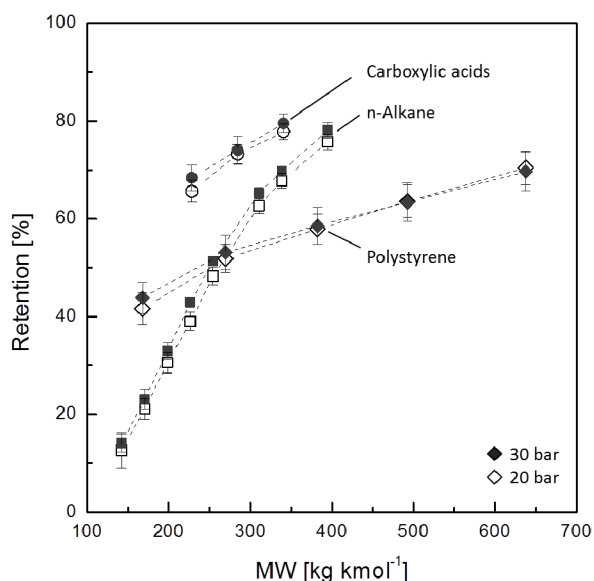


Fig. 2.7: Retention of polystyrene ($\diamond$), carboxylic acids ($\circ$) and n-alkanes ($\square$) dissolved in pure n-hexane at 20 and 30 bar transmembrane pressure

The retention curve of polystyrene does not show such a steep slope as the retention curve of n-alkanes. The retention of polystyrene is in the range of 40 % (MW = 162 kg kmol⁻¹) to 70 % (MW = 640 kg kmol⁻¹) whereas the retention of n-alkanes is in the range of 15 % (MW = 142 kg kmol⁻¹) to 78 % (MW = 394 kg kmol⁻¹). The highest retention was achieved by

using n-hexane as solvent with carboxylic acids as solute. Myristic acid is retained by the membrane to 68 % and behenic acid to 80 %. However, the influence of the pressures is low for all retention curves.

Table 2.6 presents the retention values for the different solutes at around 270 kg kmol⁻¹ and the values for $|\delta_{\text{Membrane}} - \delta_{\text{Solute}}|$. In addition, the difference between the solubility parameter of n-hexane and membrane is shown, which is relatively low (0.63 MPa^{0.5}). However this value is smaller than the values for $|\delta_{\text{Membrane}} - \delta_{\text{Solute}}|$, so the retention is generally high because the solvent is preferably dissolved in the membrane and has a high diffusion coefficient due to its small size. Also for this solvent, the deconvolution of solubility and diffusion coefficient is not straight forward.

Table 2.6: Dependence of the retention at 30 bar transmembrane pressure for different solutes dissolved in n-hexane and values for $|\delta_{\text{Membrane}} - \delta_{\text{Solute}}|$

Solute	MW (kg kmol ⁻¹)	Retention (30bar) (%)	$ \delta_{\text{Membrane}} - \delta_{\text{Solute}} $ (MPa ^{0.5})	$ \delta_{\text{Solute}} - \delta_{\text{n-Hexane}} $ (MPa ^{0.5})	$ \delta_{\text{Membrane}} - \delta_{\text{n-Hexane}} $ (MPa ^{0.5})
Octadecane	256	51.33	1.0	1.63	
Stearic acid	284	74.52	1.1	1.73	0.63
Polystyrene	269	53.17	3.2	3.83	

2.4.2.3 Isopropanol

Below we will show that using a solvent with less affinity to the membrane material will change the retention behavior considerably. The effects of differences in membrane solubility become much more obvious. Fig. 2.8 shows the retention of polyethylene glycol, carboxylic acids and different n-alkanes dissolved in isopropanol. Polystyrene is not soluble in isopropanol and could not be measured.

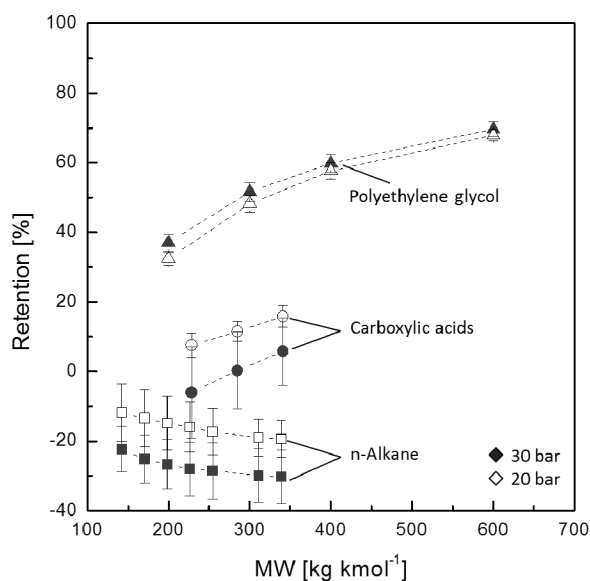


Fig. 2.8: Retention of polyethylene glycol (Δ), carboxylic acids (O) and n-alkanes ($\square$) dissolved in isopropanol at 20 and 30 bar transmembrane pressure

The retention of polyethylene glycol ranges from 37 % to 70 % and there is no significant influence of the pressure on the retention. The retention of different carboxylic acids is much lower. The highest retention (15 %) is achieved with behenic acid (340 kg kmol^{-1}) at 20 bar transmembrane pressure. Surprisingly, with n-alkanes as solute and isopropanol as solvent the retention is completely negative and decreases even with increasing molecular weight. Whether or not this negative retention would turn positive with higher molecular weight goes beyond the experimental program and would require more precise experiments. The influence of the pressure also becomes more prominent at these low retentions. For the alkanes: they become even more negative at higher feed pressure. Concentration polarization as reason for the negative rejections can be excluded because of the low concentrations used in the experiments and the high cross flow velocities (1.2 m s^{-1}). Here, a Reynolds number of around 5000 was observed and experiments show no dependence of the retention of the feed flow. So, again solubility parameters are used to explain the differences in retention, in particular for the negative retentions. In Fig. 2.9 the retention is illustrated depending on the solubility parameter. It is obvious that the solubility parameter of carboxylic acids and n-alkanes are close to the solubility parameter of the membrane. In contrast, the difference between the solubility parameter of the membrane and isopropanol is larger ($|\delta_{\text{Membrane}} - \delta_{\text{Isopropanol}}| = 8$). Consequently, the used carboxylic acids and n-alkanes have a high affinity for the membrane whereas the affinity for isopropanol is lower. This difference is likely to be responsible for the lower or even negative retention.

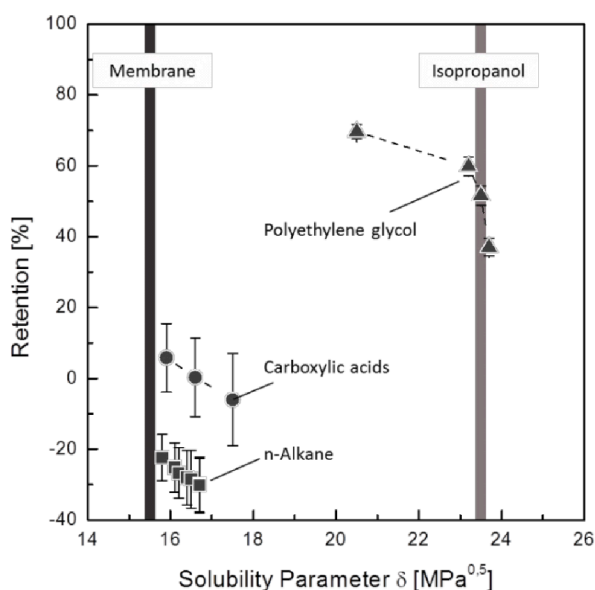


Fig. 2.9: Retention of polyethylene glycol (Δ), carboxylic acids (O) and n-alkanes ($\square$) dissolved in isopropanol as a function of solubility parameters at 30 bar transmembrane pressure

A higher retention is observed by using polyethylene glycol. As it is shown in Fig. 2.9 also the difference between the solubility parameter of this solute and the membrane is higher

($|\delta_{\text{Membrane}} - \delta_{\text{PEG}}| = 5-8.2$) and close to the difference between the solubility parameter of isopropanol and membrane. Additionally, PEG has a hydrophilic character in contrast to the hydrophobic membrane material. These two effects are reasons for the higher retention.

2.4.2.4 Methanol

Negative retentions were also observed by using methanol as solvent instead of isopropanol. The measured retentions of polyethylene glycol, carboxylic acids and different n-alkanes dissolved in methanol are shown in Fig. 2.10. Polystyrene and behenic acid are not soluble in methanol. However, using n-alkanes and myristic acid or stearic acid as solute negative retention was achieved. Moreover, the same effect was observed as in isopropanol: The retention decreases with increasing molecular weight. Also, with increasing pressure the retention for n-alkanes is reduced whereas the retention for carboxylic acid and polyethylene glycol increases.

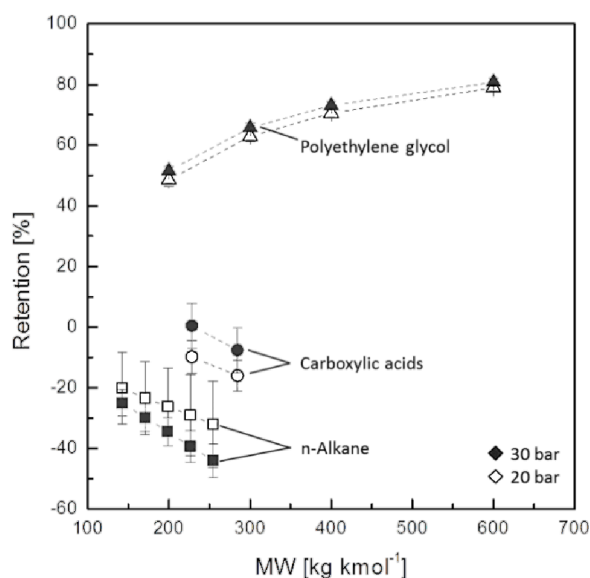


Fig. 2.10: Retention of polyethylene glycol (Δ), carboxylic acids (O) and n-alkanes (□) dissolved in methanol at 20 and 30 bar transmembrane pressure

Fig. 2.11 presents the retention as a function of solubility parameter. As mentioned before, the difference between the solubility parameter of n-alkanes or carboxylic acids and membrane is small ($|\delta_{\text{Membrane}} - \delta_{\text{n-Alkanes}}| = 0.3-1.2$ or $|\delta_{\text{Membrane}} - \delta_{\text{Carboxylic acids}}| = 0.4-1.1$); these solutes have a high affinity for the membrane. Nevertheless, methanol is used in these measurements as solvent, which has a relatively high solubility parameter. This means that the difference is also large ($|\delta_{\text{Membrane}} - \delta_{\text{Methanol}}| = 14.2$) and the affinity for the membrane is very low. As a result, the retention is extremely negative, with a minimum of -44 % for octadecane.

The difference between the solubility parameter of PEG and membrane is relatively high ($|\delta_{\text{Membrane}} - \delta_{\text{PEG}}| = 5-8.2$) which explains the positive and high retention. However, using PEG or n-alkanes as solutes, the difference between the solubility parameters of these

solutes and membrane is increased, whereas the retention decreases. Related to the retention of n-alkanes, this could be explained by the increasing polarity with growing chain length. Accordingly, the larger alkanes are preferably dissolved in the hydrophobic membrane material and thus have lower retention. The dominating effect describing the retention behavior of PEG seems to be molecular size. As usual, the retention decreases with decreasing molecular weight even though the affinity of PEG for the membrane is larger, as shown in Fig. 2.11.

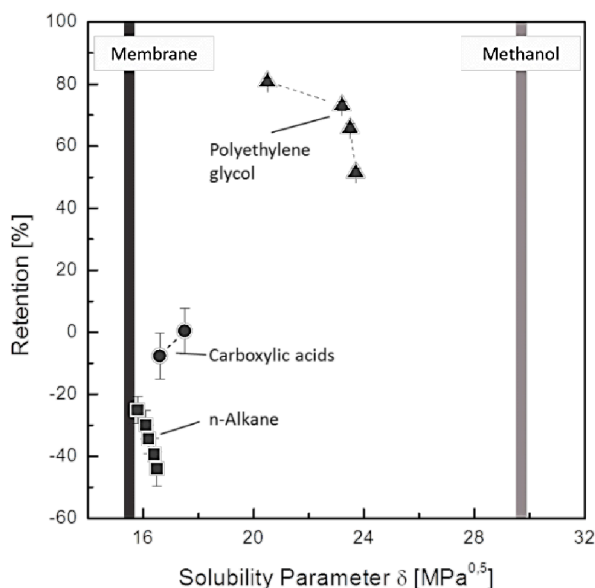


Fig. 2.11: Retention of polyethylene glycol (Δ), carboxylic acids ($\circ$) and n-alkanes ($\square$) dissolved in methanol as a function of solubility parameters at 30 bar transmembrane pressure

2.4.3 Influence of pressure on negative retentions

From the previous figures, it also became apparent at low and negative retentions that the pressure has a strong influence on the permeation of the solutes. Surprisingly, the retentions become even more negative with increasing molecular weight of the solute, i.e. decreasing diffusion coefficient. Using the solution-diffusion model however, this apparent contradiction can be easily resolved. As the flux of the solute scales with the chemical potential, we need to examine the effect of pressure and molar volume on the driving force for the solute [31].

$$J_i \propto RT(\ln x_i + v_i \Delta p)$$

With increasing molar volume as well as increasing feed pressure, the driving force for the solute increases. This influence becomes more clear at low to negative retentions of the solute. Whether or not the negative retentions surpass a minimum with increasing molecular weight depends on the balance between the decrease of the diffusion coefficient

and the increase in driving force with increasing molar volume of the solute in the solvent swollen membrane.

2.4.4 Influence of the solvent

With the previously shown measurements, the influence of the solvent can also be demonstrated. To illustrate the difference in the retention by using one solute but different solvents, Fig. 2.12 shows exemplary the retention of n-alkanes dissolved in the four different solvents at 30 bar transmembrane pressure.

The highest retention of n-alkanes is achieved by using n-hexane as solvent but there is only a minor difference compared to toluene. The measured retention was negative for all molecular weights when using alcohols (isopropanol or methanol) as a solvent. Moreover, the retention of n-alkanes dissolved in isopropanol or in methanol decreases by increasing molecular weight.

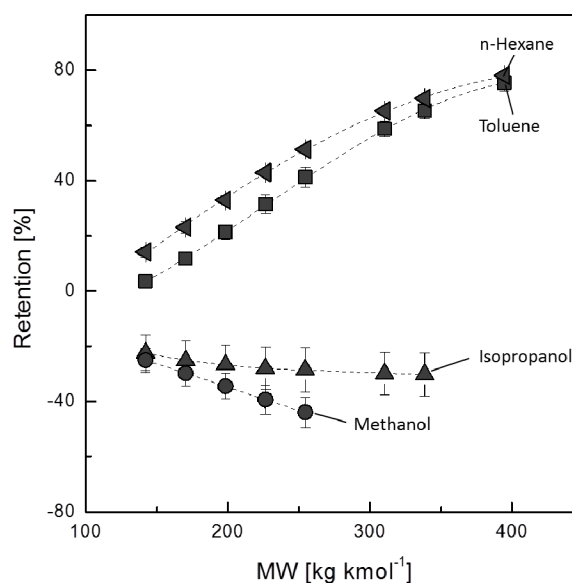


Fig. 2.12: Retention of n-alkanes dissolved in n-hexane ($\blacktriangleleft$), toluene ($\square$), isopropanol (Δ) methanol (O) at 30 bar transmembrane pressures and room temperature

Table 2.7 compares the retention of octadecane at 30 bar transmembrane pressure with the differences between the solubility parameters of the solvent and membrane or solvent and solute. It is shown, that with increasing difference for all solubility parameters the retention decreases. The retention of octadecane dissolved in n-hexane is around 51 % due to the high interaction between the solvent and the membrane ($|\delta_{\text{Membrane}} - \delta_{\text{Solvent}}| = 0.63 \text{ MPa}^{0.5}$). Accordingly, n-hexane is preferably dissolved in the membrane, so the retention is high. In general, as can be seen in Table 2.7, the lower the affinity of the solvent to the membrane, the lower the retention. For instance, when solving octadecane in methanol the retention is

negative (-44 %). This can be explained by the high affinity of the solute to the membrane, and with the low interaction of the solvent with the membrane.

In summary, it can be concluded that the retention of one solute group is mainly affected by the difference between affinity of the solvent but also of the solute for the membrane material. If this difference is large, the retention is low or even negative.

Table 2.7: Retention of octadecane $MW = 254.5 \text{ kg kmol}^{-1}$ at 30 bar transmembrane pressure with different solvents depending on the value for $|\delta_{\text{Membrane}} - \delta_{\text{Solvent}}|$ and $|\delta_{\text{Solvent}} - \delta_{\text{Solute}}|$

Solvent	Retention (30 bar) (%)	$ \delta_{\text{Membrane}} - \delta_{\text{Solvent}} $ ($\text{MPa}^{0.5}$)	$ \delta_{\text{Solvent}} - \delta_{\text{Solute}} $ ($\text{MPa}^{0.5}$)	$ \delta_{\text{Membrane}} - \delta_{\text{Octadecane}} $ ($\text{MPa}^{0.5}$)
n-Hexane	51.33	0.63	1.63	1.0
Toluene	41.25	2.73	1.73	
Isopropanol	-28.48	8.0	7.0	
Methanol	-43.98	14.2	13.2	

2.5 Conclusion

In this work retention behavior and especially negative retentions are investigated. Negative retentions are observed while using isopropanol or methanol as solvent and n-alkanes or linear carboxylic acids as solutes, whereas positive retention was measured with polyethylene glycol as solute. In contrast, using toluene or n-hexane as solvent, all observed retentions were positive.

Solubility parameters explain the different retentions and the strong dependence of the retention on the used solvent and solute. In general, negative retentions can be achieved, if the solute is preferably dissolved in the membrane material. This means that the difference between the solubility parameter of the solute and the membrane must be smaller than the difference between the solubility parameter of the solvent and the membrane. Other properties of the solute such as solute size or molar volume can affect the diffusive resistance as well as driving force.

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CHAPTER 3

MULTICOMPONENT MASS TRANSPORT IN ORGANIC SOLVENT NANOFILTRATION WITH SOLVENT MIXTURES

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3.1 Introduction

Over the last years, organic solvent nanofiltration (OSN) has become a viable alternative to conventional thermal separation process. To use the full potential of OSN, a thorough understanding of the separation mechanism is essential. It is commonly understood that the membrane performance is influenced by solvent properties, solvent composition but also by solute properties [1-5]. Some authors have observed even negative retentions, where the larger solute molecule is enriched in the permeate [6, 7].

An investigation with different single solvents (n-heptane, cyclohexane, xylene) and solutes (iron(III) acetylacetonat, 9,10-diphenylanthracene) in the range of 84 to 612 kg kmol⁻¹ using a dense PDMS membrane was carried out by Tarleton et al. [8]. They observed the highest retention using xylene as solvent while the lowest retention was measured with n-heptane as solvent. Zwijnenberg et al. [9] studied the retention behavior of polyisobutylene (PIB) and polystyrene oligomers (PS) dissolved in n-hexane and toluene. They measured higher retentions of PIB and n-hexane as solvent compared with toluene as solvent using a PDMS membrane.

Previous studies investigated the influence of different solvent mixtures on the flux and on the retention. Geens et al. [10] studied for instance the retention behavior of raffinose (MW 504 kg kmol⁻¹) with different membranes and diverse binary mixtures of water, methanol and ethanol. Different permeabilities depending on the solvent and on the solvent mixtures were found. They also observed different retentions of raffinose using varying composition of the binary mixtures. A minimum in retention was found for instance while using a MPF-50 membrane and a water/methanol mixtures at 25 wt-% methanol.

Using the binary mixtures of methanol/toluene and ethyl acetate/toluene an increasing permeate flux with increasing toluene amount was observed by Silva et al. [11]. In this study a STARMEMTM 122 membrane showed no significant change in the retention of TOABr while using the mixture toluene/ethyl acetate. Only a slight increase was measured while using the binary mixture of methanol and toluene.

Recently, Schmidt et al. [12] published results using five different solutes (n-hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, phenyldodecane, 2,6-diisopropyl-naphthalene, triphenylphosphine) in binary and ternary mixtures of toluene, isopropanol and n-hexane. They observed a strong influence of the used solvent on the retention with two different membranes, namely STARMEMTM 122 (polyimide based) and PuramemTM 280 (silicone coated polyimide). Using the binary mixtures of n-hexane and isopropanol for example, a maximum of retentions was observed at 25 wt-% isopropanol. But only a small difference was measured regarding the retention of the five dissolved compounds using the same solvent or solvent mixtures [12].

The dependence of the retention on solute properties is studied for instance by Zheng et al. [13]. They measured the retention of linear alkyl acetates, branched alkyl acetates and cyclohexyl acetates dissolved in methanol. Three different membranes (STARMEMTM 122,

STARMEMTM 240, MPF-44) were used but the same trend could be seen: cyclic and branched molecules shows a higher retention up to 88 % compared to linear solutes (1 %). The molecular shape apparently has a significant impact on the retention.

Even negative retentions were observed by Zeidler et al. [14] and Darvishmanesh et al. [15] using organic solvents and a polymeric membrane. Zeidler et al. [14] investigated the retentions of two, three and four ring-type core substances with different functional groups dissolved in ethanol, n-heptane and tetrahydrofuran using a GMT-oNF-2 membrane (PDMS/PAN). A strong dependence of the retention on the used solvent was observed while even negative retentions were measured using ethanol as solvent. Negative retention was also observed by Darvishmanesh et al. [15]. They investigated the retention of STARMEMTM 122 with various dyes dissolved in six different solvents. The retentions of these dyes were strongly influenced by the solvent used. Using for instance n-hexane as solvent, negative retentions were observed up to -70 %. Both authors based this observation on the difference of solubility parameters of solvent and solutes and on high interactions between solvent and membrane.

Negative retention was also addressed before in chapter 2. Here negative retention of three different linear carboxylic acids ($MW = 228\text{--}340 \text{ kg mol}^{-1}$) and of n-alkanes with different chain length ($MW = 142\text{--}339 \text{ kg mol}^{-1}$) dissolved in pure isopropanol and methanol was found while positive retention was measured using pure toluene and n-hexane as solvents. In general, this study discussed the influence of solvent and solute properties on the retention using four different solvents and solutes. Here, positive as well as negative retentions were observed depending on the used solvent.

Based on the chapter before the rigorous characterization of mass transport behavior of solute mixtures in binary solvent will be addressed here. Thus this study experimentally investigates the retention behavior of mixtures of n-alkanes with different chain length in binary solvent mixtures of toluene/isopropanol and toluene/methanol.

3.2 Experimental

3.2.1 Materials

Three different solvents namely toluene, isopropanol, and methanol are used in this work. Table 3.1 summarizes the main properties of the above mentioned solvents.

Table 3.1: Physicochemical properties of the used solvents [16, 17]

Solvent	Formula	Molecular weight (kg kmol ⁻¹)	Viscosity (mPa·s)	Surface tension (mN m ⁻¹)	Molar volume (m ³ mol ⁻¹)	Dielectric constant (-)	Solubility parameter (MPa ^{0.5})
Isopropanol	C ₃ H ₇ OH	60.10	2.04	21.7	76.92	18.30	23.7
Methanol	CH ₃ OH	32.04	0.60	22.6	40.40	32.60	29.7
Toluene	C ₇ H ₈	92.14	0.59	28.5	106.85	2.38	18.3

As solutes, n-alkanes with different chain lengths were used. A summary of the used n-alkanes are shown in Table 3.2.

Table 3.2: Different n-alkanes used as solutes [17, 18]

Formula	Name	Molecular weight (kg kmol ⁻¹)	Solubility parameter (MPa ^{0.5})
C ₁₀ H ₂₂	Decane	142.28	15.8
C ₁₂ H ₂₆	Dodecane	170.34	16.1
C ₁₄ H ₃₀	Tetradecane	198.39	16.3
C ₁₆ H ₃₄	Hexadecane	226.45	16.5
C ₁₈ H ₃₈	Octadecane	254.5	16.6
C ₂₂ H ₄₆	Docosane	310.61	16.7
C ₂₄ H ₅₀	Tetracosane	338.66	16.7

As membrane a development product of Evonik Industries was used. This composite membrane consists of a polymeric ultrafiltration membrane made of polyimide as support layer and a thin film of silicone acrylates with defined properties as active layer. In the patent of Evonik Industries, a membrane similar to the membrane used in this work is described [19]. Properties were reported in chapter 2.

3.2.2 Experimental procedure

A cross-flow set-up delivered by Evonik MET was used to perform different experiments. Fig. 3.1 shows the schematic of this set up. Herby two test cells are connected in series with a membrane area of 52.81 cm² each. The feed is pressurized with nitrogen and pumped with a gear pump (60 l h⁻¹) through the test cells.

Before a measurement was performed, the membrane was immersed in toluene for 24 h and in the used solvent for 2 h. This procedure was evaluated by several studies [1, 20, 21].

Thereafter, the membrane was installed in the test cell, so the operating pressure could be applied for 30 min to ensure a steady state. For the retention measurements, two permeate samples per test cell and one feed sample was taken.

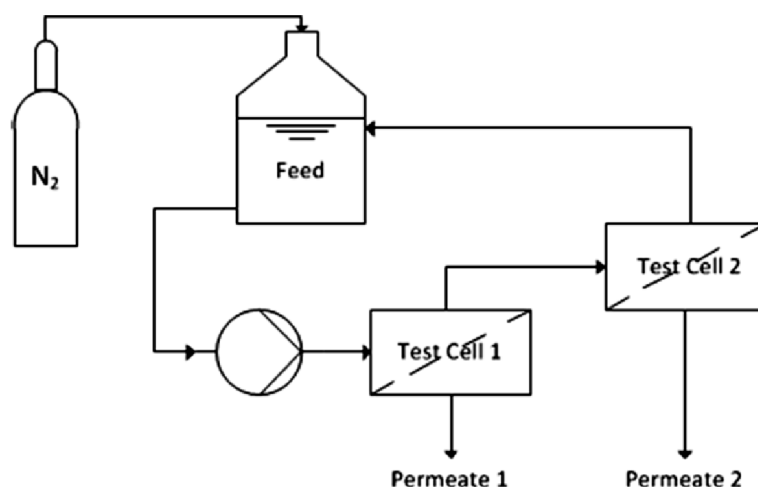


Fig. 3.1: Schematic of the cross-flow filtration set-up

The first experiments were carried out with pure toluene at 10, 20, 30 and 40 bar. Afterwards the experiments with three different binary solvent mixtures (25 wt.-%, 50 wt.-%, 75 wt.-%) of toluene/isopropanol were carried out at 20 and 30 bar. Subsequently, the pure solvent flux of isopropanol could be measured at 10, 20, 30 and 40 bar. Different n-alkanes were added to isopropanol and the retentions were measured in pure isopropanol and in different compositions (25 wt.-%, 50 wt.-%, 75 wt.-%) of the binary mixtures toluene/isopropanol at 20 and 30 bar. Finally, the retention of n-alkanes solved in pure toluene was measured. The same method was used for the experiments using methanol or the binary mixture with toluene or isopropanol as solvent. Table 3.3 shows a summary of all realized experiments.

In general, MWCO curves were measured with different n-alkanes solved in pure solvents and in solvent mixtures where a total concentration of 1 wt.-% of all fractions in the same ratio of n-alkanes is maintained. All experiments were performed at room temperature.

Table 3.3: Summary of the performed experiments

Solvent 1	Solvent 2	Solute	TMP
Toluene	-	-	10,20,30,40 bar
Toluene	Isopropanol	-	20,30 bar
-	Isopropanol	-	10,20,30,40 bar
Toluene	Isopropanol	n-Alkanes	20,30 bar
-	Methanol	-	10,20,30,40 bar
Toluene	Methanol	-	20,30 bar
Toluene	Methanol	n-Alkanes	20,30 bar
Isopropanol	Methanol	-	20,30 bar
Isopropanol	Methanol	n-Alkanes	20,30 bar

3.3 Analytics

The compositions of the solvent mixtures were determined with an Abbe refractometer. The refractive indices of the pure solvents are summarized in Table 3.4.

Table 3.4: Indices of refraction for the used pure solvents at 293 K

Solvent	Refractive index (lit) [22]	Refractive index (this work)
Toluene	1.497	1.496
Isopropanol	1.377	1.379
Methanol	1.328	1.328

So to determine the permeate fluxes of each component J_i the total flux J_{total} and the composition of that flux was measured. Using the following relation the flux of each component could be calculated:

$$J_i = J_{total} \cdot w_i$$

To determine the concentration of n-alkanes in the solvents a gas chromatography (GC 6890 system - Agilent, CA, USA) was used in this work. Detailed description of the analytic method can be found in chapter 2.

Using these measured concentrations, the retention can be calculated with the following equation:

$$R_i = 1 - \frac{c_i(\text{Permeate})}{c_i(\text{Retentate})}$$

According to this, negative retention can be observed, when higher concentration of the solute is found in the permeate than in the retentate.

3.4 Results and discussion

3.4.1 Measurements with pure solvents

Pure solvent fluxes of toluene, isopropanol and methanol are discussed in chapter 2. Here, the observed flux of toluene is much higher than the flux of isopropanol and methanol, whereas the permeate flux of isopropanol is slightly lower than the observed flux of methanol. This observation was based on different affinity of the solvent to the membrane material due to different solubility parameter.

The retention of n-alkanes with different chain length dissolved in the above mentioned solvents toluene, isopropanol and methanol was also discussed before and summarized in Fig. 3.2.

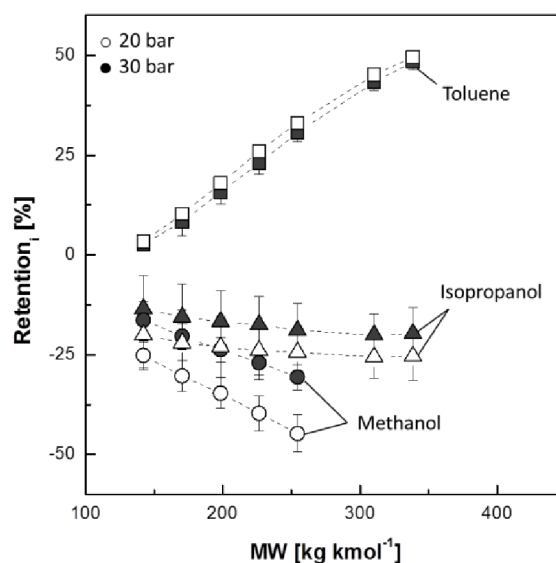


Fig. 3.2: Retention of n-alkanes with different chain length dissolved in toluene ($\square$), isopropanol (Δ) and methanol ($\circ$) at 20 and 30 bar and room temperature

Positive retention of n-alkanes was observed only while using toluene as solvent. Otherwise negative retention was measured with isopropanol and methanol. In this case the retention was even more negative with higher transmembrane pressure. Using methanol as solvent negative retention up to -45 % was reached while -25 % retention was measured using isopropanol. The retentions even decrease with increasing molecular weight.

Summarizing, using a solvent with less affinity to the membrane material than the used solutes, negative retention is observed.

3.4.2 Measurements with binary solvent mixtures

Investigations with the binary system of toluene/isopropanol, toluene/methanol and methanol/isopropanol are carried out with three different compositions (25 wt. %, 50 wt. %, 75 wt. %) at 20 and 30 bar transmembrane pressure. First of all total fluxes as well as the partial fluxes are measured. In addition to the flux measurement of single solvents and their binary mixtures, retentions of n-alkanes with different chain length dissolved in each of the solvents as well as in the binary mixtures of these solvents were investigated. These experiments were performed at 20 and 30 bar respectively and 1 wt-% n-alkanes in total.

Toluene / Isopropanol

The total fluxes as well as the partial fluxes of toluene and isopropanol in the binary mixture was measured at 20 and at 30 bar transmembrane pressure. Fig. 3.3 shows the permeate fluxes as a function of the composition of toluene and isopropanol.

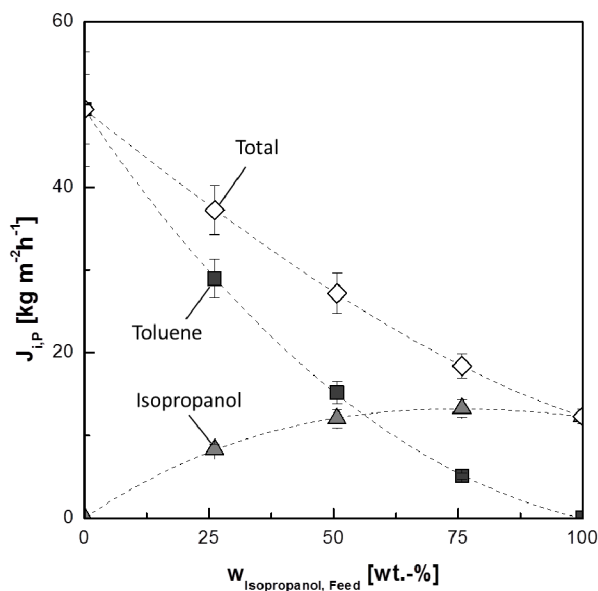


Fig. 3.3: Measured total flux ($\diamond$) and partial fluxes of toluene ($\square$) and isopropanol (Δ) or toluene ($\square$) and methanol ($\circ$) at 30 bar and room temperature

The total flux as well as the partial flux of toluene decrease with decreasing toluene amount while the isopropanol flux increases. However, in contrast to the flux of toluene only a slight increase for isopropanol was measured. Up to 50 wt-% isopropanol a sharper increase of the partial flux of isopropanol was observed, while no significant change was measured from 50-wt. % to 100-wt % isopropanol.

Fig. 3.4 shows the retention behavior of toluene and isopropanol in the mixture at 20 and 30 bar transmembrane pressure. Since toluene passes preferentially through the membrane due to the higher affinity to the membrane material (reasoned by a smaller difference in solubility parameter) (see chapter 2) a higher concentration of this solvent in

the permeate than in the retentate was observed. This is represented in Fig. 3.4 as negative retention.

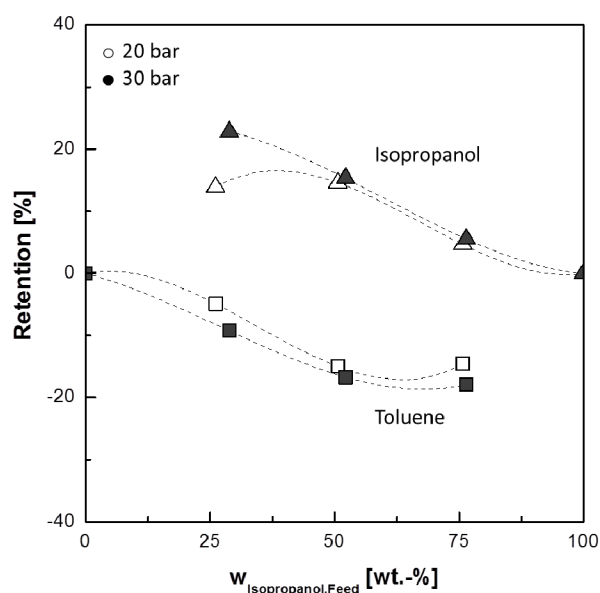


Fig. 3.4: Retention of toluene ($\square$) and isopropanol (Δ) at 20 and 30 bar and room temperature

The observed retention behavior of isopropanol is vice versa: Isopropanol is retained by the membrane up to 23 % at 25% isopropanol amount in the mixture at 30 bar transmembrane pressure due to less solubility in the membrane. It should also be note that the pressure influence changes: With higher pressure a larger amount of toluene passes through the membrane in relation to isopropanol. So the retention of toluene is even more negative while the retention of isopropanol is slightly higher. In addition to the flux measurements, the retention of n-alkanes in the binary mixtures at 20 and 30 bar transmembrane pressure was investigated. Fig. 3.5 shows the experimental data at 30 bar. The retention of n-alkanes decreases with increasing amount of isopropanol to the point of completely negative retention. The measured retentions using 75 wt-% isopropanol or pure isopropanol show no significant influence of the molecular weight anymore.

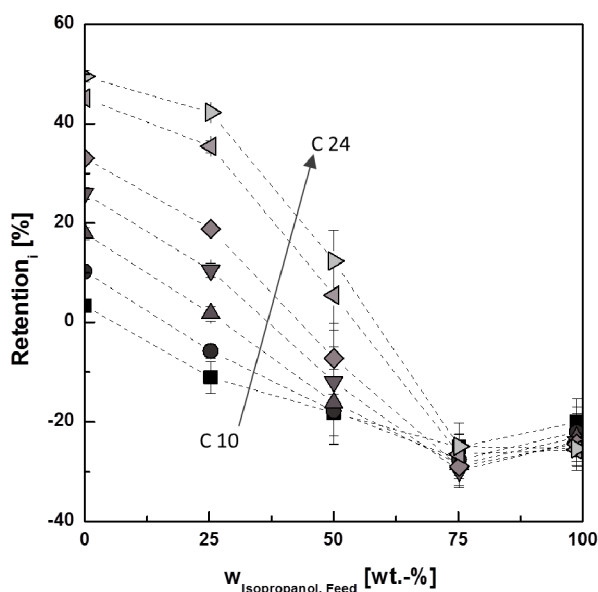


Fig. 3.5: Experimental retention of n-alkanes dissolved in different mixtures of toluene and isopropanol at 30 bar pressure

When isopropanol is used as a solvent with less affinity to the membrane material than toluene and the used n-alkanes, the solutes transport through the membrane is preferred. So, with higher isopropanol amount in the mixture the retention get negative due to higher affinity of the solutes in contrast to the solvent.

Toluene / Methanol

Measurement with toluene and methanol in binary mixtures are also carried out at 20 and 30 bar transmembrane pressure. Fig. 3.6 shows the experimental determined total as well as the partial fluxes of toluene and methanol.

A similar behavior like it is described before for the mixture toluene/isopropanol could be observed regarding the fluxes of toluene and methanol in the mixture: Again the partial flux of each component increases with increasing amount of this component in the mixture. In contrast to the partial flux of toluene, only a slight increase was observed for the methanol flux.

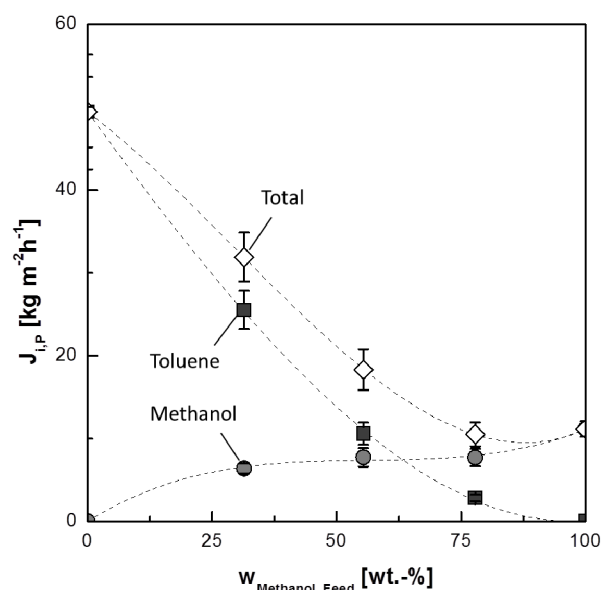


Fig. 3.6: Retention of toluene (□) and methanol (○) at 20 and 30 bar and room temperature

The retention of toluene and methanol in the binary mixture of them is shown in Fig. 3.7. A same behavior was observed as in the case of using the mixture of toluene and isopropanol. As described before, toluene as a solvent with high affinity to the membrane material is enriched in the permeate and negative retentions up to -30 % were observed. In contrast to this, positive retentions of methanol up to 36 % were measured.

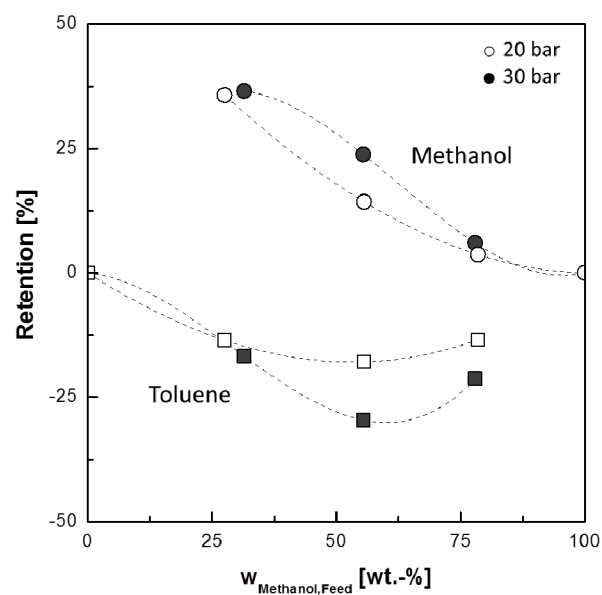


Fig. 3.7: Retention of toluene (□) and methanol (○) at 20 and 30 bar and room temperature

Further experiments using n-alkanes with different chain length dissolved in varying mixtures of toluene and methanol was carried out. Fig. 3.8 shows the experimentally determined retention of each n-alkane as a function of the composition of the solvent mixture of toluene and methanol.

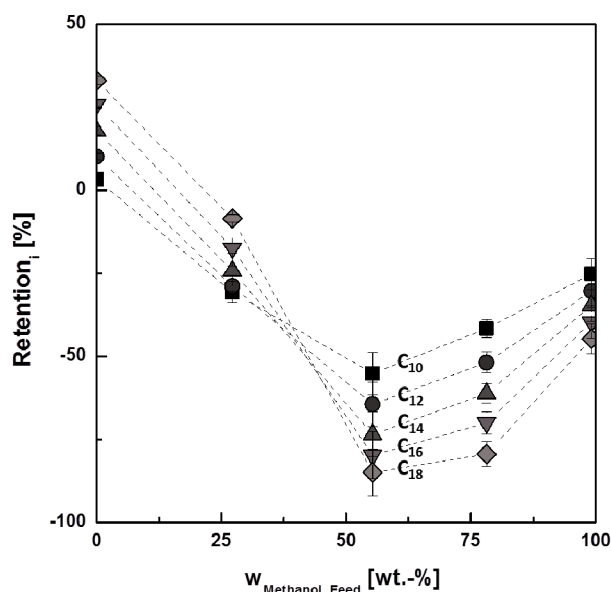


Fig. 3.8: Experimental retention of n-alkanes dissolved in different mixtures of toluene and methanol at 30 bar pressure

Here, the retention is completely negative except for the retention of n-alkanes dissolved in pure toluene. Furthermore a minimum was found at 53 wt-% methanol. Also the influence of the molecular weight changes: The retention increases with increasing molecular weight but only while using pure toluene or a mixture with 25 wt-% methanol. The retention decreases with increasing molecular weight in the range between 50 wt-% and 100 wt-% methanol.

Isopropanol / Methanol

The same experimental procedure as described before was applied using the binary mixture of isopropanol and methanol. The experimental permeate fluxes as a function of compositions are shown in Fig. 3.9.

A slight decline of the total flux was observed with increasing isopropanol content. The partial flux of each component increases with increasing amount of that component in the mixture. In general, fluxes are much lower than fluxes with higher toluene amount and no large different between isopropanol and methanol flux was observed. Due to this, none of the two solvents show significant retentions in the mixture and this is not illustrated here.

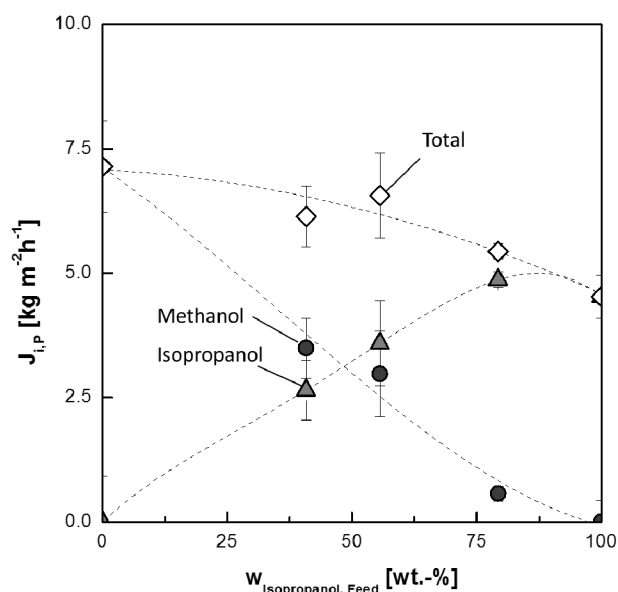


Fig. 3.9: Measured total flux (◇) and partial fluxes of isopropanol (Δ) and methanol (○) at 30 bar and room temperature

However, Fig. 3.10 shows the retention of different n-alkanes. Since dodecane and tetracosane are not soluble in methanol these were not investigated in this mixture. The retentions of C10 to C18 show no significant difference over the entire concentration range. The retention of C16 for instance varied between -28 % and -33 %. Nevertheless, the retention decreases with increasing molecular weight.

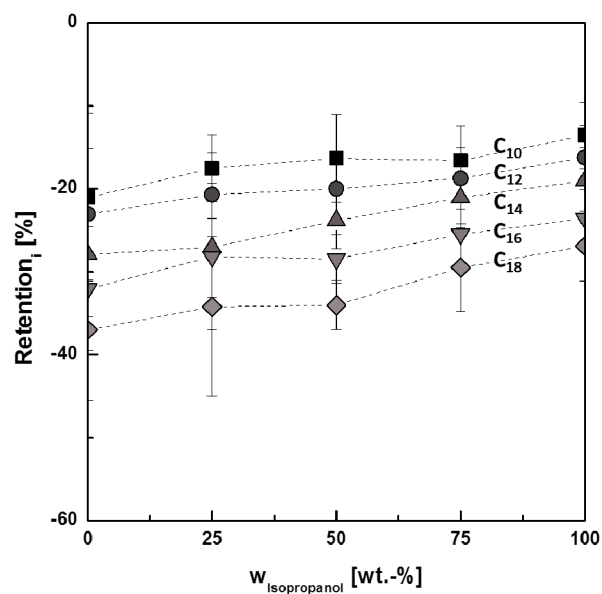


Fig. 3.10: Experimental retention of n-alkanes dissolved in different mixtures of isopropanol and methanol at 30 bar pressure

This result clearly indicates that the affinity of the solvent to the membrane material mainly influence solvent-solute-membrane interactions. The change in retention of the solute is considerable if a solvent with high affinity to the membrane material is used. But there is no significant difference in the retention of n-alkanes if isopropanol and methanol as pure solvents or in the binary mixtures are used, due to the low and almost similar affinity to the membrane material.

3.5 Conclusion

In this work the influence of solvent mixtures on the retention of different n-alkanes as solutes is investigated. Using methanol and isopropanol as pure solvents or in binary mixtures with toluene, negative retentions are observed. A significant minimum in retentions was found for all n-alkanes with different chain length in the binary mixture of toluene and methanol. In contrast, using toluene as pure solvent positive retention is observed. Only a slight increase is found in retentions of different n-alkanes with increasing isopropanol amount in the mixture with methanol.

This investigation shows that changes in solvent properties due to different solvent mixtures influenced membrane-solvent-solute interactions. This leads to significant changes in flux and retention behavior.

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CHAPTER 4

INFLUENCE OF SOLUTE-SOLUTE MIXTURES ON RETENTIONS

4.1 Introduction

Transport phenomena in dense polymeric nanofiltration membranes using organic solvents need still further improvements in order to completely understand the separation mechanism using organic solvent nanofiltration membranes. In recent years, many works were published with respect to organic solvent nanofiltration processes [1-3], development of new solvent resistant nanofiltration membranes [4-8] and mathematical description of nanofiltration using organic solvents [9-11]. However, still very few data are available regarding the influence of solute/solute mixtures using different solute groups in one solution and only few studies are published discussing the influence of solvent mixtures on the retention.

Machado et al. [12] characterized transport behavior of MPF-50 membrane using pure but also mixed solvents. Different alcohols, paraffins, ketones, acetates, and water as well as their binary mixtures were used in this study as solvent. A non-linear flux dependence on mixtures composition was observed. Using acetone/paraffins mixtures for instance, minima in flux were found. Viscosity and surface tension were found as major properties influencing the permeation behavior.

The permeation of different alkanes, alcohols and ketones through dense PDMS/PAN membranes were investigated by Dijkstra et al. [13] In this study pentane-decane and pentane-dodecane were used as binary solvent mixtures. An increasing flux was observed with increasing pentane amount in the mixtures, while a maximum was observed in partial flux of dodecane. Due to these measurements they conclude, that both diffusive and viscous flow has to be taken into account to describe these permeation measurements.

Silva et al. [14] investigated the transport of toluene/methanol and toluene/ethyl acetate as binary solvent mixtures through Starmem 122 and Koch MPF-50 membranes. They observed a decreasing flux with increasing toluene amount using Starmem 122 while the retention of TOABr seems to be not influenced by different solvent mixtures and stayed constant at around 99 %.

Retention of raffinose for different membranes (Desal-5-DK, N30F, MPF-50) in water/ethanol, water/methanol and ethanol/methanol mixtures were measured by Geens et al [15]. A clear dependence of retention on the solvent mixture was observed. For instance retention decreases with increases ethanol amount due to different membrane-solvent- solute interactions.

Schmidt et al. [16] used multi-component solvent mixtures to characterized two commercial polyimide-based membranes (StarmemTM122 and PuramemTM280). Five different solutes were dissolved in binary but also in ternary solvent mixtures of toluene, n-hexane and 2-propanol. The influence of solvent mixtures on the retention could be observed for all solutes. Even maxima in retentions were measured in mixtures containing 2-propanol. They concluded that these results were observed due to differences in solubility parameter, membrane swelling and the solute critical diameters.

Membranes made of glassy polymer PTMSP (poly[1-(trimethylsilyl)-1-propyne]) were used to investigate the retention of two different pairs of dyes as solutes dissolved in ethanol by Volkov et al. [17]. On the one hand Organe II as anionic and Solvent Blue 35 as neutral solute were used as one solute pair while on the other hand Remazol Brilliant Blue R as anionic and Oil Red O as neutral component were used as solute mixtures. Both pairs of dyes were dissolved in ethanol. Negative retentions were observed for both neutral components while Organe II and Remazol Brilliant Blue R were positive rejected by the membrane at the same time.

In this thesis, chapter 2 and 3 discusses transport phenomena in organic solvent nanofiltration membranes and negative retention. First of all, the influences of different solute classes as well as different solvents on the retention were investigated in chapter 2. Afterwards the effect of different solvent/solvent mixtures on the retention was discussed in chapter 3. Negative retention using solvents with low affinity to the membrane material was found while positive retentions were measured using solvents with high affinity to the membrane material. This was explained due to different solubility parameter: with higher affinity of the solute to the membrane material compared to the solvent, the solute is preferably dissolved in the membrane. As a consequence the solute is concentrated in the permeate and negative retention could be observed.

Additionally, the presented chapter compares retention measurements of single solute groups with measurements using two solute groups simultaneous. These measurements were carried out with two solvents (methanol or isopropanol) as pure solvents and as binary mixtures. Solutes and solvents are selected to obtain high positive retention for one solute group, while the other solute group should pass through the membrane. Thus, the influence of the presence of one solute group on the retention behavior of another solute group due to solute-solute interaction is investigated.

4.2 Experimental

4.2.1 Material

In this work, two different solvents (isopropanol and methanol) were used. To carry out retention measurements, polyethylene glycol with different molecular weights (PEG 200 - PEG 850) and n-alkanes with different chain length ($C_{10}H_{22}$ - $C_{18}H_{38}$) were used as solutes.

The most important properties of the used solvents and solutes are summarized in Table 4.1, while the structures of the investigated solutes are shown in Fig. 4.1.

Table 4.1: Physicochemical properties of the used solvents [18-21]

Solvent/ Solute	Formula	Molecular weight kg kmol^{-1}	Molar Volume $\text{cm}^3 \text{mol}^{-1}$	Dielectric constant -	Solubility Parameter $\text{MPa}^{0.5}$
Isopropanol	C_3H_7OH	60.10	76.92	18.3	23.7
Methanol	CH_3OH	32.04	40.40	32.60	29.7
PEG	$[C_2H_4O]_n$	282 - 854	117.9 - 759.9	15.5-11.0	23.7-20.5
n-Alkanes	$C_nH_{(2n+2)}$	142 - 254	180.4 - 318.8	~ 2.0	15.8-16.7

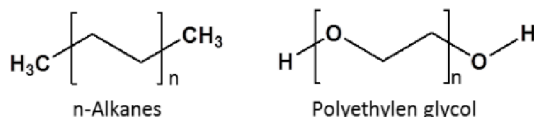


Fig. 4.1: Chemical structures of the used solutes

A composite silicon-based membrane with a support layer made of polyimide was used in this work. A detailed description can be found in chapter 2.

4.2.2 Experimental Procedure

The experiments were performed in a cross-flow set-up which was described in detail in chapter 2. The setup is shown in Fig. 4.2. Two test cells are connected in parallel with a membrane area of 100 cm^2 each. In this experimental study additionally 80 mil diamond type feed spacers are used. Two different pumps were used: A piston pump to pressurize the feed solution and a gear pump to circulate the solution up to 400 kg h^{-1} .

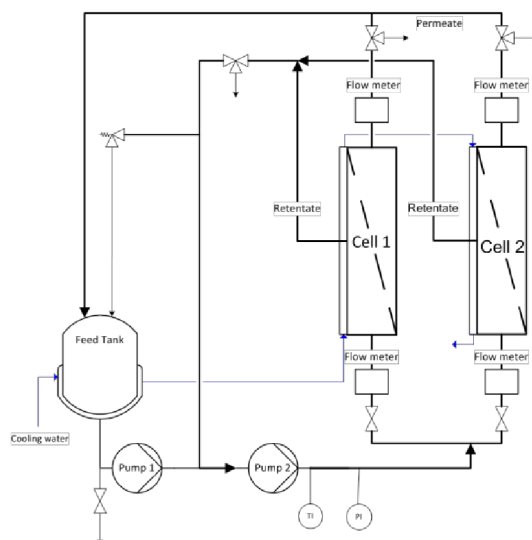


Fig. 4.2: Schematic of the used nanofiltration set-up

A membrane pretreatment was realized in this investigation. The membrane was immersed in toluene for 24 h and for 2 h in the used solvent before starting the experiments. Afterwards the membrane was pressurized for 2 h to reach the steady state.

To determine the retention, three retentate and permeate samples per test cell were taken during the experiments. Accordingly, the results for the retention measurements shown in this study are averages of six samples. To verify the experiments, also feed samples at the beginning and at the end of each experiment were taken.

First of all, fluxes of pure solvents and of the binary solvent mixtures using three different composition of solvent mixtures (25 wt-%; 50 wt-%, 75 wt-%) were measured. Afterwards, one single solute group (PEG or n-alkanes) was added with a total amount of 1 wt-% respectively and the same ratio of every single monomer. Retentions in pure solvents and in the binary mixtures of the used solvents were measured. Next, both solute groups are mixed and a total amount of 1 wt-% was dissolved in pure methanol, isopropanol or in the binary mixture.

All measurements were performed at 20 and 30 bar transmembrane pressure. Table 4.2 summarizes the performed experiments.

Table 4.2: Summary of the performed experiments

Solvent 1	Solvent 2	Solute 1	Solute 2
Isopropanol	-	-	-
Isopropanol	Methanol	-	-
-	Methanol	-	-
Isopropanol	-	n-Alkanes	-
Isopropanol	Methanol	n-Alkanes	-
-	Methanol	n-Alkanes	-
Isopropanol	-	-	PEG
Isopropanol	Methanol	-	PEG
-	Methanol	-	PEG
Isopropanol	-	n-Alkanes	PEG
Isopropanol	Methanol	n-Alkanes	PEG
-	Methanol	n-Alkanes	PEG

4.3 Analytics

The compositions of the solvent mixtures were determined with an Abbe refractometer. Detailed description can be found in chapter 3.

The determination of n-alkane concentration is carried out by gas chromatography (GC) with a flame ionization detector (FID). This method was already described in detail in chapter 2 and only summarized here. For the quantitative determination of PEGs in organic solvents, a high performance liquid chromatography (HPLC) combined with a refractive index detector (RID), or an evaporation light scattering detector (ELSD) is used similar to the method described by Li et al. [22]. In order to determine the concentration of PEG in a mixture with n-alkanes a new stepwise method was developed and is described in the following chapter.

Table 4.3 summarizes the analytic method depending on the solute or the solute mixtures.

Table 4.3: Summary of different analytic methods depending on the solute

Solute	Method
n-Alkanes	GC-FID
PEGs	HPLC + ELSD
n-Alkanes + PEGs	n-Alkane: HPLC + RID PEGs: HPLC + ELSD

4.3.1 Determination of n-alkanes concentration by gas chromatography

The gas chromatography (GC) system used in the work was a GC 6890 system (Agilent, CA, USA) with liquid auto sampler, splitless injection and flame ionization detector (FID). An Agilent HP-5 column was used, 30 m length, 0.32 mm inner diameter and 0.25 μm thickness. The injector temperature was 280 °C. 2 μl of each sample were injected splitless. Each sample was measured at least twice. Substances were identified by retention times of the particular alkane. The Calibration range was 0-80 mg/l for each alkane. All samples diluted up to the calibration range. All procedures were carried out in at least three replications while the standard deviation of all measurements was usually < 1% . A detailed description can be found in chapter 2.

4.3.2 Determination of PEG oligomers by HPLC

An Agilent-HPLC (series 1100) system was used to determine PEGs dissolved in different solvents. This system consists of a solvent degasser, binary pump, evaporation light scattering detector (ELSD), auto sampler, column thermostat and Agilent Chemstation-software. PEG-oligomer standards were delivered by PSS, Mainz, Germany.

The column used was a Kromasil-C18-5 μm -125mm-3mm ID delivered by CS – Chromatographie Service GmbH. As mobile phase a water/acetonitrile mixture with a flow rate of 0.5 ml min⁻¹ at 30 °C was used. At the beginning the eluent consists of 95 % water. The composition is gradually changed up to 95% acetonitrile. Therefore, the chemical properties of the eluent changes from polar to less polar, so the polar components of the samples are eluted at the beginning, whereas the less polar components are eluted at the end of the separation.

In order to identify single PEG oligomers, a HPLC-mass spectrometry was used in additional experiments with the same chromatographic conditions. So each peak in the chromatogram could be related to defined molecular weights. PEGs with lower molecular weight eluted faster compared with larger PEGs that remain in the separation column for a longer time. Fig. 4.3 shows exemplarily a HPLC-chromatogram of different PEG oligomers.

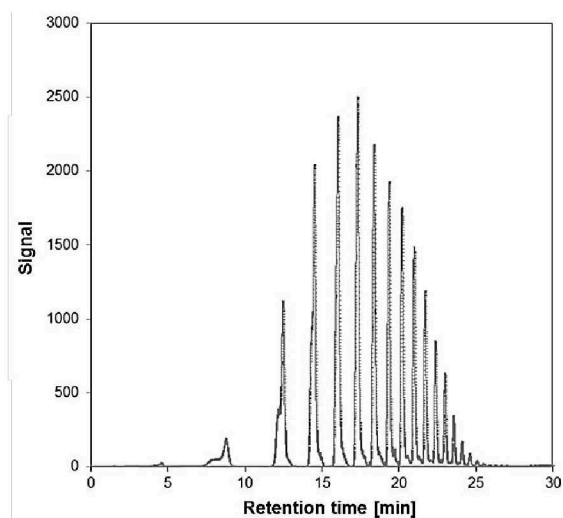


Fig. 4.3: HPLC-chromatogram of different PEG oligomers.

4.3.3 Determination of n-alkanes and PEG oligomers in one mixtures

Analytic methods to determine PEGs and n-alkanes in their mixture and dissolved in organic solvents is quit challenging. In this work a method is developed, to analyze PEG without influencing the n alkanes. So, subsequently the concentration of n-alkanes can be determined.

To analyze PEGs in this mixture, the same procedure is used as above described using HPLC with ELSD. However, the methods differ with respect to the mobile phase: Water and acetonitrile are also used as eluent, but with a different gradient. This method is used only to analyze the PEGs in the mixture. Alkanes elute late and unseparated.

The concentration of n-alkanes can be determined in the mixture with PEGs using an additional HPLC method. As a separation column Multochrom C18-BDS-100-3 μm -250 mm-3 mm ID and pure methanol as eluent is used. The flow rate of this eluent is adjusted to 0.5 ml min⁻¹. Calibration is performed with external standards over a range of 0 2000 mg L⁻¹ for all alkanes. The samples were diluted before being analyzed. The components can be detected using a refractive index detector.

This described method is used only to analyze the alkanes which are contained in the sample of the mixture with PEG. In this case the PEG oligomers are eluted unseparated at the beginning of the separation and they were not analyzed.

4.4 Results and discussion

4.4.1 Methanol and isopropanol measurements

First of all fluxes of pure methanol or isopropanol as well as fluxes of different binary mixtures were measured.

Table 4.4 summarizes the results of pure solvents which was reported and discussed in chapter 2. In general, the fluxes are low compared to fluxes using other solvents like toluene or n-hexane with high affinity to the membrane material. Furthermore, only a small difference was observed: The flux of methanol is slightly higher compared with the flux of isopropanol due to lower molar volume of methanol.

Table 4.4: Measured permeabilities of methanol and isopropanol

Solvent	Permeability ($\text{kg m}^{-2}\text{h}^{-1}\text{bar}^{-1}$)
Methanol	0.22
Isopropanol	0.20

Fig. 4.4 compares each partial flux as well as the total flux in relation to different solvent mixtures. Using different solvent mixtures an increase of each partial flux with increasing solvent amount respectively was observed for both solvents. Accordingly a slight decrease was measured with increasing isopropanol content regarding the total flux.

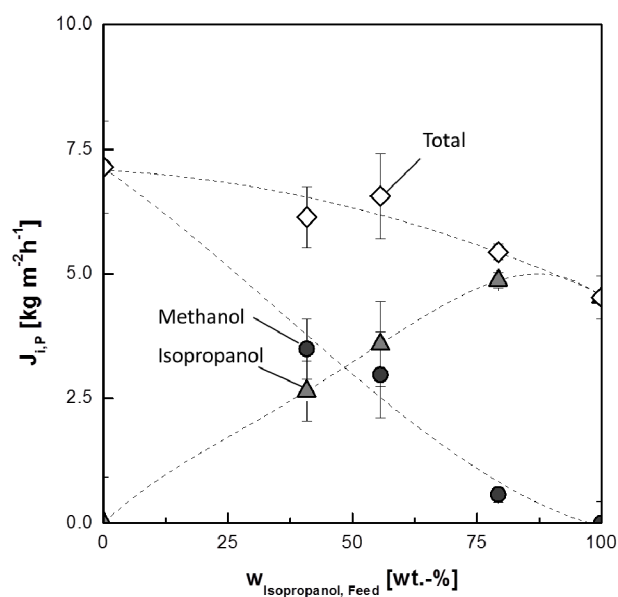


Fig. 4.4: Measured total and partial fluxes of methanol (o) and isopropanol (Δ) at 30 bar TMP and 25 °C.

4.4.2 Retention measurements with pure solvents and single solute groups

In chapter 2, retentions of n-alkanes and polyethylene glycols in different solvents were shown and discussed extensively. However, Fig. 4.5 summaries the retention of these two solutes dissolved in isopropanol (Fig. 4.5 a, c) or methanol (Fig. 4.5 b, d).

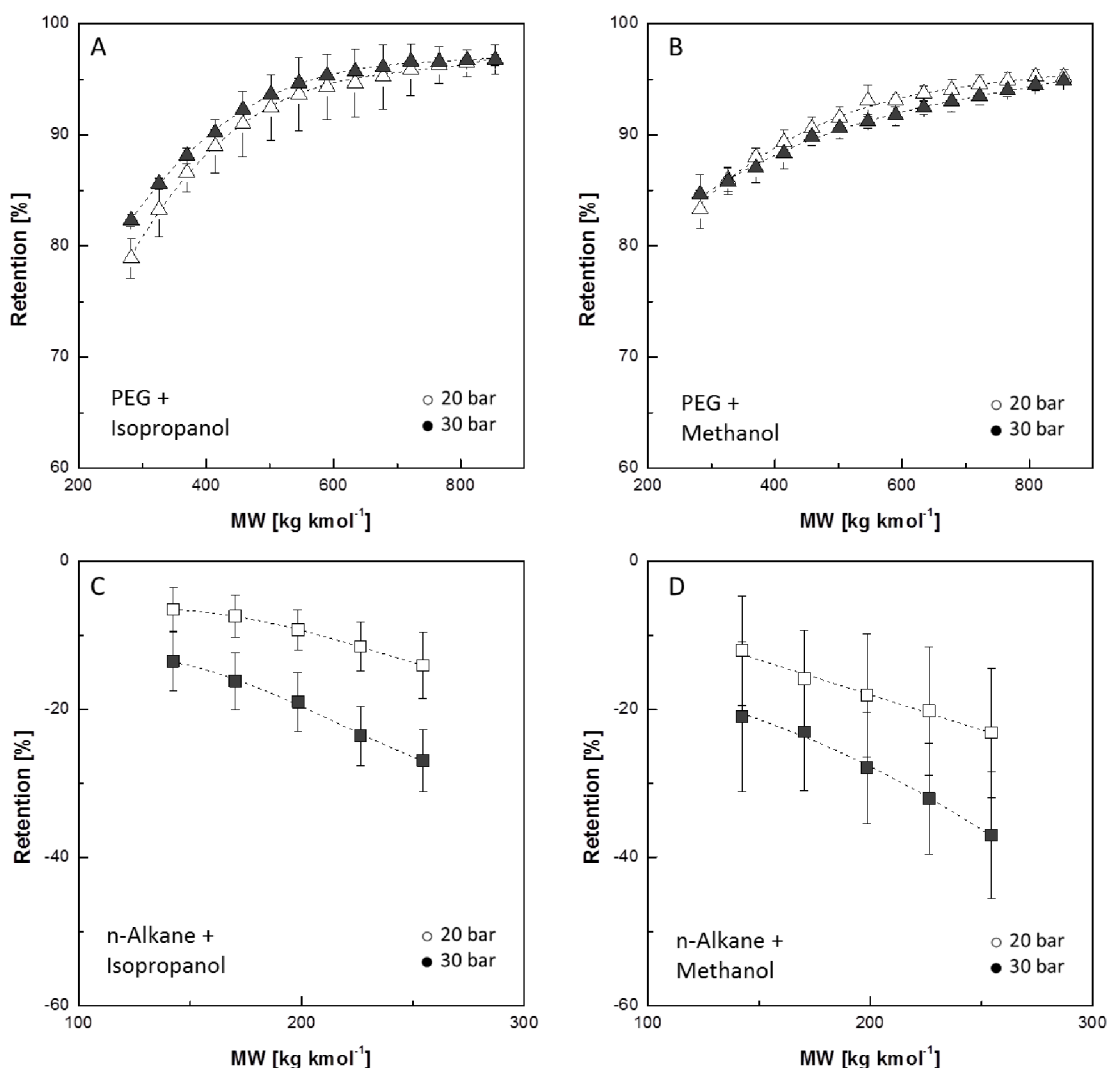


Fig. 4.5: Retentions measurements of PEGs (Δ) and n-alkanes ($\square$) dissolved in isopropanol (PEG: A, n-alkane: C) or methanol (PEG: B, n-alkane: D) at 20 and 30 bar TMP and 25 °C

Using PEGs as solute positive retentions up to 95 % were observed independent of the investigated solvent. In contrast, using n-alkanes as solutes and methanol or isopropanol as solvents with less affinity to the membrane material and low fluxes, negative retentions were observed. This result is explained, due to higher affinity of the solute to the membrane material compared to the solvent. Furthermore the retention decreases with increasing molecular weight and with increasing pressure, due to preferential solute

transport through the membrane. The dependence of solvents as well as solutes on different retentions is extensively discussed in chapter 2.

4.4.3 Retention measurements with binary mixtures and single solute groups

Retention measurements were also carried out for n-alkanes or polyethylene glycols in three different solvent mixtures (25 wt.-%, 50 wt.-%, 75 wt.-%) at 20 and 30 bar transmembrane pressure.

1 wt. % in total of each solute group was added to the solvent mixture. The influence of different solvent mixtures on the transport behavior through a nanofiltration membrane was already introduced in chapter 3. In addition this study presented the influence of methanol/isopropanol mixtures. Fig. 4.6 shows the retention of n-alkanes depending on these solvent mixtures. Only a slight increase of retentions of $C_{10}H_{22}$ to $C_{18}H_{38}$ with increasing isopropanol content was observed. The retention of $C_{16}H_{34}$ for instance varied between -28 % and -33 % over the entire concentration range. Nevertheless, the retention decreases with increasing molecular weight: Using a mixture of 50 wt.-% isopropanol $C_{10}H_{22}$ is retained up to -17 % by the membrane while even -34 % is retained using $C_{18}H_{38}$ as solute.

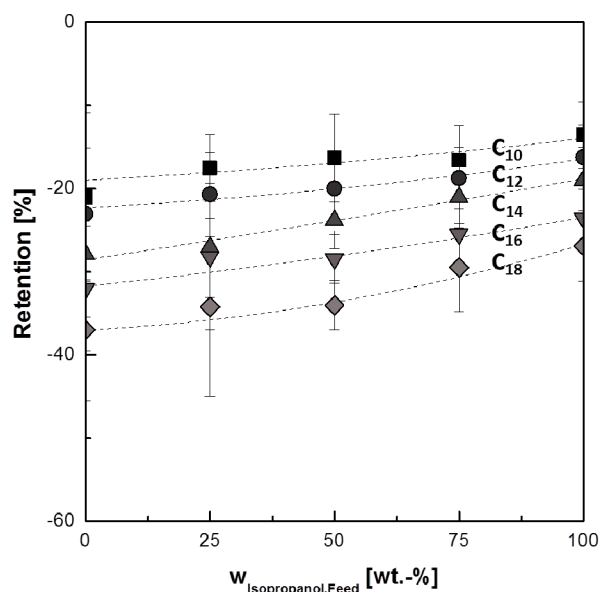


Fig. 4.6: Retentions measurements of n-alkanes dissolved in isopropanol/methanol mixtures at 30 bar TMP and 25 °C

Additionally Fig. 4.7 compares the retention of different polyethylene glycols dissolved in different methanol/isopropanol mixtures. As described before the retention is in general positive and up to 97.5 %. Again only a small change in retention over the entire

concentration range was observed. Regarding PEG with lower molecular weights a maximum at around 50 wt.-% was measured. For instance, the retention of polyethylene glycol with a molecular weight of 326 kg kmol^{-1} increases up to 90 % but decreases again with higher amount of isopropanol up to 85 %. However, the retention of PEG 854 for example varied only in the range between 94 % and 97 %.

In general, no significant difference in retentions was observed using solvents with low or almost similar affinity to the membrane material. Solutes with higher affinity to the membrane material compared to the solvent are concentrated in the permeate and negative retentions were observed. However, using solutes with low or comparable affinity to the membrane material related to the investigated solvent, high and positive retention could be observed. Due to this conclusion, no significant difference was observed in retention behavior using these different solvent mixtures.

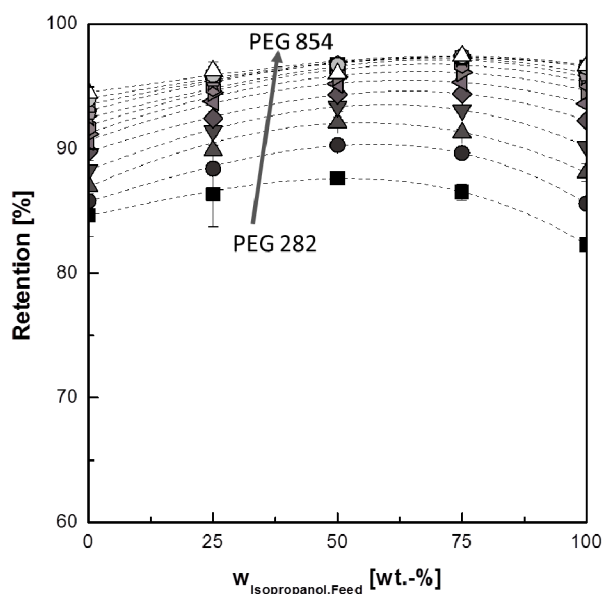


Fig. 4.7: Retentions measurements of different PEGs dissolved in isopropanol/methanol mixtures at 30 bar TMP and 25 °C

4.4.4 Measurements with pure solvents and solute group mixtures

Main focus of the presented study is to investigate the influence of different solute groups in one mixture on the separation behavior. For this investigation PEGs and n-alkanes were dissolved in isopropanol or methanol simultaneously and the retention of these solutes were measured like it is described in section 2.2.

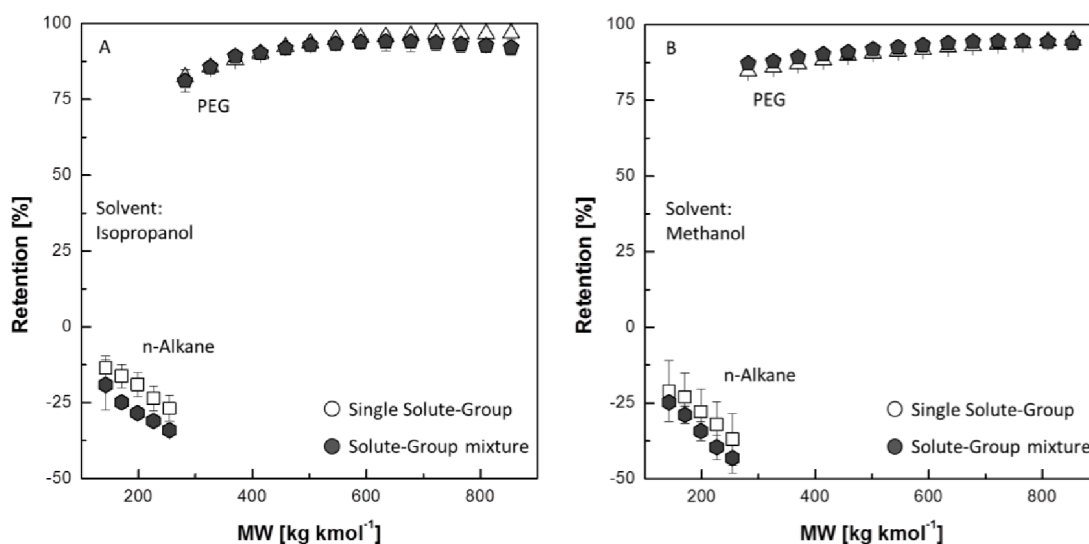


Fig. 4.8: Retention measurements using n-alkanes and PEG as single solutes or in one mixture dissolved in isopropanol (A) or methanol (B) at 30 bar TMP and 25 °C

Fig. 4.8 compares the retention of PEG and n-alkanes dissolved in isopropanol (Fig. 4.8A) or methanol (Fig. 4.8B) as single solute group with retention measurements using these solutes in one mixture. No significant change was observed whether using single solutes or solute group mixtures.

For instance polyethylene glycol with a molecular weight of 502 kg kmol^{-1} was retained up to 93.6 % in pure isopropanol while 92.9 % was retained using a solution which contains also different n-alkanes. However, the retention of n-alkanes is slightly lower while using solute group mixtures compared with single solute measurements.

Table 4.5: Retention measurements of $\text{C}_{16}\text{H}_{34}$ (C16) and PEG502 as single solutes or in a mixture dissolved in isopropanol or methanol at 30 bar TMP and 25 °C

Solvent	Solute	$R_{\text{n-Alkanes}}$ (%)	$\Delta R_{\text{n-Alkanes}}$ (%)	R_{PEG} (%)	ΔR_{PEG} (%)
Isopropanol	C16	-23.6		93.6	
Isopropanol	C16 + PEG502	-31.0	-7.4	92.9	-0.7
Methanol	C16	-32.0		90.6	
Methanol	C16 + PEG502	-39.6	-7.6	91.9	+1.3

Table 4.5 summarizes these retentions of PEG502 and $\text{C}_{16}\text{H}_{34}$ and shows additionally the absolute deviation between measurements using solute/solute mixtures with single solute measurements. As before described, the maximal deviation of 7.6 % was found for n-alkanes and smaller retentions were observed using solute/solute mixtures.

In general, no significant difference was observed between measurements using one solute group compared with the measurements using solute group mixtures dissolved in pure isopropanol or methanol. The separation mechanism of a dense nanofiltration membrane

seems to be predominated by the solute class, while solute/solute interactions do not influence the retention significantly in that presented case.

4.4.5 Measurements with binary mixtures and solute group mixtures

The influence of solvent/solvent mixtures on the retention of solute/solute mixtures was also investigated. Different methanol/isopropanol do not influence the retentions as already described before. Furthermore comparing retentions using solute groups separately with retention measurements using one solute/solute mixture, no significant change was measured. However, as described before, the retention of n-alkanes is slightly lower over the entire concentration range using the n-alkanes as solute/solute mixtures.

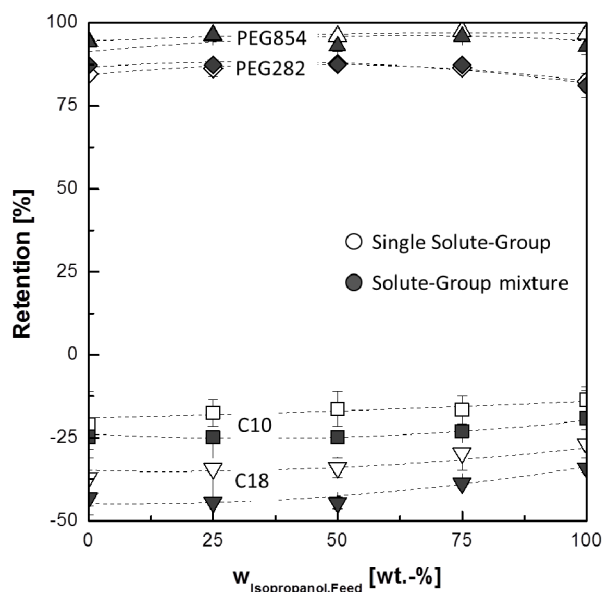


Fig. 4.9: Retention measurements of C18, C10 and PEG282, PEG854 as single solutes or in one mixture dissolved in different isopropanol/methanol mixtures at 30 bar TMP and 25 °C

These measurements indicate that solute/solvent/membrane interactions are main properties influencing separation mechanism of a dense membrane transport process, while solute/solute interaction play only a minor role.

4.5 Conclusion

This study extended a systematic investigation of solute transport through dense polymeric nanofiltration membranes. Retentions of different n-alkanes and polyethylene glycols dissolved in pure methanol or isopropanol or in different mixtures of these solvents were investigated. Negative retentions were observed for all n-alkanes dissolved in both solvents, while positive retentions up to 95 % were measured for PEG. Only a small

difference in retentions was observed whether using methanol or isopropanol as solvent. The investigated mixtures of methanol and isopropanol influenced the retentions of n-alkanes and PEGs not significantly. A slight maximum was observed regarding the PEG retention at around 50 wt.-% isopropanol.

Using the investigated solute groups in one mixture in comparison to the measurement with each solute group separately, no significant change in retention was measured.

In general the separation mechanism of a dense polymeric membrane seems to be dominated by solvent/solute/membrane interaction while solute/solute interaction do not influenced the retention significantly.

4.6 References

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CHAPTER 5

SOLVENT DEPENDENT SOLUTE SOLUBILITY GOVERNS RETENTION IN SILICONE BASED ORGANIC SOLVENT NANOFILTRATION

This chapter is in preparation for submission: Stefanie Postel, Carina Schneider, Matthias Wessling;
Solvent dependent solute solubility governs retention in silicone based organic solvent
nanofiltration

5.1 Introduction

In recent years, dense rubbery silicone based polymer membranes with high swelling tendency have gained more attention as solvent resistant nanofiltration-membrane material, due to its stability against most organic solvents. Most of the published work focuses on permeation and rejection properties. Different models are used, the most likely to govern transport through silicone-based membranes being the solution diffusion model. Actually, very little is known on the solubility of the solute partitioning in the membrane material. Thus we prove that swelling measurements are essential to understand transport phenomena using PDMS as membrane material, in particular when so-called negative retentions are observed.

Stafie et al. [1] proposes a method where a liquid solution comprising a single solvent and a single solute is used to immerse a PDMS sample in. Removal of the sample from the liquid, evaporating the volatile solvent and measuring the remaining amount of solute in the polymer allowed a first estimation of solute solubility. These measurements showed an influence of the molar volume of the penetrant, but also points already towards the influence of the solute solubility. A three dimensional relationship between solubility parameter of solute, solvent and polymer is presented in this work:

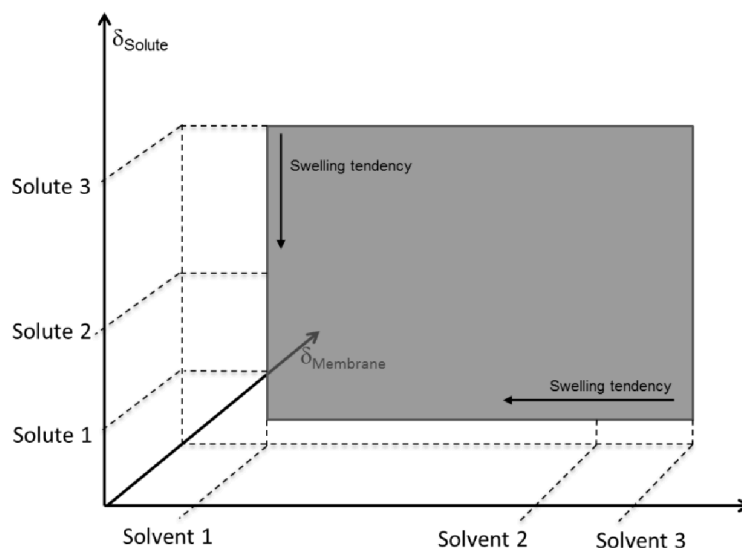


Fig. 6.1. Correlation between solubility parameter of solute, solvent and membrane adapted and redrawn from Stafie et al. [1]

Several papers were published in recent decades discussing the influence of different solvents on the swelling behavior of PDMS using different techniques [2-7]. Favre et al. [2, 8-10] extensively analyzed sorption, diffusion and permeation of different solvents and solvent mixtures through dense polydimethylsiloxane membranes varied the activity. A quasi-ideal behavior following the Flory-Huggins theory was measured using apolar

solvents, while highly non-ideal sorption behavior was observed using polar solvents. As an explanation of this non-ideal behavior they supposed at the one hand increased clustering tendency of polar solvents but on the other hand they suggested an application of more refined free volume theories.

Furthermore the influence of temperature on the swelling degree of crosslinked PDMS networks using different solvents was investigated by Favre [11]. In general, a clear relation between solubility parameter and sorption was found: The smaller the difference between solubility parameter of solvent and membrane the higher the sorption due to higher affinity of the solvent to the membrane material. This relationship using PDMS membranes or PDMS based composite membranes and different solvents but also solvent mixtures were verified by several authors [12-17]. They found a clear dependency between affinity, swelling and permeation of the solvents, while also viscosity and temperature has to be taken into account to explain the observed results.

A new technique based on spectroscopic ellipsometry allowing high pressure measurements of solvent induced swelling was recently presented by Ogieglo et al. [5]. n-Hexane sorption in PDMS was investigated in this study by applying different pressure (0.1 - 10 MPa). In this pressure range no influence of the pressure on the swelling of PDMS layer was found.

Only a few papers were published regarding sorption and swelling behavior of solutes in polymer membranes. However, Michaels et al. [18] used the solubility theories of Hildebrand and Flory - Huggins and demonstrated a predictive correlation between steroid permeability in polymers and their melting temperature using thermodynamic parameters. With respect to solubility and partitioning effects, they generally observed that a drug will be more soluble in the polymer phase as the difference in the solubility parameters of the drug-polymer becomes smaller [18].

In this presented study, swelling behavior and sorption measurements are carried out in order to complete a systematic investigation of negative retention in organic solvent nanofiltration using a dense PDMS-based membrane. Toluene, isopropanol and methanol as pure solvent and solvent mixtures as well as a selection of solutes are used in order to investigate the swelling behavior. Additionally the obtained results are interpreted using the Flory-Huggins theory.

5.2 Experimental

5.2.1 Materials

Swelling behavior was measured in order to investigate the influence of solvents and solvent mixtures on the swelling degree of the used membrane. For this measurement three different solvents were used as pure solvents but also as binary mixtures. These solvents and the most important properties are summarized in Table 6.1.

Table 6.1: Physicochemical properties of the used solvents [18, 19]

Solvent	Formula	Molecular weight (kg kmol ⁻¹)	Viscosity (mPa·s)	Molar volume (m ³ mol ⁻¹)	Dielectric constant (-)	Solubility parameter (MPa ^{0.5})
Isopropanol	C ₃ H ₇ OH	60.10	2.04	76.92	18.30	23.7
Methanol	CH ₃ OH	32.04	0.60	40.40	32.60	29.7
Toluene	C ₇ H ₈	92.14	0.59	106.85	2.38	18.3

In addition sorption measurements using different solutes dissolved in pure solvents were carry out to verify the before described retention behavior. The selected solutes and important properties are summarized in Table 6.2.

Table 6.2: Solutes properties [20-24]

Name	Formula	Molecular weight (kg kmol ⁻¹)	Solubility Parameter (MPa ^{0.5})
n-Alkanes			
Decane	C ₁₀ H ₂₂	142.3	15.8
Dodecane	C ₁₂ H ₂₆	170.3	16.1
Hexadecane	C ₁₆ H ₃₄	226.4	16.5
Tetracosane	C ₂₄ H ₅₀	338.7	16.7
Polyethylene glycol			
	C _{2n} H _{4n+2} O _{n+1}		
PEG 200	n = 4; 5	194-238	23.7
PEG 400	n = 8; 9	370-414	23.2
PEG 600	n = 13; 14	590-634	20.5
Carboxylic acids			
Myristic acid	C ₁₃ H ₂₇ COOH	228.4	17.5

In order to represent the PDMS-based membrane, a Sylgard 184 Silicone Elastomer Kit delivered by Dow Corning Corporation was used. As PDMS solubility parameter a value of 15.5 MPa^{0.5} is assumed [25].

5.2.2 Experimental Procedure

First the PDMS plates were prepared using the Sylgard 184 Silicon Elastomer Kit and a hardening agent (10:1). After the polymer was fully dissolved, the solution was cast into petri dishes and placed into vacuum oven. It takes a time of 48 h to completely harden the PDMS plates. After 48 h the initial weight of the dry polymer was measured before it was immersed either into toluene, isopropanol, methanol, three different binary mixtures of them (25%/75%, 50%/50%, 75%/25%) or in solutions of 1 wt.-% of each solute in every pure solvent.

After defined time intervals, the immersed PDMS-plates were removed, dried with filter paper and weighted. This procedure was repeated until the mass of PDMS remained constant. The swelling were calculated using the mass uptake $\Delta m(t)$ related to the initial weight of the PDMS plate m_0 .

$$\text{Swelling degree (SD)} = \frac{\Delta m(t)}{m_0} \quad [g \ g^{-1}] \quad (1)$$

To compare the results among themselves, the swelling degree at the equilibrium state ($SD(\infty)$) was used.

Once the equilibrium state was reached the PDMS plate was dried again and weighted in order to measure the sorption of different solutes. Using that procedure the amount of solute in the membrane ($w_{\text{solute}}(\text{Membrane})$) was determined and solute partition coefficient K_{solute} was calculated using the following equation and the initial concentration of solute in the immersed solution ($w_{\text{solute}}(\text{Feed})$).

$$K_{\text{solute}} = \frac{w_{\text{solute}}(\text{Membrane})}{w_{\text{solute}}(\text{Feed})} \quad (2)$$

5.3 Results and discussion

5.3.1 Solvent induced swelling using pure solvents

First, all the swelling degrees of PDMS using different pure solvents were investigated. The total amount of swelling as a function of time is shown in Fig. 6.2. The well established order of swelling (Toluene>Isopropanol>Methanol) can be clearly observed. A five times higher swelling degree was observed using toluene as solvent compared with isopropanol. Using methanol as solvent, almost no swelling could be observed while the difference between isopropanol and methanol is again not that high. These measurements could be explained by different affinity of the used solvent to PDMS. In Table 6.3 these different affinities expressed as differences in solubility parameter compared to the swelling degree at equilibrium state is shown.

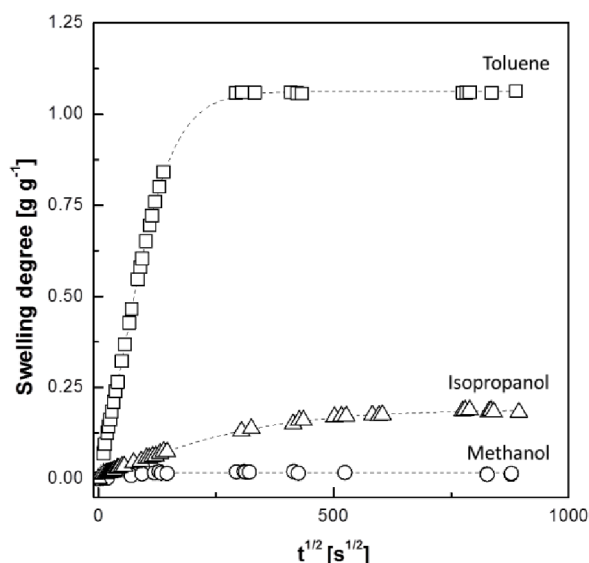


Fig. 6.2: Swelling degree of PDMS using toluene ($\square$), methanol (O) or isopropanol (Δ) as a function of time

Table 6.3: Comparison of swelling degree at equilibrium state ($SD(\infty)$) to differences between solubility parameter and permeabilities reported in chapter2

Solvent	$SD(\infty)$ g g^{-1}	$ \sigma_{\text{Solvent}} - \sigma_{\text{Membrane}} $ MPa ^{0.5}	Permeability $\text{kg m}^{-2}\text{h}^{-1}\text{bar}^{-1}$
Toluene	1.06	2.7	1.75
Methanol	0.02	14.2	0.49
Isopropanol	0.18	8.0	0.38

Small differences in solubility parameter between polymer and solvent correlate well with a high degree of swelling. Furthermore, the swelling behavior is in line with flux measurements discussed in the previous chapter. Table 6.3 summarizes the permeabilities of the investigated solvents. A large permeability was measured using toluene, as solvent with high swelling degree while low permeabilities were measured using methanol or

isopropanol, as solvent with low swelling tendency. However, methanol permeability was higher compared to the permeability of isopropanol even though the swelling degree of methanol is lower. This result shows that not only sorption determine the transport but also diffusion properties as represented by molar volume and viscosity of the solvent.

5.3.2 Solvent induced swelling using solvent mixtures

Additionally the influence of solvent mixtures on swelling behavior of PDMS was investigated. In order to compare different swelling behavior of PDMS using solvent mixtures, the swelling degree at equilibrium state ($SD(\infty)$) is calculated as described before. First, binary mixtures using toluene and isopropanol or toluene and methanol were investigated and $SD(\infty)$ as function of weight fraction of toluene is illustrated in Fig. 6.3A.

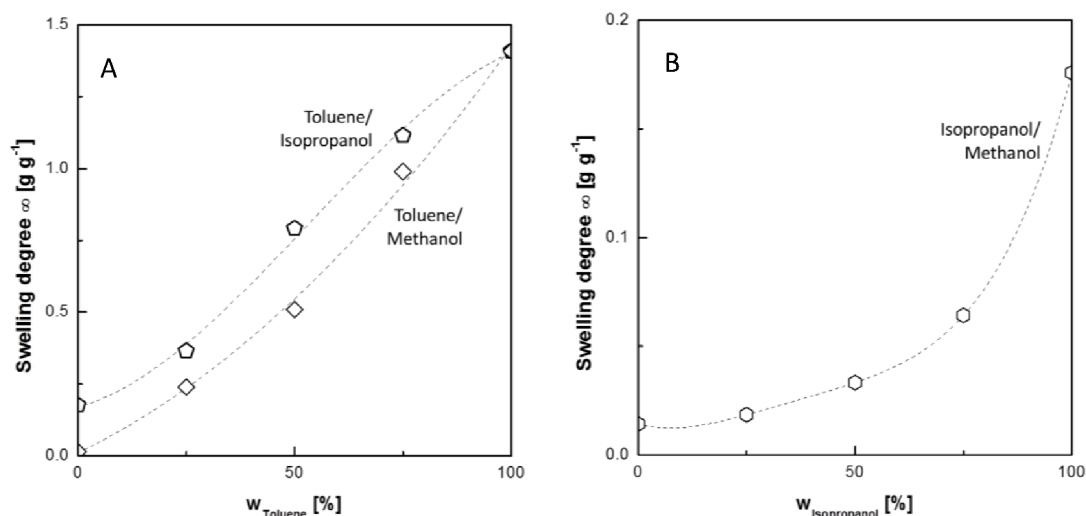


Fig. 6.3: Swelling degrees at equilibrium state ($SD(\infty)$) as a function of toluene (A) or isopropanol (B) weight fraction using different toluene/isopropanol (A), toluene/methanol (A) or isopropanol/methanol (B) mixtures.

The same trend was observed for both mixtures: With increasing toluene amount swelling of PDMS increases due to the high affinity of toluene to PDMS. Furthermore, an almost linear correlation was observed using these mixtures over the entire concentration range.

Also, the swelling behavior of PDMS using isopropanol/methanol mixtures was investigated. Fig. 6.3B illustrates the correlation between swelling degree at equilibrium state and isopropanol amount in the binary mixtures with methanol.

Swelling degrees of PDMS using isopropanol, methanol as well as their mixtures were several times lower compared with swelling degrees of PDMS using toluene or toluene-rich mixtures. For their solvent mixtures, the swelling degree increases with increasing isopropanol amount in a highly non-linear manner with a sharp increase after 75 wt.-% isopropanol.

5.3.3 Influence of different solutes on swelling of PDMS

Sorption experiments with a selection of different solutes were carried out in order to cover three different solute classes. These selected solutes are separately dissolved in the three solvents toluene, isopropanol and methanol. Swelling degree and partition coefficients were determined like it is described in section 5.2.2.

Toluene

Three different polyethylene glycols (PEG200, PEG400, PEG600), myristic acid (MyrAc) and n-alkanes with different chain length ($C_{10}H_{22}$ (C10), $C_{16}H_{34}$ (C16), $C_{24}H_{50}$ (C24)) were separately dissolved in pure toluene. Fig. 6.4A compares different overall swelling degrees of any solute over time with the swelling degree of PDMS using only pure toluene. No significant change could be observed for the swelling behavior of PDMS when solutes were added to the solvents.

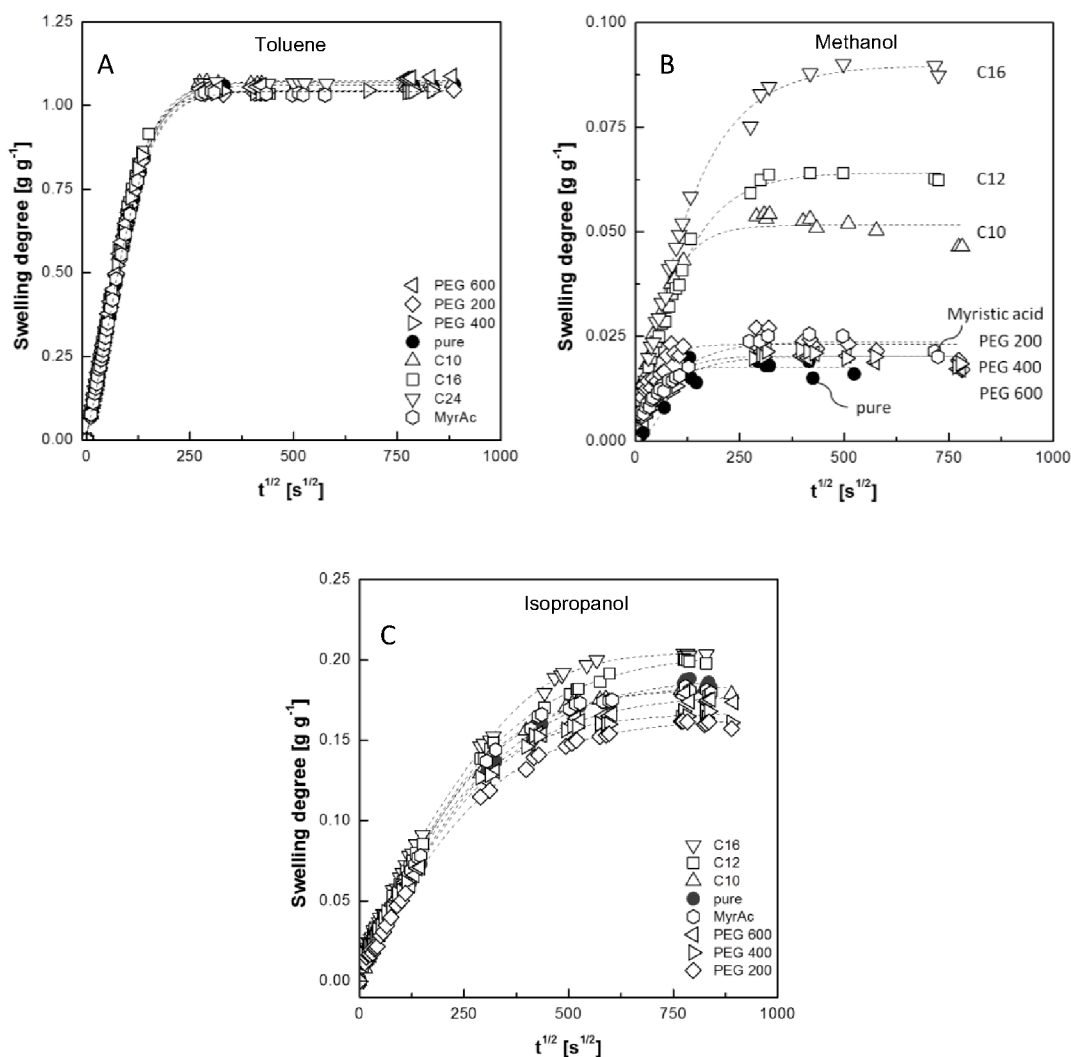


Fig. 6.4: Swelling degree of PDMS using different solution of different PEGs, n-alkanes and myristic acid (MyrAc) in toluene (A), methanol (B) and isopropanol (C) over time

The amount of solute in the PDMS can be obtained after solvent evaporation from the weight difference PDMS before and after the sorption experiment. Table 6.4 summarizes the solute weight uptake for the investigated solutes expressed as concentration of each solute in the polymer or partition coefficient. Table 6.4 also gives the differences of solubility parameters and measured retentions of these solutes, the latter being reported in chapter 2.

Table 6.4: Comparison between swelling degree at equilibrium state ($SD(\infty)$), partition coefficient (K_i) and retentions at 30 bar TMP of different solutes dissolved in toluene

Solute	$w_{\text{Solute,Membrane}}$ (%)	K_{Solute} (-)	$ \delta_{\text{PDMS}} - \delta_{\text{Solute}} $ ($\text{MPa}^{0.5}$)	Retention (%)
PEG 200	0.24	0.193	8.2	43.03
PEG 400	0.08	0.066	7.7	74.14
PEG 600	0.20	0.161	5.0	84.87
Myristic acid	0.62	0.500	2.0	63.5
$\text{C}_{16}\text{H}_{34}$	1.15	0.917	1.0	31.46
$\text{C}_{24}\text{H}_{50}$	1.05	0.838	1.2	65.38

In general, the observed sorption of the hydrophilic PEGs is lower compared to the hydrophobic n-alkanes, while the partition coefficient of myristic acid is between these both solute classes. The PEGs have the largest difference in solubility parameter and their retentions are high. The alkanes show lower values in solubility parameter difference, hence their retentions are lower as well. Within a class of solutes the influence of molar volume and hence diffusion coefficient becomes apparent. As smaller molecules have larger diffusion coefficients, their retention decreases with decreasing molar volume.

Methanol

Fig. 6.4B illustrates the swelling degree over time using different solutes dissolved in pure methanol. In general, the swelling degree remains lower compared to measurements with toluene. No significant differences could be observed between measurements using pure methanol and measurements using solutions with different PEGs or myristic acid in methanol. In contrast, for the different n-alkanes the observed swelling degrees increased significantly and an increase with increasing chain length was observed. Higher affinities of these solutes to PDMS can be concluded and correlated with smaller differences in solubility parameters.

Fig. 6.5A summarizes the swelling degrees at equilibrium state ($SD(\infty)$) as a function of molecular weights of the investigated solutes. The values of $SD(\infty)$ using different PEGs are lower compared with that of pure methanol, which is in line with the reported retention discussed in chapter 2: PEGs were retained by the membrane up to 95 %. Furthermore higher $SD(\infty)$ -values for PDMS using solution of n-alkanes in methanol compared to pure methanol are shown in Fig. 6.5A. In comparison with the previously presented retention of n-alkanes dissolved in methanol, their higher sorption values in PDMS give a consistent interpretation: because of preferential sorption, n-alkanes were enriched in the permeate

and negative retentions were observed. Moreover, decreasing retentions with increasing chain length were reported in chapter 2. Swelling measurements are also consistent with these results due to increasing swelling degrees with increasing chain length. For instance the measured $SD(\infty)$ value using $C_{16}H_{34}$ as solute is 0.08 g g^{-1} which is one and a half times higher compared with the $SD(\infty)$ value using $C_{10}H_{22}$ as solute (0.05 g g^{-1}). This is in line with the retention measurements: $C_{16}H_{34}$ is retained to -40 % while $C_{10}H_{22}$ is retained to -25 %.

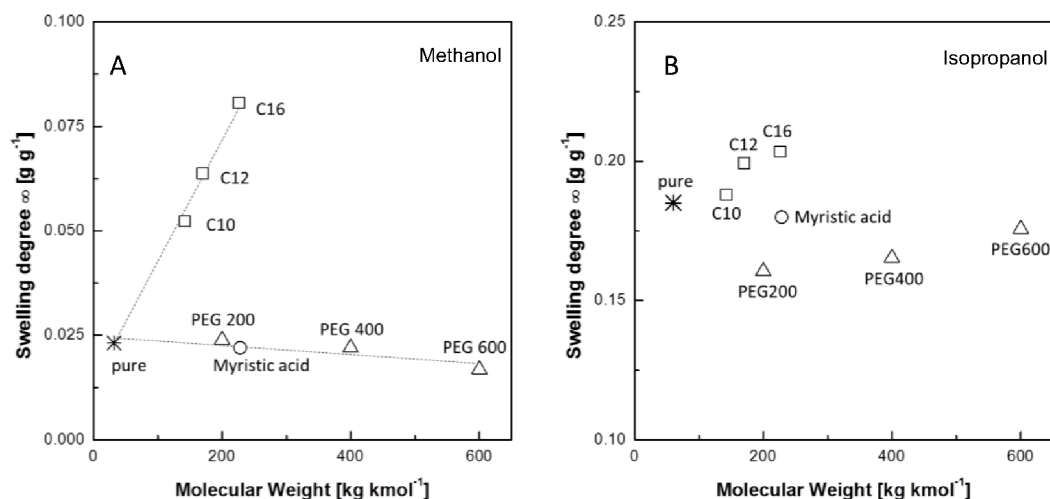


Fig. 6.5: Swelling degree at equilibrium state as a function of molecular weight using solution of different solutes in methanol (A) or isopropanol (B)

Isopropanol

Swelling behavior of PDMS was investigated as well for solutions of previously described solutes in isopropanol. Fig. 6.4C shows the observed swelling degree over time. Only a small change in swelling degree was observed, comparing the swelling degree for the pure isopropanol as compared to mixture containing n-alkanes, PEGs or myristic acid. Fig. 6.5B illustrates the swelling degree at equilibrium state in a range between 0.1 and 0.25 g g^{-1} in correlation to the molecular weights of the used solvents. For n-alkanes with different chain length, swelling degrees at equilibrium state were higher compared to pure isopropanol: it increases with increasing chain length. However, less swelling was observed using different PEGs and myristic acids compared with measurements using pure isopropanol. These results are consistent with retention measurements: negative retentions were observed using n-alkanes, while positive and high retentions were measured for different PEGs.

In order to visualize this correlation between retention and swelling behavior, Fig. 6.6 shows the retentions of different PEGs and n-alkanes as a function of the difference between swelling degree in the mixture and pure solvent. Using solution of PEGs in isopropanol lower swelling degrees were observed compared to the solvent and high retentions were measured. In contrast, higher sorption of the solute compared to the solvent was observed using different n-alkanes. In general, this clarifies the importance of solvent/solute-relation: lower swelling degrees using dissolved solutes compared to pure

solvents results in positive retention, while higher swelling degrees compares to the solvent leads to low or even negative retentions.

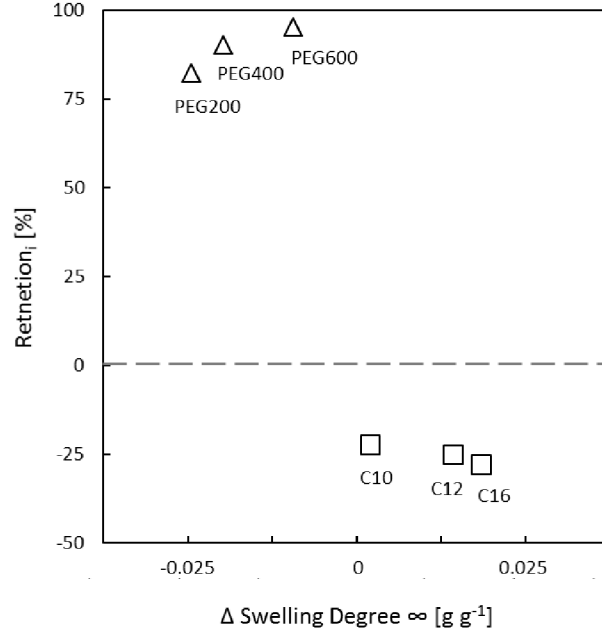


Fig. 6.6: Measured retentions of PEGs and n-alkanes at 30 bar TMP as a function of the difference between swelling degree at equilibrium state of solute and solvent (SD^∞ (Solute) - SD^∞ (Solvent))

5.4 Interpretation using the Flory Huggins theory

Swelling data were also used to calculate Flory-Huggins interaction parameter. According to the Flory-Huggins theory activities a are related as follows to volume fraction ϕ in the membrane using a binary system consisting of one component (1) and polymer (P) [26].

$$\ln(a_1) = \ln\phi_1 + \left(1 - \left(\frac{V_1}{V_P}\right)\right) \phi_P + \chi_{1P} \phi_P^2 \quad (3)$$

Assuming that $V_P \gg V_1$ and $a_1 = 1$ based on swelling a polymer in pure solvent, the polymer-solvent interaction parameter χ_{1P} can be calculated as follows:

$$\chi_{1P} = -\frac{\ln \phi_1 + \phi_P}{\phi_P^2} \quad (4)$$

Using a ternary mixture with two components 1 and 2 and one polymer p the following extensions was defined by Flory [26]:

$$\ln a_1 = \ln\phi_1 + (1 - \phi_1) - \left(\frac{V_1}{V_2}\right) \cdot \phi_2 - \left(\frac{V_1}{V_P}\right) \cdot \phi_P + \left((\chi_{1,2}\phi_2 + \chi_{1,P}\phi_P) \cdot (\phi_2 + \phi_P)\right) - \chi_{2,P} \cdot \left(\frac{V_1}{V_2}\right) \cdot \phi_2 \cdot \phi_P \quad (5)$$

$$\ln a_2 = \ln \phi_2 + (1 - \phi_2) - \left(\frac{V_2}{V_1}\right) \cdot \phi_1 - \left(\frac{V_2}{V_P}\right) \cdot \phi_P + \left(\left(\chi_{1,2} \phi_1 \cdot \left(\frac{V_2}{V_1}\right) + \chi_{2,P} \phi_P \right) \cdot (\phi_1 + \phi_P) \right) - \chi_{1,P} \cdot \left(\frac{V_2}{V_1}\right) \cdot \phi_1 \cdot \phi_P \quad (6)$$

$$\phi_1 + \phi_2 + \phi_P = 1 \quad (7)$$

In order to predict volume fraction in the membrane, interaction parameter χ_{1P} , χ_{2P} , χ_{12} have to be known. Since swelling measurements were conducted with pure solvents (toluene, isopropanol and methanol) $\chi_{\text{solvent,Polymer}}$ could be determined using equation (4). Table 6.5 summarizes these interaction parameters.

Table 6.5: $\chi_{\text{solvent,Polymer}}$ calculated using equation (4)

	Toluene	Isopropanol	Methanol
χ_{IP}	0.73	1.29	2.73

The interaction parameter follow the order $\chi_{\text{Toluene,PDMS}} < \chi_{\text{Isopropanol,PDMS}} < \chi_{\text{Methanol,PDMS}}$. The closer the value of chi to 0.5, the better is the solvent quality and the higher will be the degree of swelling. Hence, toluene's interaction with PDMS is highest, followed by isopropanol: methanol has the lowest affinity.

To determine solute-polymer interaction parameter and solute-solvent interaction parameter an equation based on Hansen solubility parameter δ was used [20]:

$$\chi_{i,j} = \alpha \frac{V_1}{RT} \left((\delta_{i,d} - \delta_{j,d})^2 + 0.25(\delta_{i,p} - \delta_{j,d})^2 + 0.25(\delta_{i,hb} - \delta_{j,hb})^2 \right) \quad (8)$$

With respect to a systematic investigation of different α -values by Lindvig et al. [27] a value of 0.6 is assumed in this work. Table 6.6 summarizes the calculated interaction parameter.

Table 6.6: Calculated interaction parameter $\chi_{\text{Solute,Polymer}}$ and $\chi_{\text{Solvent,Solute}}$

Solute	Solvent			
		Toluene	Isopropanol	Methanol
	χ_{IP}	χ_{ij}	χ_{ij}	χ_{ij}
PEG200	1.10	0.04	1.19	1.38
PEG400	2.19	0.04	1.20	1.39
PEG600	3.23	0.04	1.22	1.41
C ₁₀ H ₂₂	0.68	0.12	1.40	1.59
C ₁₂ H ₂₆	0.80	-	1.41	1.60
C ₁₆ H ₃₄	1.09	0.11	1.42	1.61
C ₂₄ H ₅₀	1.44	0.07	-	-
Myristic acid	1.38	0.12	0.58	0.91

These values clearly show that the interaction between toluene and PDMS is higher than the interaction between the investigated solutes and PDMS. This indicates a preferential sorption of toluene which could explain the before described swelling degrees and also the

positive retentions. Using methanol as solvent, interaction between different n-alkanes and PDMS is higher than the interaction between methanol and PDMS. This leads to the assumption that n-alkanes are preferential sorbed into the membrane and due to this negatively retained. This is consistent with the above discussed swelling degrees. However, using PEG 200 or PEG 400 interaction parameter between these solutes and PDMS were also slightly lower than $\chi_{\text{Methanol,PDMS}}$, which is not consistent with measured retention or swelling behavior. This indicates that also solvent-solute interaction and diffusion have to be taken into account.

Using these calculated interaction parameters and the Flory-Huggins theory for ternary mixtures (Equation (5), (6)), volume fractions can be predicted. Table 6.7 compared the experimental determined volume fraction with calculated volume fraction using the above described Flory-Huggins theory.

Table 6.7: Comparison of experimental determined or calculated (Flory-Huggins (FH)) volume fractions

	ϕ_{Solvent}		ϕ_{Solute}		ϕ_{PDMS}	
	exp.	FH	exp.	FH	exp.	FH
Toluene +						
C ₁₀ H ₂₂	0.553	0.541	0.001	0.005	0.445	0.451
C ₁₆ H ₃₄	0.553	0.540	0.015	0.002	0.432	0.457
C ₂₄ H ₅₀	0.553	0.543	0.013	0.008	0.434	0.459
Isopropanol +						
C ₁₀ H ₂₂	0.191	0.027	0.005	0.020	0.804	0.953
C ₁₂ H ₂₆	0.191	0.027	0.0045	0.020	0.804	0.953
C ₁₆ H ₃₄	0.191	0.026	0.011	0.019	0.798	0.955
Methanol +						
C ₁₀ H ₂₂	0.029	0.027	0.001	0.020	0.970	0.953
C ₁₂ H ₂₆	0.029	0.027	0.011	0.020	0.960	0.954
C ₁₆ H ₃₄	0.029	0.026	0.057	0.019	0.914	0.955

For clarity reasons only different n-alkanes dissolved in toluene, isopropanol or methanol are presented. Experimental volume fractions were determined assuming constant solvent volume fraction calculated in the binary mixture (pure solvent, PDMS). Comparing these experimental determined solvent volume fractions with these calculate using the Flory-Huggins theory, a maximal relative deviation of 12 % was observed. The deviations between experimental determined volume fractions of PDMS and calculated PDMS volume fraction were also very low. However, the solute volume fraction was insufficient predicted using the above described method.

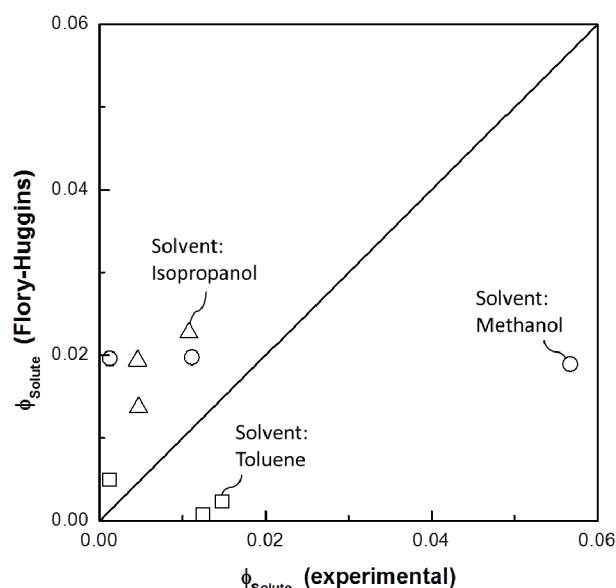


Fig. 6.7: Comparison of experimental or calculated (Flory-Huggins theory (FH)) volume fraction of different n-alkanes in PDMS dissolved in toluene ($\square$), methanol (O) or isopropanol (Δ)

Fig. 6.7 compared the experimental and the calculated volume fractions of different n-alkanes dissolved in toluene, isopropanol or methanol. Most of the solute volume fractions were overestimated using the Flory-Huggins theory. Only $\phi_{C_{16}H_{34}}$ or $\phi_{C_{24}H_{50}}$ were underestimated using toluene or methanol as solvent.

The described methods using Hansen solubility parameter in order to calculate Flory-Huggins interaction parameter gives adequate results for ϕ_{Solvent} and ϕ_{PDMS} whereas ϕ_{Solute} is insufficient calculated with this method. Hence, future thermodynamic research needs to focus on the prediction of solute solubility in polymers in the presence of solvents.

5.5 Conclusion

In this study swelling behavior of PDMS using different solvent and solvent mixtures were investigated. The influence of different solutions of n-alkanes, PEGs or myristic acids in the investigated solvents on swelling degrees of PDMS was discussed.

A clear correlation between swelling degree and solubility parameter was found: the higher the differences of solubility parameter of the component and PDMS the lower the swelling degree of PDMS. This dependency could be related to permeability and retention measurements. A lower solubility of one component results in lower permeability. Solutes with higher sorption tendency compared to the used solvents are enriched in the permeate and negative retention as described in other publications can be correlated. The swelling measurements were also used to calculate Flory-Huggins interaction parameter using an

approach based on solubility parameter. It was found that higher interaction leads to higher swelling degrees and due to this mostly to negative retentions. However, the predicted volume fractions of solutes using the Flory-Huggins theory were insufficient and require further improvements.

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CHAPTER 6

DO SILICON-BASED MEMBRANES PERMEATE OR REJECT SALTS?

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6.1 Introduction

The potential and the application range for nanofiltration increased steadily over the last decades. Nanofiltration processes in water application are often reported and implemented in large industrial systems [1-3]. New application opportunities in organic solvent permeation have emerged by developing solvent resistant membranes [4-7]. Non-porous silicone-based membranes are recently developed as robust membrane materials [8, 9]. However, their mass transport properties have only been investigated for classical single solvent systems or solvent mixtures with organic solutes. Yet, there exists a class of potential application which is little investigated so far: mixed solvents of alcohols and water containing different salts. Such mixtures often occur in pharmaceutical and agro-chemical synthesis processes. Here we report a comprehensive experimental study on the retention and flux behavior of non-porous silicone-based composite nanofiltration membranes. We contrast these experimental findings to the behavior of state-of-the-art hydrophilic polyamide composite membranes.

6.2 Background

Water, methanol, ethyl acetate and toluene were used as pure solvents in the experimental study presented by Yang et al. [10]. Retentions are reported for one negatively charged (Orange II), one positively charged (Safranin O) and one neutral (Solvent Blue 35) solutes, using different hydrophilic and hydrophobic membranes. The observed retentions of all solutes were higher in aqueous solution than in organic solvents. Complexation of water molecules with the solutes is suggested to enlarge the effective solute size of these molecules [10].

Zhao and Yuan [11] presented a similar study. Ethanol as an additional solvent and different organic charged and neutral solutes in a range of 180 - 600 kg kmol⁻¹ were used. A higher retention was found for all solutes in aqueous solution using Desal-DK, MPF-44 membranes but also hydrophobic Starmem membranes. However, using these Starmem membranes the retention is in most cases lower compared with the hydrophilic membranes [11].

Hydrophilic and hydrophobic membranes were compared using binary water, methanol and ethanol mixtures by Geens et al. [12]. Using raffinose as solute, higher retention in water occurs as compared to any alcohol solution. This observation was explained by a change in solvent-solute-membrane interactions as well as a reduced hydration shell decreasing the effective solute and decreasing the retention. Solvation of the membrane was also discussed, while hydrophobic membranes are more stable in organic solvents than hydrophilic membranes [12, 13].

Bowen et al. [14, 15] characterized nanofiltration membranes in aqueous solutions by using salts as well as uncharged solutes and developed mathematical models for a predictive

purpose. In their experimental section retention measurements using a PES-membrane and KCl, NaCl as well as LiCl as salts were carried out. The observed retention follows the order $R(\text{KCl}) > R(\text{NaCl}) > R(\text{LiCl})$ due to increasing diffusivity of the cations [14, 15].

Peeters et al. [16] compared the retention of Na_2SO_4 , CaCl_2 and NaCl using 21 different polymeric membranes and lab-made $\gamma\text{-Al}_2\text{O}_3$ membranes. Different salt retentions were observed following either the order $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{CaCl}_2)$ for negatively charged membranes or the order $R(\text{CaCl}_2) > R(\text{NaCl}) > R(\text{Na}_2\text{SO}_4)$ for positively charged membranes due to Donnan exclusion mechanism. The order $R(\text{Na}_2\text{SO}_4) > R(\text{CaCl}_2) > R(\text{NaCl})$ was also identified for some membranes which was explained by differences in diffusion coefficients [16].

A characterization of polymeric nanofiltration membranes with aqueous solution of Na_2SO_4 , CaCl_2 and NaCl was also described by Boussu et al. [17]. Retentions for each salt following the order $\text{Na}_2\text{SO}_4 > \text{CaCl}_2 > \text{NaCl}$ were observed as well and explained similar to Peeters et al. due to differences in dimensions of the hydrated ions [17].

Déon et al. [18] developed and validated a transport model considering a charge distribution along the membrane pores. The experimental study shows a higher retention of CaCl_2 than of NaCl in aqueous solution using a Desal 5DK membrane. A stronger influence of divalent cations (Ca^{2+}) than of monovalent cations (Na^+) on the dielectric constant was suggested to influence this behavior. Using solutions containing divalent cations, the dielectric constant as well as the retention of the Desal 5DK membrane increases [18].

The retention of NaCl was investigated in water and water/ethanol mixtures up to 13 vol.-% ethanol by Labanda et al. [19]. Using a Toray UTC-70UB nanofiltration membrane the observed NaCl retention decreases with increasing amount of ethanol. A decreasing dielectric constant with higher ethanol content is suggested to modify the interactions between NaCl and membrane [19].

Recently Geise et al. [20] published a review paper regarding the water and salt transport properties of polymeric materials. The paper summarizes the influence of solvation/hydration and dissociation on different salt permeabilities. Also the differences in salt transport depending on the water uptake were extensively discussed. [20]

Marchetti et al. [21] presented experimental results using different single salts and acids (NaCl, KCl, LiCl, NaI, NaF, HCl, trifluoroacetic acid, TFA-H) dissolved in water but also in various organic/water mixtures. Using hydrophilic ceramic membranes ($\text{TiO}_2/\text{Al}_2\text{O}_3$), an increasing retention of NaCl in pure water with increasing solvent flux is established, while the retention of NaCl decreases with increasing solvent flux in organic/water mixtures. Indeed negative NaCl rejections were observed. Hansen solubility parameters were used to explain this observation as well as the differences in retention using various cations and anions. Preferential solvation of salts in solution changes the molecule hydration degree and the hydrophilic/hydrophobic interaction with the membrane. Due to this change, different salt retentions could be explained [21].

In this chapter desalination of different salts in binary mixtures of methanol and water using a non-porous silicone-based nanofiltration membrane in comparison to a commercial, hydrophilic PA-based membrane is investigated. We ask the question whether a very hydrophobic material such as the used silicone-based membrane material permeates or rejects salts when dissolved in different aqueous/methanol mixtures. Since the solvent permeabilities for water or methanol are low, composite membranes were analyzed as opposed to thicker silicone-based films without a support membrane. In some cases the behavior for the hydrophobic membrane is juxtaposed to hydrophilic polyamide based composite membranes for comparison.

6.3 Experimental

6.3.1 Materials

Two different composite membranes were tested in this study. On the one hand, as a hydrophilic membrane, a commercial available Desal-DK membrane from Osmonics made of thin film polyamide active layer, sulfonated polysulfone intermediate layer and microporous polysulfone support layer [22, 23]. As a hydrophobic membrane a composite membrane made of polyimide as support layer and silicone acrylates as active layer is used. A similar one is described in the patent of Evonik Industries [24] and thoroughly characterized in [25]. To compare both membranes the Desal-DK membrane is called "PA-based" and the hydrophobic membrane is abbreviated "silicone-based".

Methanol and deionized water were used as solvent in this work. Table 6.1 summarizes important properties of these solvents.

Table 6.1: Properties of used solvents [12, 26]

	MW (kg kmol ⁻¹)	V _{mol} (cm ³ mol ⁻¹)	Viscosity (mPa s)	Dielectric constant (-)
Water	18.02	18.07	0.93	82.75
Methanol	32.04	40.56	0.57	32.04

Geens et al. [12] investigated the viscosity and the dielectric constant of methanol and water in their mixture. Increasing methanol amount decreases the dielectric constant. A maximum was observed regarding the viscosity at 24 mol.-% methanol. Detailed description and further information regarding viscosities, dielectric constants as well as diffusion coefficients of the solvent depending on the composition of methanol and water can be found in the Appendix.

Retention measurements were carried out with three different salts: NaCl, LiCl and CaCl₂. The most important properties of these salts are summarized in Table 6.2.

Table 6.2: Properties of used salts [16, 27-30] (Solubilities were measured at 298 K)

	D_{∞} ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	MW (kg kmol^{-1})	V_{mol} ($\text{cm}^3 \text{ mol}^{-1}$)	Solubility in water (wt.-%)	Solubility in methanol (wt.-%)
NaCl	1.61	58.44	26.93	26.46	1.375
LiCl	1.37	42.39	20.48	84.65	43.58
CaCl ₂	1.45	110.98	51.61	74.50	

Table 6.3 shows the diffusivity as well as the stokes and the hydrated radii of each ion, while the order of hydration values for the monovalent cations with chloride as anion follows the order $\text{Li}^+ > \text{Na}^+$ [31].

Table 6.3: Properties of used cations and anions [14, 16, 27, 32]

	D_{∞} ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	Stokes radius (Å)	Hydrated radius (Å)
Na^+	1.33	1.84	3.58
Li^+	1.03	2.38	3.82
Ca^{2+}	0.92	3.10	4.12
Cl^-	2.03	1.21	3.32

6.3.2 Experimental procedure

The cross-flow set-up shown in Fig. 6.1 delivered by Evonik MET was used to carry out the different flux and retention experiments. Two test cells with a membrane area of 52.81 cm^2 each are connected in series. Nitrogen is used to pressurize the system while a gear pump (60 l h^{-1}) is used to recirculate the feed and retentate stream.

Before starting an experiment, the hydrophobic membrane was first immersed in methanol for 24 h and pressurized for 30 minutes. Different precondition methods for the Desal-DK membrane were tested but show no significant influence on the flux nor on the retention.

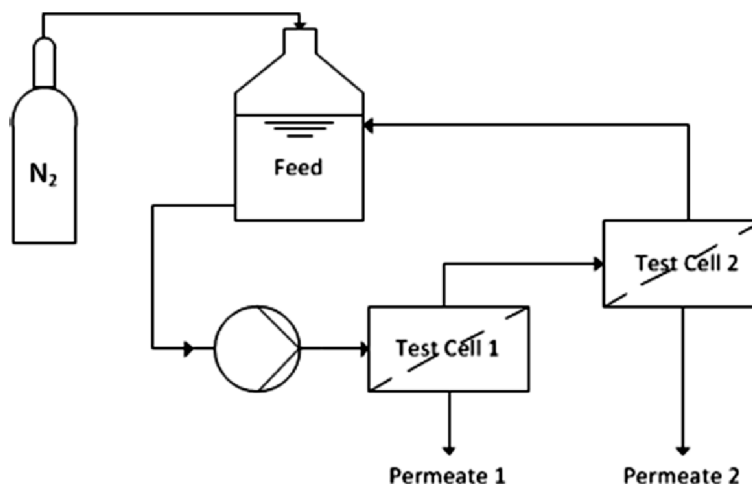


Fig. 6.1: Schematic of the cross-flow filtration set-up

Prior to the retention measurements, the pure solvent fluxes of water and methanol as well as the fluxes of the binary mixtures were investigated. First of all, the pure methanol flux was measured at 20, 30, 40 and 50 bar transmembrane pressure (TMP) before adding water. Five different mixtures (90 wt.-%, 80 wt.-%, 70 wt.-%, 60 wt.-%, 25 wt.-% methanol) were studied at 30 and 50 bar TMP before pure water fluxes were measured at 20, 30, 40 and 50 bar TMP. The same experimental procedure was carried out for both membranes and for the retention measurements. For these measurements 1 wt.-% of the investigated salt was dissolved in pure water, in methanol as well as in the binary mixtures as described before.

6.4 Analytics

The amount of water and methanol in the binary mixture was determined with a refractometer (Optilab DSP) delivered by Wyatt Technology.

In order to determine the concentrations of the different salts dissolved in water, methanol or mixtures of them, a WTW Inolab Cond 7110 was used to carry out conductivity measurements. Conductivities of the investigated salts NaCl, LiCl and CaCl_2 in pure solvents are shown in Fig. 6.2.

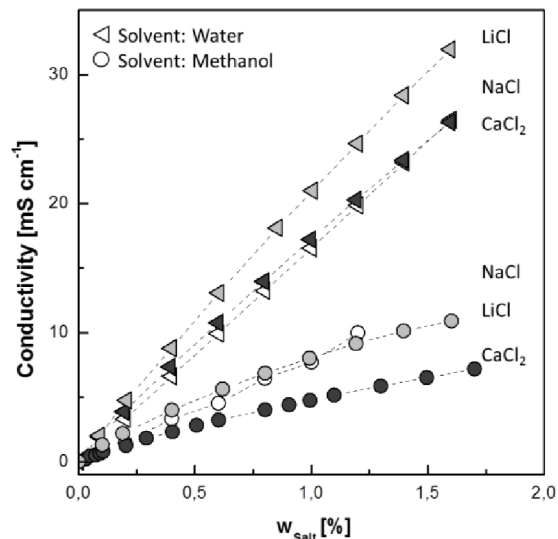


Fig. 6.2: Measured conductivity of NaCl, LiCl and CaCl₂ in water (Δ) and methanol (○) as a function of salt concentrations

Using the conductivities (L), the dissociation constants (K) as well as dissociation degrees (α) can be calculated using the following equations [33]:

$$L = K \Lambda_0^2 \left(\frac{C}{L} \right) - K \Lambda_0 \quad (1)$$

and

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{L}{\Lambda_0 C} \quad (2)$$

where Λ_0 represents the limiting conductance and C the molar concentration. Fig. 6.3A shows the conductivities measurements for 1 wt.-% NaCl, LiCl or CaCl₂, dissolved in different water/methanol mixtures. The degree of dissociation is then calculated and illustrated in Fig. 6.3B. Further conductivity measurements using water/methanol mixtures and different salt concentration are given in the appendix.

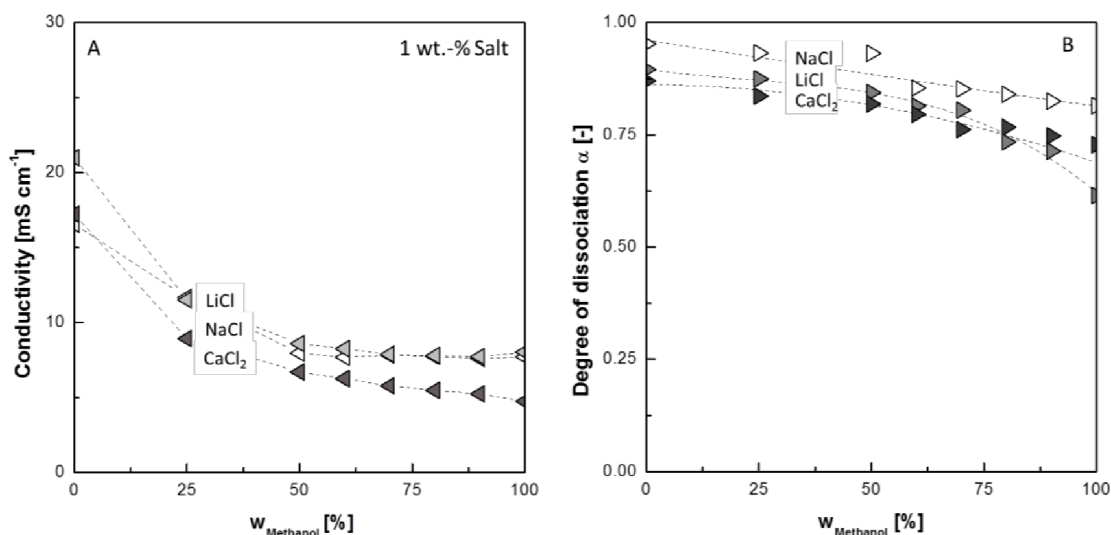


Fig. 6.3: Measured conductivity (A) and calculated degrees of dissociation (B) of 1 wt. % NaCl (white symbols), LiCl (gray symbols) or CaCl₂ (black symbols) dissolved in different water/methanol mixtures

6.5 Results and discussion

6.5.1 Water and methanol flux

Pure water and methanol fluxes were measured using the hydrophobic, silicone-based membrane in comparison with the hydrophilic PA-based membrane. The results of this investigation are shown in Fig. 4. The flux of both pure water and methanol is considerably lower for the silicone-based membrane (Fig. 4 A) as compared to the PA-based membrane (Fig. 4 B), due to the difference in hydrophobicity of the membrane materials: The affinity of polar solvents to the hydrophilic, PA-based membrane is much higher than the affinity of these polar solvent to the hydrophobic, silicone-based membrane. However, the hydrophobic membrane is methanol selective while the hydrophilic membrane is water selective. Since the polarity of methanol is less than that of water, the affinity of methanol to the non-polar hydrophobic membrane material is higher. As a consequence the pure methanol flux is up to 10 kg m⁻²h⁻¹, while the water flux is very low at around 0.4 kg m⁻²h⁻¹. In contrast, using the hydrophilic PA-based membrane both fluxes are much higher. The maximum flux was measured using water as solvent. At 30 bar TMP, the observed methanol flux is around 50 kg m⁻²h⁻¹ while the water flux reaches 136 kg m⁻²h⁻¹. This again relates to the difference in polarity of the solvents in comparison to the hydrophilic character of the membrane material.

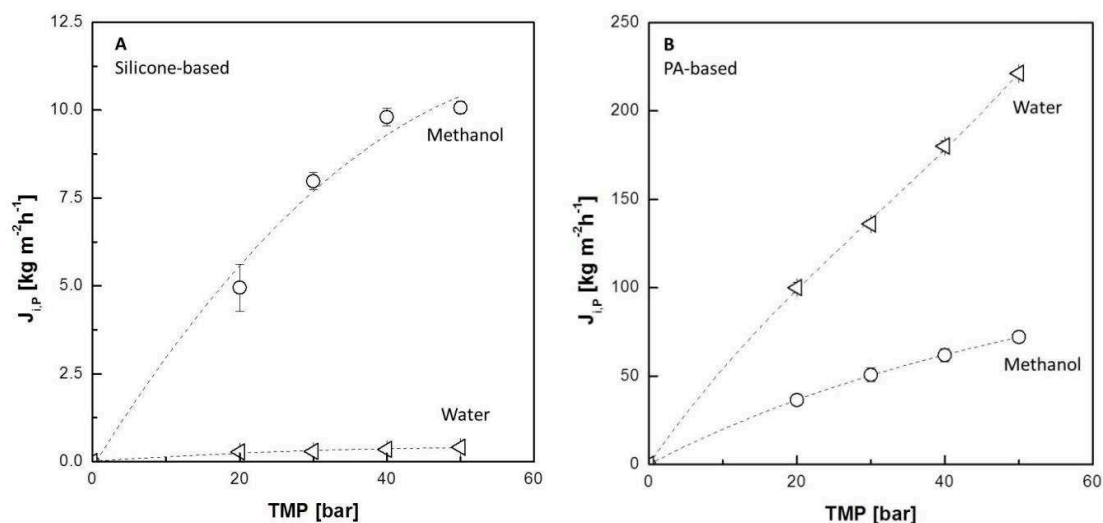


Fig. 6.4: Pure water (<) and methanol (o) flux using a silicone-based (A) or a PA-based membrane (B)

Measurements with different binary mixtures were carried out as well with both membranes. Fig. 6.5 A shows the partial fluxes of methanol and water using the silicone-based membrane as a function of the methanol mass fractions in the mixture with water. No significant change in fluxes compared with pure water as solvent was observed, while using a mixture with high amount of water (25 wt.-% methanol). Further addition of methanol leads to an increase of the methanol flux at least up to $8 \text{ kg m}^{-2} \text{h}^{-1}$ in pure methanol. The partial flux of water shows only a slight increase up to 60 wt.-% methanol up to around $0.75 \text{ kg m}^{-2} \text{h}^{-1}$ but decreases again. In general the partial flux of water is lower than the flux of methanol over the entire concentration range. However, the partial flux of methanol is reduced to 70 % by adding only 10 wt.-% water.

Similar observations were made by Geens et al. [12]. They explain such a behavior due to the high polarity of water: significant changes were observed by adding only a small amount water. This leads to a lower affinity of the mixture to the hydrophobic membrane material and a considerable decline of the flux.

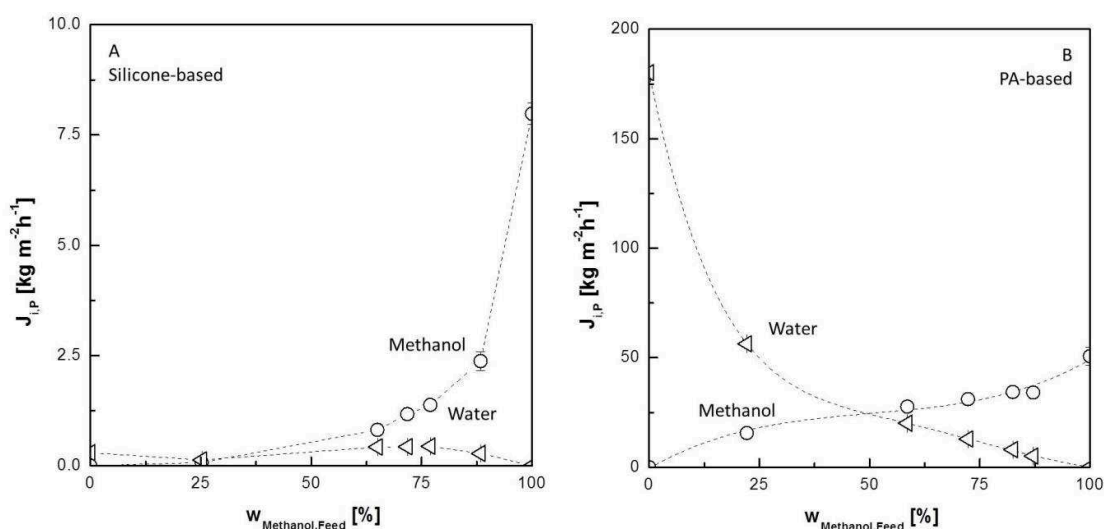


Fig. 6.5: Partial fluxes of water ($\triangleleft$) and methanol (o) at 30 bar and room temperature using a silicone-based membrane (A) or a PA-based membrane (B)

Fig. 5 B shows also the partial flux of water and methanol for the PA-based membrane. The observed fluxes show an opposite behavior compared to the behavior of the silicone-based membrane: the partial flux of water declines dramatically by adding only 25 wt.-% methanol and shows a further decrease with higher amount of methanol. In contrast, the methanol flux increases with increasing methanol and become even higher than the partial flux of water beyond 60 wt.-% methanol. Using a hydrophilic PA-based membrane the above described effect, namely the partial flux changes for different water/methanol mixtures, is reversed. This is in line with the conclusions drawn in many previous publications that the solubility of the solvent in the membrane material is a major factor affecting the overall solvent flux.

6.5.2 NaCl retentions in water and methanol

NaCl retentions were measured in pure water and methanol as well as in the binary mixture of these solvents. Fig. 6.6 compares the retention of NaCl dissolved in pure methanol or water using either the silicone-based or the PA-based membrane.

Retentions of sodium chloride using the PA-based membrane were higher compared to the NaCl retentions of the silicone-based membrane, due to higher affinity of the investigated solvents to the PA-based membrane material. So the ratio of NaCl permeation to solvent permeation is much smaller using the PA-based membrane. Consequently, NaCl retentions of the PA-based membrane were higher due to high solvent affinities.

Furthermore, higher NaCl retentions were measured over the entire pressure range while using methanol as solvent compared to water for both membranes. Retentions up to 88 % or 75 % were reached using the hydrophilic or hydrophobic membrane respectively for sodium chloride dissolved in methanol. For water as a solvent, NaCl is retained only for

60 % using the PA-based or to 23 % using the silicone-based membrane. With respect to the higher NaCl retention in methanol compared with the retention in water, we suggest less dissociation and ion-pair formation (association) in the organic solvent resulting in a lower NaCl transport rate [21, 34, 35].

Using the conductivity measurements and equations (3) and (4), the dissociation degree α of NaCl dissolved in water or in methanol can be calculated. Since the degree of dissociation of 1 wt.-% NaCl is higher in aqueous solution (0.95) than in methanol (0.82) solution, less ions are formed but ion pair formation occurs. The ion pair formation inside the solution can cause a reduce partitioning into the polymer as well as a decrease in overall diffusivity through the polymer network. Both lead to a reduced ion flux and hence to higher retention.

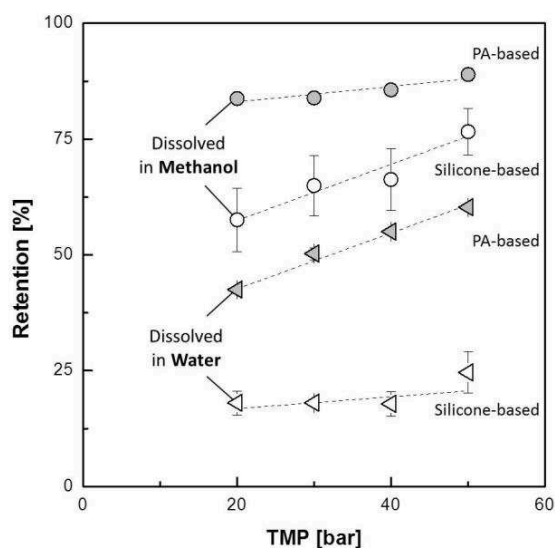


Fig. 6.6: Retention of NaCl dissolved in water ($\blacktriangle$) and methanol (o) at 30 bar and room temperature using a PA-based (filled symbols) or a silicone-based (unfilled symbols) membrane

This effect is also illustrated in Fig. 6.7. Here NaCl retentions as a function of varying water/methanol mixtures are shown for the hydrophilic or hydrophobic membrane material.

For the pure solvents the retention of the PA-based membrane is higher compared with the retention of the silicone-based membrane. For the PA-based membrane, the retention scales slightly convexly for the mixtures between the retention values for the pure solvents. The addition of the second solvent affects the retention significantly and retentions drop to a minimum of about 28 %. This significant influence of methanol was also seen before in Fig 5B which shows the partial fluxes as a function of water/methanol mixtures. Here a significant flux decrease with increasing methanol amount was shown. Depending on the total flux also the retention drops significantly, as described before. In contrast, using methanol-rich mixtures, ion-formation occurs, which results in increasing retentions due to bigger molecule size. Both these effects result in a convex retention curve for the PA-based

membrane. However, the silicone-based membrane behaves very differently. Using the silicone-based membrane a significant increase in NaCl retentions with increasing methanol amount was measured. The observation for both membranes holds also for higher pressures. However, data are not shown for clarity reasons.

Interestingly, the development of the salt flux as a function of feed composition is very different as shown in Fig. 6.7B. While the retentions have comparable trends for medium to high weight fractions of methanol, the partial salt flux is very different. While the silicone-based membrane shows an increasing salt flux at higher methanol concentrations, the PA-based membrane shows a decreasing salt flux at high methanol concentrations. Currently, we can only speculate on the reason behind this different behavior. The silicone-based membrane swells significantly at high methanol concentrations which may facilitate NaCl transport. For the PA-based membrane, ion pairing as discussed below may cause an increase in effective molecular size and hence hinder the transport of NaCl.

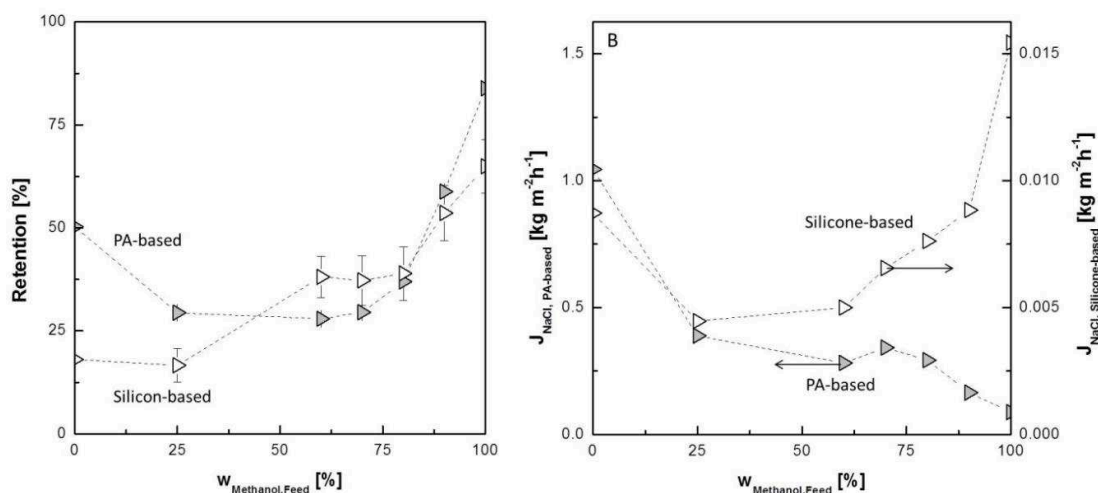


Fig. 6.7: Retention (A) and mass flux (B) of NaCl dissolved in different water/methanol mixtures at 30 bar and room temperature using a silicone-based membrane (unfilled symbols) or a PA-based membrane (filled symbols)

6.5.3 Retentions of different salts using a silicone-based membrane

We continue this study with the analysis of the salt transport properties of the silicone-based membrane using LiCl and CaCl_2 as well. As previously done, retention measurements were also carried out in methanol and water as well as in their mixtures.

Fig. 6.8 compares the retention of the three salts dissolved in pure water or pure methanol. Significantly higher retentions for all salts were measured in methanol than in aqueous solutions.

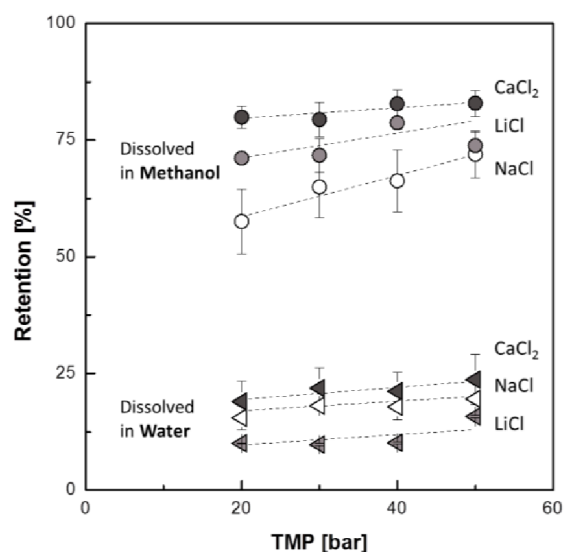


Fig. 6.8: Retentions of NaCl (white symbols), LiCl (gray symbols) and CaCl₂ (black symbols) dissolved in pure water (<) and methanol (o) at different transmembrane pressures and room temperatures using the silicone-based membrane

The methanol flux is 20 times higher than the water flux. Higher methanol solubility in the membrane material compared with that of water governs the permeability (see section 6.5.1). Using water as solvent, the investigated salts permeate the silicone-based membrane to a larger extent. Although the membrane is not swollen by water, ions can permeate: apparently the affinity of the salt ions in the hydrophobic membrane is high enough to partition into the membrane material most likely as undissociated ion pairs. This latter interpretation requires experimental verification through sorption experiments.

In methanol, ion-pair formation can occur and this appears to be correlated to a higher retention in methanol than in water due to the bigger solute sizes. Again conductivity measurements were used to calculate the dissociation constant and the degree of dissociation [33]. Table 6.4 compares the degree of dissociation α using 1 wt.-% salt with the retention at 30 bar TMP. Here the correlation between association and retention is visible: the lower the degree of dissociation the higher the retention.

Table 6.4: Degree of dissociation of different salts dissolved in water or methanol compared with retentions at 30 bar TMP

	NaCl		LiCl		CaCl ₂	
	Water	Methanol	Water	Methanol	Water	Methanol
Degree of dissociation α (-)	0.95	0.82	0.90	0.61	0.87	0.73
Retention (%)	18.1	65.0	13.8	71.1	21.8	86.3

For both solvents, calcium chloride is retained most: as a bivalent salt, calcium chloride has the biggest molar volume as well as the maximum Stokes and hydrated radius. The order of

retention in pure methanol follows the order $R(\text{CaCl}_2) > R(\text{LiCl}) > R(\text{NaCl})$ according to the order of Stokes radii ($r(\text{Na}^+) = 1.8 \text{ \AA}$, $r(\text{Li}^+) = 2.4 \text{ \AA}$, $r(\text{Ca}^{2+}) = 3.1 \text{ \AA}$). The observed retention of lithium chloride is lower than that of sodium chloride in water. So the order in aqueous solution changes: $R(\text{CaCl}_2) > R(\text{NaCl}) > R(\text{LiCl})$. This retention for salts dissolved in water could be correlated with the different molecular weights ($\text{MW}(\text{LiCl}) = 42 \text{ g mol}^{-1}$, $\text{MW}(\text{NaCl}) = 58 \text{ g mol}^{-1}$, $\text{MW}(\text{CaCl}_2) = 111 \text{ g mol}^{-1}$).

Fig. 6.9 shows the influence of solvent mixture on the retention of the investigated salts at a feed pressure of 30 bar TMP. The retention of all three salts CaCl_2 , NaCl and LiCl increases with increasing methanol amount. So the lowest retentions were found in pure water while the highest retention up to 86 % was observed in pure methanol for CaCl_2 . The retention curves of NaCl and CaCl_2 show a similar behavior.

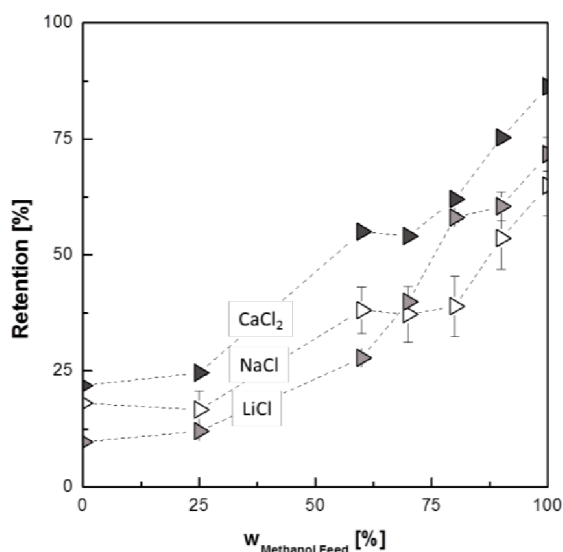


Fig. 6.9: Retentions of CaCl_2 (black symbols), LiCl (gray symbols) and NaCl (white symbols) dissolved in different water/methanol mixtures at 30 bar transmembrane pressure and room temperature using the silicone-based membrane

As the order of retentions of NaCl and LiCl changes for the pure solvents, the retention of lithium chloride intersects the retention curve of sodium chloride at around 60 wt.-% methanol. Using a water-rich mixture LiCl is retained least. But raising the methanol content higher than 60 wt.-% methanol the retention follows the order $R(\text{CaCl}_2) > R(\text{LiCl}) > R(\text{NaCl})$.

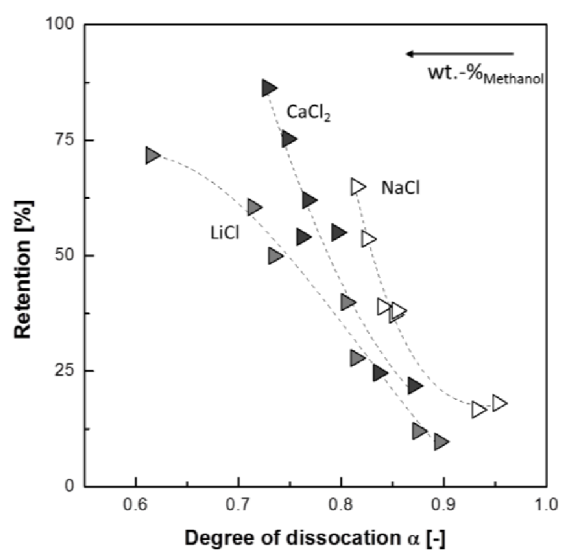


Fig. 6.10: Retention of 1 wt. % CaCl₂ (black symbols), LiCl (gray symbols) and NaCl (white symbols) dissolved in different water/methanol mixtures as a function of dissociation degree using the silicone-based membrane

The degree of dissociation has a strong influence on the retention as shown before. Fig. 6.10 now compares the retention for all three salts in different solvent mixtures. For all three salts, increasing degree of dissociation correlates with a decreasing retention. Sodium chloride shows the highest retentions at constant degree of dissociation.

While the degree of dissociation gives a strong indication for the retention, it is insufficient to fully explain the differences between the salts at equal degree of dissociation. To fully comprehend the permeation of salts through the hydrophobic polymer, one needs to ultimately know the magnitude of partition for the ion pairs as well as the partitioning and its dissociation into the membrane matrix. Then, one needs to know the state of the ions inside the membrane: will equal, extra or less ion pairing occur when the ions transfer from the solution to the membrane matrix? What are the values for diffusion coefficients for the dissociated ions and the paired ions inside the matrix? Such questions are difficult to answer since our fundamental understanding of ions in non-aqueous solutions is still not comprehensive [36]. The state and the mobility of ions in slightly swollen hydrophobic polymers are even less understood.

6.6 Conclusion

In this chapter, the retention behavior of a hydrophobic silicone-based membrane was investigated and compared with a hydrophilic PA-based (Desal DK) membrane using water, methanol as well as different water/methanol mixtures and NaCl as salt. Furthermore retention of NaCl, LiCl and CaCl_2 using the silicone-based membrane was measured in pure solvents but also in water/methanol mixtures.

Higher retention of NaCl was observed in methanol solution than in aqueous solution using the silicone-based membrane but also the PA-based membrane. Moreover, a minimum was measured at 60 wt.-% methanol using NaCl and the PA-based membrane. The retention of NaCl was compared with the retention of LiCl and CaCl_2 using the silicone-based membrane. The observed salt retention follows the order: $R(\text{CaCl}_2) > R(\text{LiCl}) > R(\text{NaCl})$ in methanol but $R(\text{CaCl}_2) > R(\text{NaCl}) > R(\text{LiCl})$ in aqueous solution. In general, retention up to 86 % regarding CaCl_2 in methanol was observed using a silicone-based membrane.

In this study, lower dissociation degrees were calculated for the investigated salts in methanol than in water, resulting in ion-pair formation. The ion pair formation inside the solution can change the partitioning into the polymer to the better or worse as well as it decreases the overall diffusivity through the polymer network. In their combination it leads to a reduced ion flux and hence to higher salt retention.

6.7 Appendix

6.7.1 Properties of water/methanol mixtures

Geens et al [12] investigated the properties of water and methanol in their mixture. Results are shown in Fig. 6.11 .

Water as extreme polar component has a high dielectric constant (83) but adding methanol with a lower dielectric constant (32) this decreases linearly. This behavior is shown in Fig. 6.11 A. However a maximum can be observed regarding the viscosity (Fig. 6.11 B). First the viscosity increases by adding methanol to pure water up to around 30 wt.-% methanol. By increasing the methanol amount the viscosity decreases again up to 0.57 mPas in pure methanol.

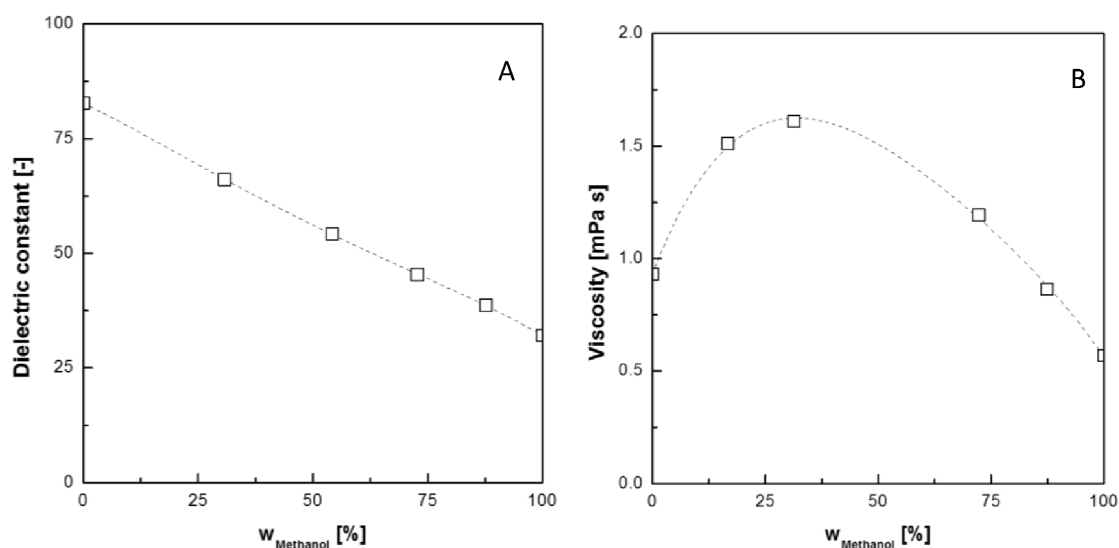


Fig. 6.11: Dielectric constant (A) and viscosity (B) of methanol/water mixtures adapted from Geens et al. [12]

In addition Fig. 12 shows the different diffusion coefficients of water and methanol in their mixtures. Hawlicka and Swiatla-Wojcik [37] observed a slight decrease of both diffusion coefficients up to 25 mol % methanol while the coefficients then increase again by adding methanol. Only a small difference was observed between these both diffusion coefficients at water-rich compositions. In this case the diffusion coefficient of water is slightly higher than that of methanol while no significant difference was measured between the coefficients using high methanol amount.

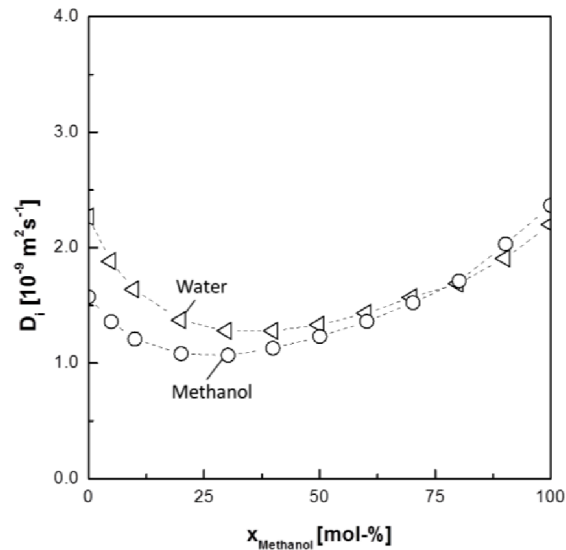


Fig. 6.12: Diffusion coefficients of water and methanol in their binary mixtures adapted from Hawlicka and Swiatla-Wojcik [37]

6.7.2 Properties of water/methanol/NaCl mixtures

Hawlicka and Swiatla-Wojcik [37] as well as Chowdhuri and Chandra [38] investigated the dynamic properties of NaCl in water-methanol mixtures. Fig. 6.13 shows as one of their results the diffusion coefficients of Na^+ and Cl^- as a function of different methanol/water mixtures [37, 38]. The anion diffusion is higher than the cation diffusion in pure water. However, adding methanol to this solution, no significant difference between the Cl^- - and the Na^+ -diffusion coefficient could be observed.

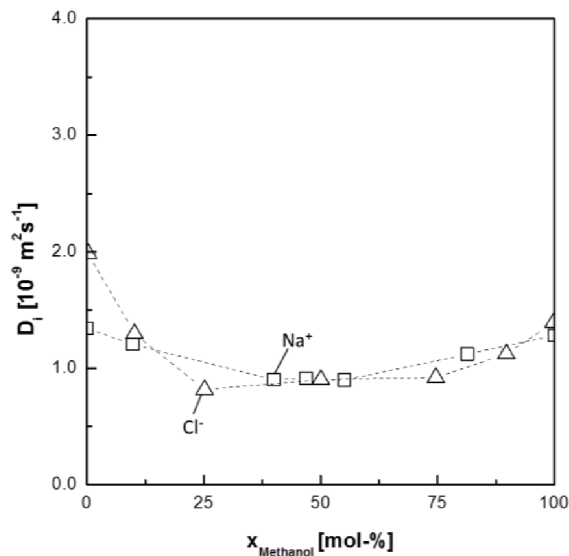


Fig. 6.13: Na^+ - and Cl^- -diffusion coefficient in water/methanol mixtures adapted from Hawlicka and Swiatla-Wojcik [37]

A drastic decrease of NaCl solubility could be observed by Pinho et al [29] by increasing the methanol amount to an aqueous solution (Fig. 6.14). While 26.5 wt.-% NaCl could be dissolved in pure water, only 1.4 wt.-% NaCl could be dissolved in pure methanol. Furthermore, the conductivity decreases with increasing methanol content as shown in Fig. 6.15. However, using a mixture with more than 50 wt.-% methanol, no change in conductivity could be observed any more. So a higher mobility of NaCl is observed in pure water or in mixtures with high water content, while a constant and low mobility is measured in methanol-rich mixtures.

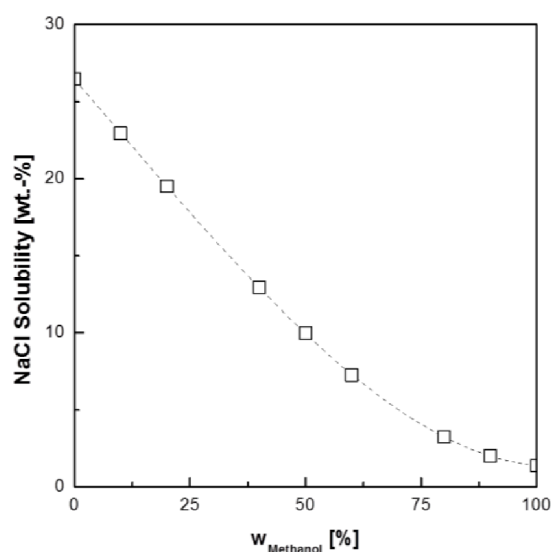


Fig. 6.14: Solubility of NaCl in different water/methanol mixtures adapted from [29]

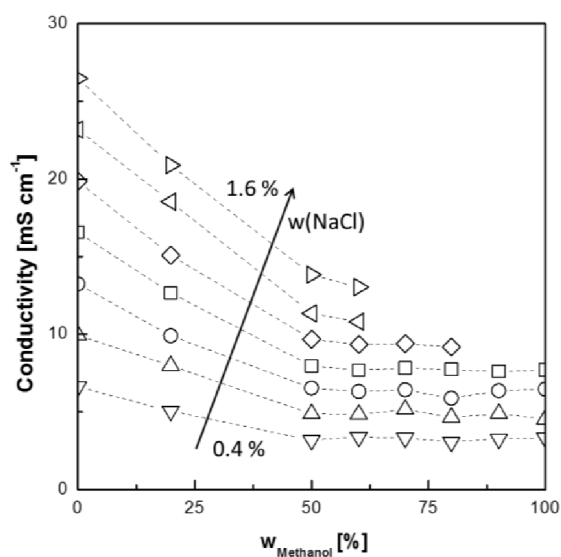


Fig. 6.15: Measured conductivity of NaCl in different water/methanol mixtures

6.7.3 Properties of water/methanol/salt mixtures

A comparison between the solubility of NaCl and LiCl in different water/methanol mixtures is shown in Fig. 6.16. A higher solubility was reported over the entire concentration range of water/methanol mixtures for LiCl than for NaCl by Pinho and Macedo as well as by Li et al. [29, 30]. However, the solubility of LiCl as well as the solubility of NaCl decreases with increasing methanol amount.

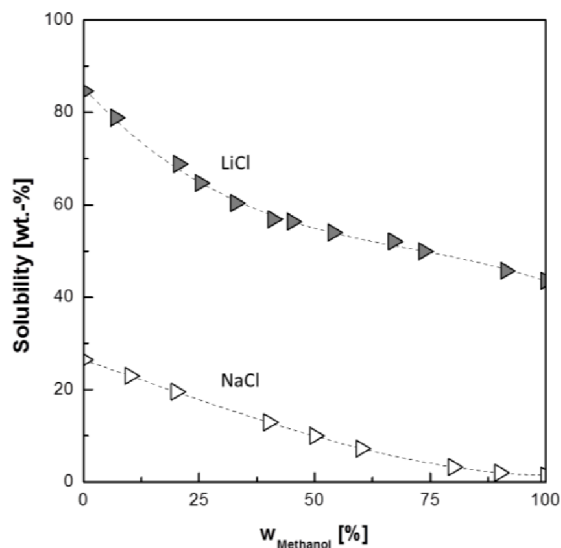


Fig. 6.16: Solubility of NaCl and LiCl at 298 K dissolved in different water/methanol mixtures adapted [29, 30] from

The influence of different methanol/water mixtures was shown above for NaCl and for LiCl as well as for CaCl_2 in Fig. 6.17. Fig. 6.17 shows the significant difference of conductivity between dissolving the investigated salts in water or in methanol. A higher conductivity was measured using water as solvent than methanol. So the lowest conductivity was measured for CaCl_2 dissolved in methanol while the highest conductivity was observed for LiCl dissolved in water (see also Fig. 6.2). A decrease of conductivity could be measured using LiCl or CaCl_2 with increasing methanol content like it is describe above for NaCl. Again the conductivity remains almost constant up to 50 wt.-% methanol.

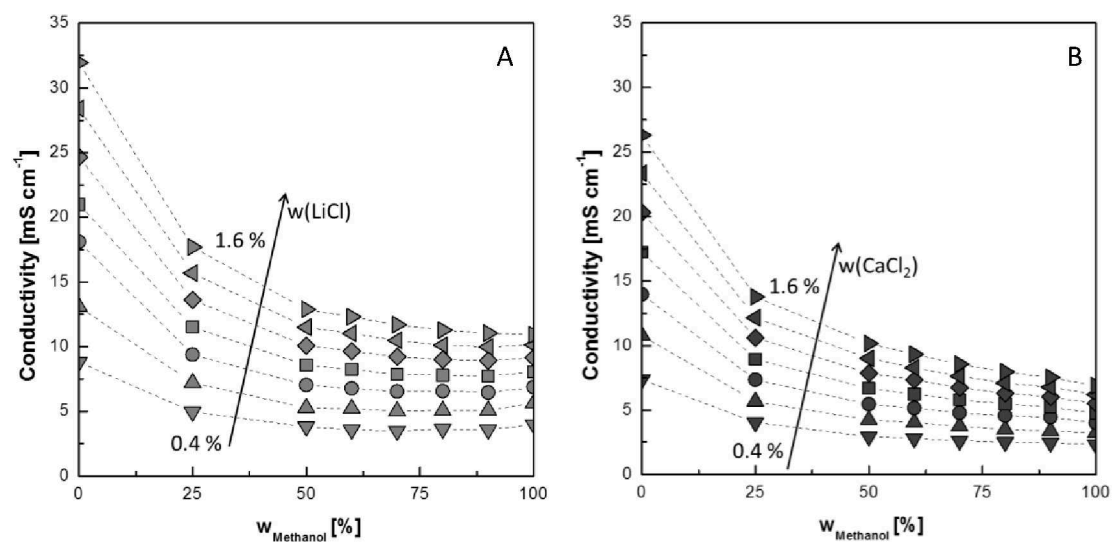


Fig. 6.17: Measured conductivity of, LiCl and CaCl₂ in various water/methanol mixtures using different salt concentrations

6.8 References

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CHAPTER 7

MODELLING OF MULTICOMPONENT MASS TRANSPORT IN OSN WITH SOLVENT MIXTURES

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7.1 Introduction

Organic solvent nanofiltration offers a large potential as an energy efficient separation process in chemical industries. In order to bring this technology to efficient applications, the systematic experimental investigation has to be enhanced with a mathematical model. For this mathematical description of nanofiltration processes with organic solvents, the solution diffusion model (SDM) or extensions of this model are commonly used. [1, 2]

Peeva et al. [3] measured the flux and retention of TOABr with different concentrations dissolved in toluene. They found a good agreement between the experimental and calculated data using the SDM. Silva et al. [4] compared a pore flow model and the solution-diffusion model in their publication. Both, the flux of the binary mixtures of toluene/ethyl acetate and the flux of the mixtures of toluene/methanol are well represented by the solution-diffusion model.

The solution-diffusion model is often extended with convective contribution based for instance on imperfections in the membrane. Furthermore, some authors use the Maxwell-Stefan equation, to avoid simplifying assumptions which are included in the Solution-Diffusion model. Dijkstra et al. [5] compared this extended solution-diffusion model with a Maxwell-Stefan equation. They found a good agreement with both models between the measured fluxes through dense PDMS/PAN membranes of different binary mixtures of pentane, decane and dodecane and calculated data. The Maxwell-Stefan flux model was also used by Hesse et al. [6] for the prediction of different single solvents fluxes and fluxes of solvent mixtures. They showed very good agreement between the calculated data and the experimental data for the measured fluxes but also for the partial fluxes of ethyl acetate and isopropanol in various compositions. Schmidt et al. [7] used a phenomenological permeation model based on the solution diffusion model with imperfection and extended this model with diffusive and convective coupling fluxes. A good agreement between simulated and experimental data was reported for retention experiments with different solutes dissolved in binary but also in ternary solvents mixtures. Straatsma et al. [8] also use also the Maxwell-Stefan model to model the retention of glucose, different single salt solutions (NaCl , CaCl_2 , Na_2SO_4) and ternary ion mixtures of these salts. Here, the experimental results are described well by this model. They also reported that negative Na^+ retention can be represented by the model. However, in such aqueous electrolyte systems, the negative retentions of some ions stem from the coupling of the ionic species and the requirement of electro neutrality.

The rigorous characterization of mass transport behavior of solute mixtures in binary solvent is yet unexplored and will be addressed here. Thus this study experimentally investigates the retention behavior of mixtures of n-alkanes with different chain lengths in binary solvent mixtures of toluene/isopropanol and toluene/methanol. A Maxwell-Stefan model is used to describe solvent as well as solute mixture fluxes showing positive as well as negative retentions. This chapter will show potentials and limitations of extracting model

parameters from single solvent/solute mixtures and predicting binary solvent/solute mixtures.

7.2 Theoretical background

Several models have been developed to describe the permeation of organic solvents through dense polymeric membranes. Of these all, the solution-diffusion model presented 1965 by Lonsdale and Merten [9] is most commonly used and widely accepted for this purpose. The concept of this model conceives the transport as consecutive three separate steps. First, the permeating component dissolves in the membrane. Once dissolved in the polymer network, the dissolved penetrant molecules diffuse through the membrane and, in a third step, desorb from the membrane at the side of the lower chemical potential. Accordingly, different components are separated due to differences in sorption and diffusion.

Wijmans and Baker [10] gave an excellent review about the experimentally observed phenomena and their description using the solution diffusion model. Relevant for our contribution is that the apparent pressure difference between feed and permeate sides give rise to differences in chemical potential of all components in the mixture. Assuming thermodynamic equilibrium between the components in the fluid phase and the membrane, the chemical potential in the fluid phase is sufficient to quantify the driving force. Recently, Ogieglo et al. [11] proved the validity of the solution diffusion model through ellipsometry measurements comparing static pressure and non-equilibrium measurements with hexane permeation through PDMS. The regular solution-diffusion model assumes that the dissolved penetrant molecules in the polymer matrix diffuse independently of each other making any cross-coupling terms superfluous. To describe the transport of solutes in organic solvents and the effect of negative retention, the before mentioned cross-coupling term should be taken into account, as also reported in previous works [5, 8, 12, 13].

Therefore, we suggest using the generalized Maxwell-Stefan equation (Eq. (1)). Using this fundamental equation also mutual cross-coupling effects are taken into account by considering the individual species in a mixture. Here the friction forces on the right side of this equation are described by $\zeta_{i,j}$ as diffusive friction coefficient between different components i,j or as mutual friction coefficient $\zeta_{i,M}$ between molecules i and membrane M . This friction force has to be equal to the driving forces F_i at steady state flux.

$$F_i = \sum_{\substack{j=1 \\ i \neq j}}^n [x_j \zeta_{ij} (u_i - u_j)] \quad (1)$$

For a nanofiltration process with a non-porous membrane the driving force can be described by the chemical potential gradient across the membrane $d\mu/dz$. The diffusive

velocity u_i can be replaced by the molar flux N_i and the friction force $\zeta_{i,j}$ can be substituted by Maxwell-Stefan diffusions coefficient Θ_{ij} :

$$\Theta_{ij} = \frac{RT}{\zeta_{ij}} \quad (2)$$

So the following equation can be used to calculate the flux N_i of one component i in a multicomponent mixture: [14]

$$-\frac{d\mu_i}{dz} = \frac{RT}{c_{\text{tot}} \bar{x}_i} \sum_{\substack{j=1 \\ i \neq j}}^n \left[\frac{1}{\Theta_{ij}} (N_i \bar{x}_j - N_j \bar{x}_i) \right] + \frac{N_i}{\Theta_{iM}} \quad (3)$$

Using the standard definition of the chemical potential difference over the membrane (Eq.(5)) the flux N_i of a component i can be expressed by the following equation:

$$\frac{c_{\text{tot}} \bar{x}_i \Theta_{iM}}{\Delta z} \left(\ln \frac{a_{iM}}{a_{iP}} + \frac{\tilde{V}_i}{RT} \Delta p \right) = N_i + \Theta_{iM} \sum_{\substack{j=1 \\ i \neq j}}^n \left[\frac{1}{\Theta_{ij}} (N_i \bar{x}_j - N_j \bar{x}_i) \right] \quad (4)$$

with

$$\Delta\mu_i = (RT \cdot \Delta \ln a + \tilde{V}_i \cdot \Delta p) \quad (5)$$

This equation can be used to calculate solvent but also solute fluxes through dense polymeric nanofiltration membranes in consideration of interactions of solute, solvent and membrane. The estimation procedure to extract and quantify the model parameter for this set of equations will be described below.

7.3 Experimental methods

In order to validate the model, experiments with toluene, isopropanol and methanol as well as the binary mixtures toluene/isopropanol and toluene/methanol as solvents were carried out. Retention measurement with different n alkanes were used to evaluate the before described model. A silicone based composite membrane is used for all described experiments. The Evonik MET setup was used to perform the different measurements, working with two test cells in series with a membrane area of 52.81 cm² each.

The used materials and the experimental procedure are described in Chapter 3 in detail

7.4 Modeling

The transport model described in section 6.2 was implemented in Aspen Custom Modeler®. To determine the unknown parameters $\bar{D}_{iM}$ and P_{iM} , a least square fit routine was used. Solvent and solute properties like activity, molar volume or diffusions coefficient between solute and solvent are taken from Aspen Properties®.

The diffusion coefficient of the pure solvent inside the membrane was calculated according to equation (4) using the experimental determined fluxes of this work as well as sorption data from Stamatialis et al. [15] and Favre et al [16]. For the model-based prediction of fluxes of binary solvent mixtures, only the parameter set of the pure components was used. Hence, to calculate solvent fluxes of mixtures the unknown model parameters were combined into the permeability coefficient as following:

$$\frac{c_{\text{tot}} \bar{x}_i \bar{D}_{iM}}{\Delta z} = P_{iM} \quad (6)$$

To calculate the solute fluxes both, this factor P_{iM} and the diffusion coefficient of the solute within the membrane $\bar{D}_{iM}$ were fitted (see Eq. (4)). Implicitly the solubility of the solute into the membrane was therefore also fitted using Eq. (6). For this estimation the experimental flux of the different n-alkanes dissolved in a single solvent was used. In these experiments all solutes are dissolved in one single solvent. So using for instance toluene with seven different n-alkanes ($C_{10}H_{22}$ - $C_{24}H_{50}$) as solutes, an equation system with 8 components has to be solved. However, during the estimation of the solute parameters the solvent parameters are not adjustable but remain equal to the value of the solvent only. It must be clarified that the resulting parameters for the solute permeability however depend on the single solvent used.

To calculate the solute fluxes and the retention in the mixture of two solvents, mixing rules have to be used. In this work a simple mixing rule was used to calculate any value b in a mixture (*Mix*) with pure component values b_{ii} :

$$b_{\text{Mix}} = \sum x_i b_{ii} \quad (7)$$

Fig. 6.1 illustrates this modeling procedure and a detailed scheme demonstrating the fitting method can be found in appendix.

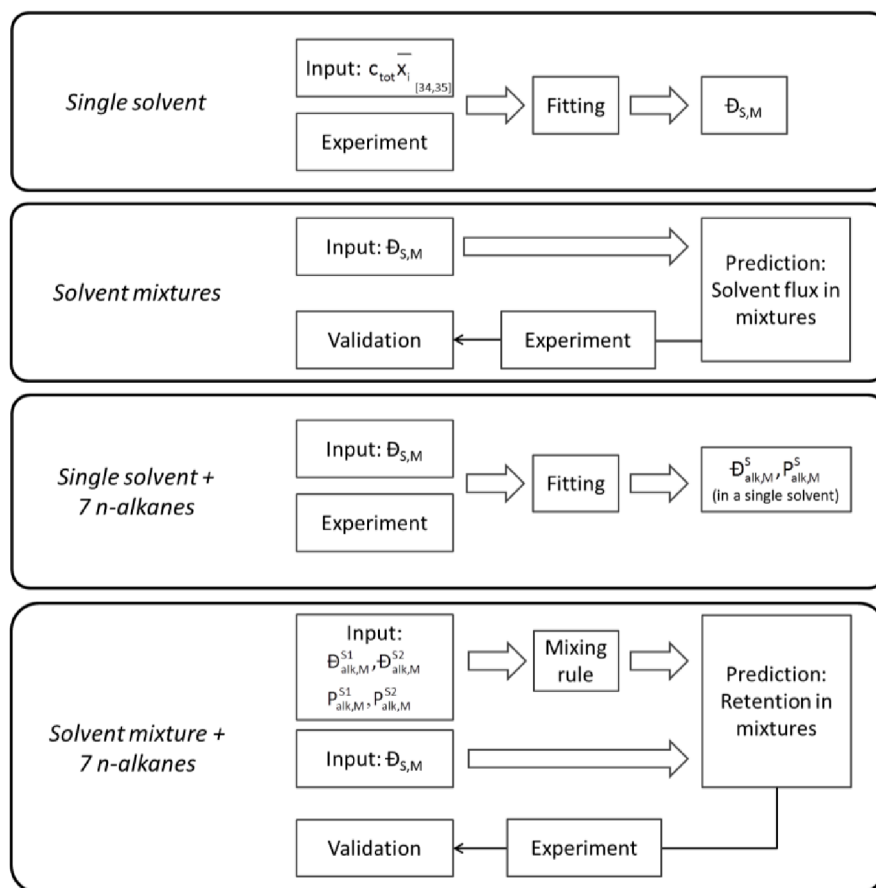


Fig. 6.1: Schematic illustration of the modeling procedure. Here, index "S" refers to single solvent and index "alk" refers to different n-alkanes

7.5 Results and discussion

7.5.1 Flux measurements of pure solvent fluxes

First of all fluxes of the pure solvents toluene, isopropanol and methanol were measured at different applied transmembrane pressures (TMP). With these data, the diffusion coefficient of each solvent in the membrane was fitted as it is described before. The results are shown in Fig. 6.2.

Not surprisingly, due to the simplicity of the equation for only one component, the calculated curves in Fig. 6.2 agree well with the experimental data. Generally, Fig. 6.2 shows that the permeability follows the order toluene > isopropanol > methanol although no significant difference between isopropanol and methanol was measured.

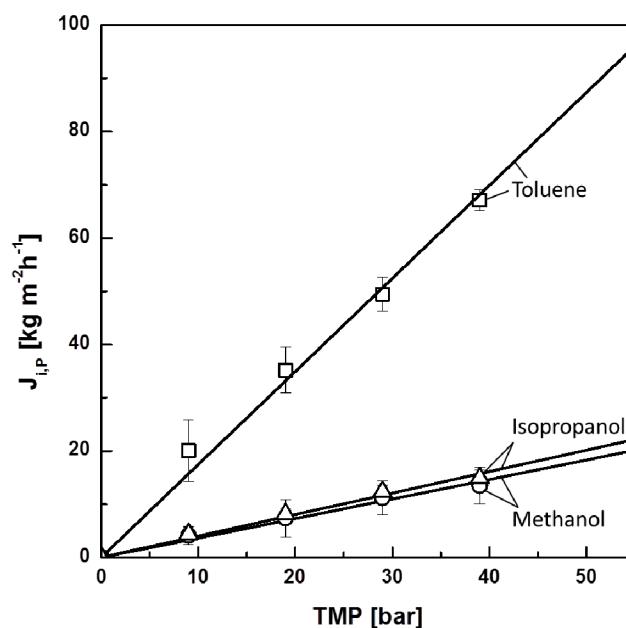


Fig. 6.2: Measured (symbols) and calculated (solid line) pure solvent fluxes of toluene ($\square$), isopropanol (Δ) and methanol ($\circ$) at different transmembrane pressures and room temperature

The estimated diffusion coefficients for each solvent are shown in Table 6.1. As expected, D_{SM} increases with decreasing molecular weight and decreasing permeability for the solvent. Due to this increasing diffusion coefficient the reduction in permeability must be caused by different sorption behaviors of these solvents like it is discussed in chapter 2.

Table 6.1: Estimated diffusion coefficient of pure solvents

Solvent	$D_{SM} \cdot 10^{-9}$ $\text{m}^2 \text{s}^{-1}$
Toluene	1.92
Isopropanol	2.16
Methanol	8.05

7.5.2 Flux measurements of binary solvent mixtures

Permeate fluxes of binary mixtures of toluene/isopropanol and toluene/methanol can be predicted with the estimated diffusion coefficients of pure solvents. For this purpose, the Maxwell-Stefan equation has to be expanded to two components and applied to the entire concentration range.

Investigations with the binary system of toluene and isopropanol are carried out with three different compositions (25 wt.-%, 50 wt.-%, 75 wt.-%) at 20 and 30 bar pressure. The total fluxes as well as the partial fluxes are shown in Fig. 6.3. The Maxwell-Stefan model with its input parameters from the single solvent measurements slightly underpredicts all fluxes.

The non-linearity in the predictions stems from the thermodynamic data and the flux coupling terms in the MS-model.

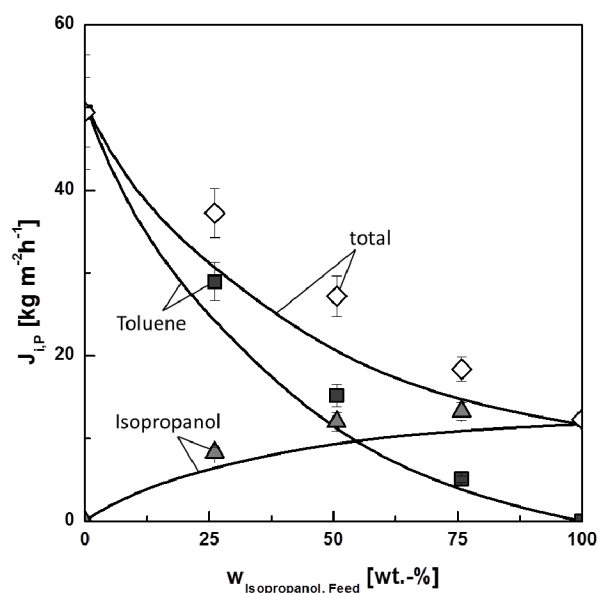


Fig. 6.3: Measured total flux ($\diamond$) and partial fluxes of toluene ($\square$) and isopropanol (Δ) and predicted fluxes (solid lines) at 30 bar and room temperature

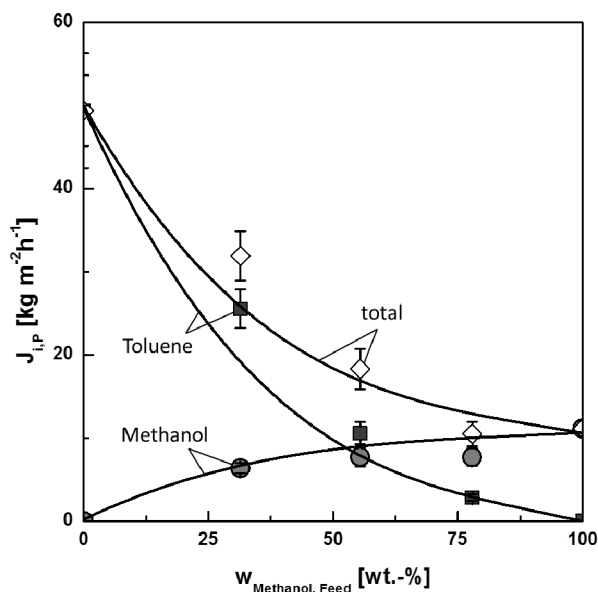


Fig. 6.4: Measured total flux ($\diamond$) and partial fluxes of toluene ($\square$) and methanol ($\circ$) and predicted fluxes (solid lines) at 30 bar and room temperature

The same procedure was applied using the binary mixture of toluene and methanol. The predicted and the experimental permeate fluxes as a function of the composition are

shown in Fig. 6.4. With increasing solvent content in the mixtures the partial flux increases for each solvent. The experimental results are discussed in detail previously in chapter 3. As already described for the mixtures toluene/isopropanol, the model based prediction gives also good results for the binary mixture of toluene and methanol. Here, the maximum relative deviation for the partial toluene flux in the mixture with methanol is 27 % and for methanol is 30 %. Using toluene and isopropanol the maximum relative deviation for the toluene permeate flux is in the same range (29 %). Regarding the permeate flux of isopropanol the maximum deviation is only 22 %. Table 6.2 compares the maximal and minimal absolute as well as relative deviations but only for the predicted values in the mixture (25 wt.-%, 50 wt.-%, 75 wt.-%).

Table 6.2: Comparison of absolute and relative deviations between experimental and predicted partial fluxes

	Toluene / Isopropanol				Toluene / Methanol			
	Absolute deviation $\text{kg m}^{-2} \text{h}^{-1}$		Relative deviation		Absolute deviation $\text{kg m}^{-2} \text{h}^{-1}$		Relative deviation	
	Toluene	Isopropanol	Toluene	Isopropanol	Toluene	Methanol	Toluene	Methanol
Min.	1.33	1.83	17 %	18 %	0.15	0.12	5 %	2 %
Max.	4.94	2.57	29 %	22 %	5.53	2.33	27 %	30 %

7.5.3 Retention measurements with single solvents

In addition to the flux measurement of single solvents and their binary mixtures, retentions of n-alkanes with different chain length dissolved in each of the solvents were measured. These experiments were performed at 20 and 30 bar respectively and 1 wt-% n-alkanes in total. The permeability coefficient $P_{alk,M}^S$ and the diffusion coefficient of one solute within the membrane $D_{alk,M}^S$ was estimated with these data points as it is described in section 7.4. Fig. 6.5 (A) shows exemplarily the experimental and the calculated fluxes of $\text{C}_{16}\text{H}_{34}$ dissolved in toluene, isopropanol and methanol, respectively, as a function of the transmembrane pressure. Furthermore, Fig. 6.5 (B) shows the measured and simulated retentions at 20 and 30 bar of this alkane also dissolved in each of these three solvents. The flux of $\text{C}_{16}\text{H}_{34}$ is three times higher using toluene as solvent compared with isopropanol or methanol as solvent. No significant difference was measured whether $\text{C}_{16}\text{H}_{34}$ was dissolved in isopropanol or in methanol. Nonetheless, a difference can be observed in the retention of $\text{C}_{16}\text{H}_{34}$: dissolving this n-alkane in methanol the lowest retention (-39 %) was reached. Using isopropanol as solvent the retention is also negative but only -21 %. These differences in retention without any significant variation in the partial fluxes of $\text{C}_{16}\text{H}_{34}$ are caused by the difference in the total permeate fluxes of methanol and isopropanol (see Fig. 6.2). Commonly measured positive retentions are found using toluene as solvent.

Nevertheless, the model parameters can be extracted from these data with the Maxwell-Stefan model resulting in fitted parameters $\mathcal{D}_{alk,M}^S$ and $P_{alk,M}^S$ for each of the different solvents.

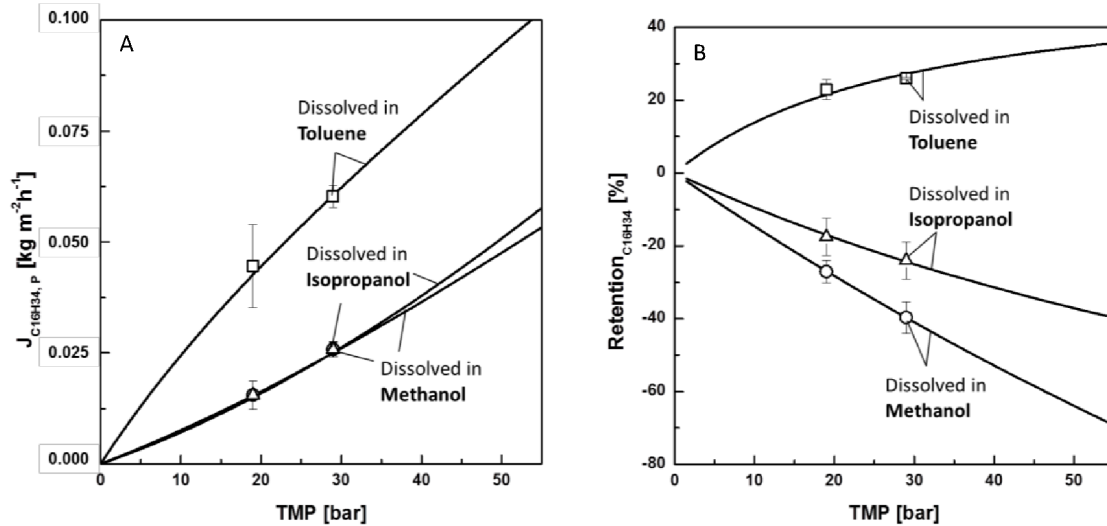


Fig. 6.5: Measured (symbols) and simulated (solid line) fluxes (A) and retentions (B) of $C_{16}H_{34}$ dissolved in toluene ($\square$), isopropanol (Δ) and methanol (O) at different transmembrane pressures and room temperature

Summarizing the retention measurements Fig. 6.6 shows the retentions at 20 and 30 bar of all n-alkanes dissolved in toluene, isopropanol and methanol, respectively. Using toluene as solvent positive retention up to 50 % was reached. Using isopropanol or methanol as solvents, negative retentions for all n-alkanes with different chain length are observed. The retentions even decrease with increasing molecular weight. It is essential to realize that the negative values and the changes in retentions are closely related to the sorption selectivity of the membrane material: using a solvent with high affinity to the membrane material like toluene, this solvent passes preferential through the membranes and the solute is retained. However, using a solvent with less solubility than the solutes, negative retention could be observed (see chapter 2).

There is a very good agreement between the model and the experimental data: the measured decreasing retentions with increasing molecular weight or with increasing pressure are represented by this model using a single set of model parameters.

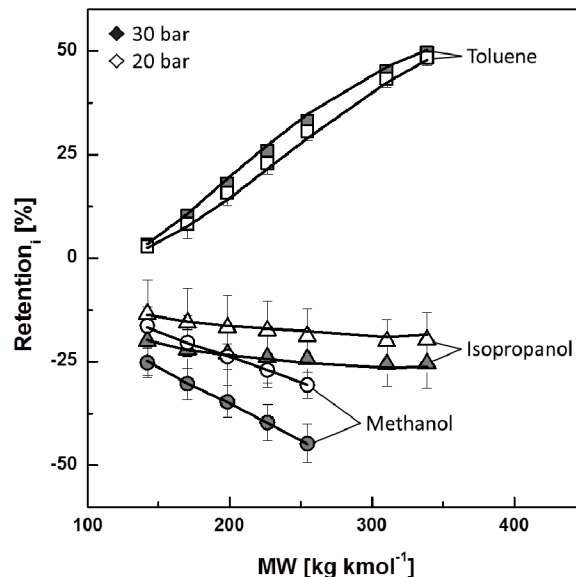


Fig. 6.6: Retention of different n-alkanes dissolved in toluene (Δ), isopropanol ($\square$) or methanol (O) at 20 and 30 bar pressure. For visualization, the solid line represents the simulated data, though the simulation refers only to the respective molecular weights.

7.5.4 Retention measurements with solvent mixtures

In order to quantify the transport of solutes in solvent mixtures, the retentions of n-alkanes with different chain lengths were also measured in the binary mixture of solvents. These experiments are discussed in detail in chapter 3.

First of all different n-alkanes were dissolved in the solvent mixture of toluene / isopropanol (Fig. 6.7). The retention of n-alkanes decreases with increasing amount of isopropanol to complete negative retention. However, no significant influence of the molecular weight was observed using 75 wt-% isopropanol or pure isopropanol.

Further experiments using n-alkanes with different chain lengths dissolved in varying mixtures of toluene and methanol were carried out and shown in Fig. 6.8. In this case, a minimum was found at 53 wt-% methanol. Only in pure toluene solution positive retentions were measured. With increasing methanol content the retentions initially decreases but raises again using methanol weight fractions higher than 53 wt.-%. Furthermore the influence of the molecular weight changes.

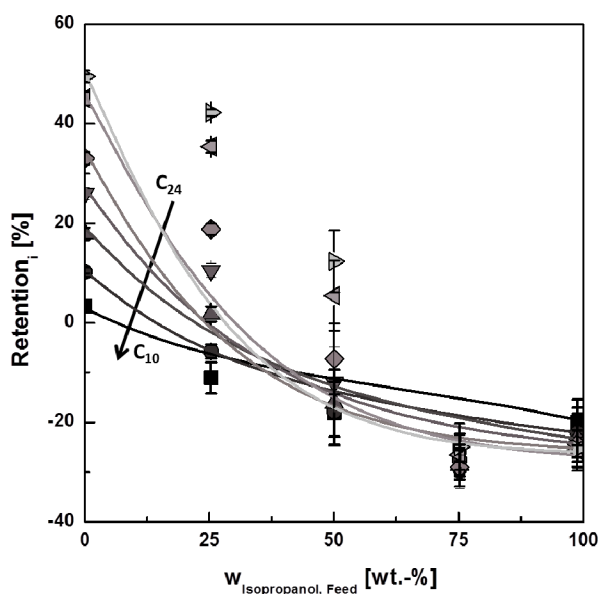


Fig. 6.7: Comparison of experimental and predicted retentions of n-alkanes dissolved in different compositions of toluene and isopropanol at 30 bar

The model-based retention prediction for the entire concentration range in the binary solvent mixtures toluene/isopropanol and toluene/methanol was performed using only the parameter set for n-alkanes dissolved in the three pure solvent. As described in section 7.4 a mixing rule was used to calculate the permeability coefficients and diffusion coefficients in the mixture. With these parameters the retention of n-alkanes in binary mixtures was predicted. Fig. 6.7 shows the results for the mixture of toluene and isopropanol. The deviation between the experimental data and the simulated curves is high, especially in the range between 25 wt.-% and 50 wt.-% isopropanol.

For the solvent mixture toluene/methanol, the predicted values are always above the experimental values as it is shown in Fig. 6.8. The minimum at 50 wt.-% methanol cannot be represented by the model. Generally, the deviation between the predicted and the experimental data is not in a satisfactory range.

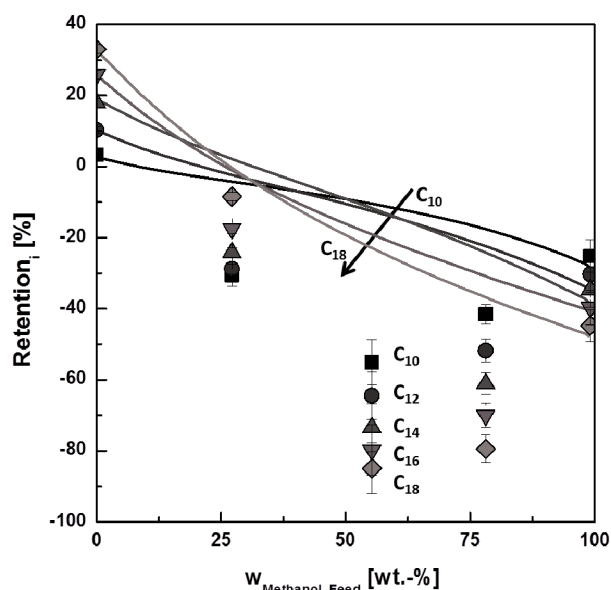


Fig. 6.8: Comparison of experimental and predicted retentions of n-alkanes dissolved in different compositions of toluene and methanol at 30 bar

The results indicate the limitations of the model. They are most likely due to two reasons: (a) single solvent based fitting data are used to predict binary solvent properties and this method is just inappropriate due to non-ideal mixing related thermodynamic effects, and (b) the estimated permeability coefficient assuming linear sorption behavior of the solute and solvents with constant partitioning coefficient. An adequate equation for the sorption has to be implemented to describe the difference in sorption due to the varying solvent compositions. A Flory-Huggins related model [11, 17] or even better a PC-SAFT model [18-20] may be an appropriate approach. However there is very little evidence how such methodologies perform to predict solubility of all components of a solute mixtures in solvent mixtures in a polymer.

7.6 Conclusion

In this study, significant changes in flux and retention behavior due to different solvent mixtures and solvent properties are shown. This leads even to negative retention due to changing membrane-solvent-solute interactions.

The Maxwell-Stefan model takes such interactions into account. Thus, this model is successfully used in this study to describe solvent as well as solute fluxes but also positive and negative retentions. Furthermore solvent fluxes in binary mixtures are well predicted with this mathematical model.

However, a further improvement is required with respect to the prediction of the retention in binary solvent mixtures. For instance suitable sorption models, which describe the sorption of solutes in PDSM membranes, should be implemented.

7.7 Nomenclature

a	Activity	-
b	Mixing Parameter	-
c	Concentration	mol m^{-3}
D	Diffusion coefficient	m^2s^{-1}
N	Molar flux	$\text{mol m}^{-2}\text{s}^{-1}$
p	Pressure	Pa
R	Gas constant	$\text{J mol}^{-1}\text{K}^{-1}$
T	Temperature	K
u	Velocity	m s^{-1}
$\tilde{V}$	Molar volume	$\text{m}^3\text{mol}^{-1}$
x	Molar fraction	-
z	Membrane thickness	m

Greek letters

μ	Chemical potential	J mol^{-1}
ζ	Friction force	-

Subscripts

alk	n-Alkanes
i,j	Components
M	Membrane
S	Solvent
tot	Total

7.8 Appendix

Fig. 6.9 and Fig. 6.10 shows detailed illustrations of the fitting procedures of single solvents and of solute mixtures dissolved in a single solvent.

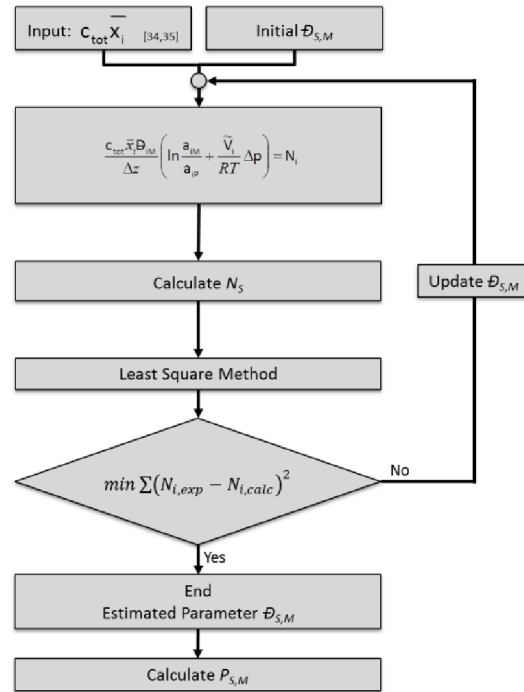


Fig. 6.9: Estimation method for pure solvents (Index "S")

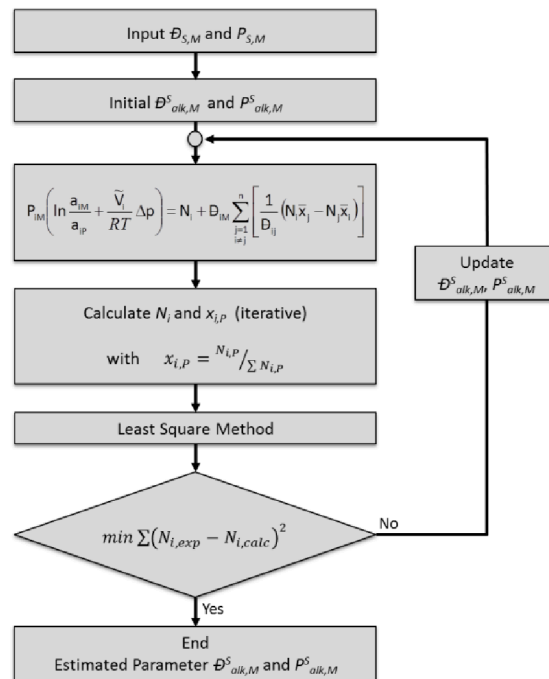


Fig. 6.10: Estimation method for n-alkane (Index "alk") dissolved in one single solvent (Index "S")

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CHAPTER 8

CONCLUSION AND OUTLOOK

8.1 Experimental investigation

The potential of organic solvent nanofiltration as energy-efficient separation process was shown in the last decade. In order to implement the OSN processes a thoroughly understanding of transport phenomena is required. Thus, this thesis systematically investigated transport behavior in organic solvent nanofiltration focused on negative retentions.

Initially, a 3-dimensional relationship between solubility parameter of solvent, solute and membrane was used. Based on this, different solvent and solutes were selected, while only one silicone-based membrane was investigated. Due to this selection, a solubility determined solute transport resulting in up-concentration of the larger solute into the permeate could be observed.

Chapter 2 described this enrichment of single solutes in the permeate resulting in negative retention. This negative retention was compared to positive retention while solubility parameters were found to explain the different retentions and the strong dependence of the retention on the used solvent and solute. Furthermore a correlation between larger transport rates for larger solute molecules and the growing contribution of the increasing partial molar volume to the chemical potential was found.

Since chapter 2 described the retention of different solutes dissolved in different pure solvents, chapter 3 investigated the transport behavior of these solutes additionally in solvent mixtures. Depending on the solvent and on the ratio of these solvents in case of binary mixtures, considerable differences in the retention behavior of these solutes were discovered. Even negative retention could be observed. Again a dependence of retention on the affinity of the solvent or solute relative to the membrane was found. However the observed minimum in retentions for n-alkanes dissolved in toluene/methanol mixtures, showed also the strong influence of solvent-solute-membrane interactions.

Additionally, chapter 4 investigated the influence of solute group mixtures on transport behavior. Summarizing this investigation no significant influence could be observed whether single solutes or solute/solute mixtures were used.

In order to verify the dependence of retention on the differences in solubility, chapter 5 reported swelling measurements using the investigated solvents and solutes. A clear correlation between swelling degree and retention was found. For instance a higher swelling degree of negatively retained components was observed compared to the swelling degree of the used solvent. This was also verified with Flory-Huggins interaction parameter. Lower interaction parameters (higher interactions) of solute or solvent and PDMS, leads to higher swelling and thus to negative retentions.

In contrast to the above described investigations using uncharged solutes in pure solvents or solvent/solvent mixtures, chapter 6 reported the influence of different salts in aqueous or in water/methanol solutions. A significant difference in retentions could be observed using the silicone-based membrane in comparison to a commercial PA-based membrane.

Moreover different retentions using three different salts (NaCl, LiCl, CaCl₂) were measured and could be correlated to ion formation.

In general Table 8.1 summarizes the performed investigations expressed as changes in retentions from positive to negative. It can be concluded that retentions depends on the affinity of the used solute, on one hand relative to the membrane, but also relative to the solvent or solvent mixtures. So, negative retentions can be achieved, if the solubility parameter of the solute is closer to the solubility parameter of the membrane compared to the solubility parameter of the used solvent. This affinity changes if components properties changes for instance if solvent mixtures are used instead of pure solvents. However solute/solute mixtures showed no significant influence of retentions compared to single solute measurements.

8.2 Modeling of OSN

In addition to the experimental investigation, a mathematical model based on the Solution-Diffusion approach combined with the Maxwell-Stefan theory was used in order to describe the experimental results.

Chapter 7 described this model and a development of a parameter fitting routine. It was shown that solvent as well as solute fluxes could be successfully predicted using model parameters from single solvent experiments. Due to the introduction of Maxwell-Stefan theory, interactions were taken into account and positive but also negative retentions could be predicted. A good agreement between experimental data and model could be achieved with pure solvent fluxes and solvent fluxes in binary mixtures. However, predictions of solute retentions in solvent mixtures based on solutes/single solvent systems was insufficient and indicates a richer transport complexity in the binary solute/solvent/membrane system.

Table 8.1: Summary of the measured retention (n.s. = not soluble; n.m. = not measured)

	Solvent					
	Isopropanol (IPA)	Methanol (MeOH)	Toluene (Tol)	n-Hexane (Hex)	Tol + IPA	Tol + MeOH
						IPA + MeOH
n-Alkanes (Alk)	negative	negative	positive	positive	pos.→ neg.	negative
Polyethylene glycol (PEG)	positive	positive	positive	-(n.s.)	-(n.m.)	positive
Carboxylic acid (CA)	neg.→ pos.	negative	positive	positive	-(n.m.)	-(n.m.)
Polystyrene (PS)	-(n.s.)	-(n.s.)	positive	positive	-(n.m.)	-(n.m.)
Alk + PEG: Alkane PEG	negative positive	negative positive	-(n.m.)	-(n.m.)	-(n.m.)	negative positive

8.3 Outlook

8.3.1 Experimental Investigation

In this thesis a systematically investigation of organic solvent nanofiltration is presented using a rubbery crosslinked PDMS membrane. However, the transfer of these gained results to other membrane materials is not proven in this work. This is highly recommended due to the complex transport behavior in organic solvent nanofiltration. The influence of different membrane materials will give further information about transport behavior and solvent-solute-membrane interactions. Like it is introduced in this thesis some authors describes negative retention using different membrane materials. However, due to missing standardized measure procedures data transfer is not possible. Accordingly, a development of such standardized measure procedures is required and recommended. This will additionally improve the potential application of OSN since such procedures allow simple and fast data transfer. Consequently, the probability of OSN implementation in existing or innovative processes will increase.

8.3.2 Mathematical description

According to the above described limitations of the used model, further developments are required. Using single solute fitting parameter, solute retentions in solvent mixtures was insufficient predicted. Improvements with respect to different mixing rules or adequate sorption theories are recommended.

In order to describe sorptions behavior and to determine the concentration of a component in the membrane the linear Henry approach is often use. This is applicable to describe the sorption in polymer membranes for low concentrations. However, using rubbery polymer membranes the solubility of the components increases with increasing concentration. To describe this phenomenon, the approach of Flory and Huggins is commonly used and introduced in chapter 5.

In order to determine the volume fraction ϕ in a multi-component mixture in the membrane, the following equation can be used [1]:

$$\ln(a_i) = \ln(\phi_i) + \sum_{j=1}^n \phi_j \left(1 - \frac{V_i}{V_j} \right) + V_i \sum_{j=1}^n \phi_j \chi_{i,j}^* - \frac{1}{2} V_i \sum_{j=1}^N \sum_{k=1}^N \phi_j \phi_k \chi_{j,k}^* \quad (1)$$

Here, the activity a , the molar volume V but also the interaction parameter χ has to be known in order to predict volume fractions in the membrane. The interaction parameter is calculated in this work using a solubility parameter approach with three different Hansen solubility parameter: σ^d (non-polar (dispersion) forces), σ^p (polar forces), σ^h (hydrogen-bonding effects) [2, 3]:

$$\chi_{i,j}^* = \frac{0.6}{RT} \left[(\delta_i^d - \delta_j^d)^2 + 0.25 \cdot (\delta_i^p - \delta_j^p)^2 + 0.25 \cdot (\delta_i^h - \delta_j^h)^2 \right] \quad (2)$$

Using this approach the interaction parameters are constant, and thus not concentration dependent. In chapter 5 we showed that this combination of Flory-Huggins theory with the Hansen solubility parameter approach, leads to good predictions of solvent or PDMS volume fractions but insufficient predictions of solute volume fraction. Further improvements have to be realized with respect to determination of Flory-Huggins interaction parameter. Moreover, extensions of Flory-Huggins theory are recommended.

The Flory Huggins model is often extended using an additional term, taking elastic forces into account [4]. This elastic term is shown in equation (3). Here the classical Flory-Huggins equation is abbreviated with "FH" and refers to equation (1) [5, 6]:

$$\ln(a_i) = FH + \frac{V_i \cdot \rho_M}{M_c} \cdot \left(1 - \frac{2M_c}{M_0} \right) \cdot \left(\phi_M^{1/3} - \frac{\phi_M}{2} \right) \quad (3)$$

The molecular weight between two cross-links M_c and the molecular weight of the polymer before cross-linking M_0 are introduced. This so called Flory-Rehner theory applies for a cross-linked polymer matrix. Due to that the application of this extension is recommended.

In order to develop a predictive approach also diffusion coefficients have to be calculated. Based on the analysis of the experimental data for the diffusion coefficient of nonelectrolytes in dilute solution, Nakanishi [7] developed the following correlation to calculate diffusion coefficient between solute i and solvent j in dilute solution:

$$D_{i,j}^{x_i \rightarrow 1} = \left(\frac{9.97 \cdot 10^{-8}}{(l_i \cdot V_i)^{1/3}} + \frac{2.4 \cdot 10^{-8} \cdot A_j S_j V_j}{l_i S_i V_i} \right) \cdot \frac{T}{\eta_j} \quad (4)$$

This correlation includes three empirical parameters which reflect various specific interactions between solute and solvent in dilute solution: A_j is an association parameter for associated solvents which is comparable to the "association parameter" published by Wilke and Chang [8]. Furthermore l_i is an interaction parameter for polar solutes and S is a shape factors for paraffins. These parameters can be found in different tables. Also the molar volume V and the viscosity η have to be known for solving this correlation.

However, to determine diffusion coefficients in the entire concentration range, mixing rules has to be used. A mixing rule developed by Darken [9, 10] for diffusion coefficients in binary mixture and extended to multicomponent mixtures by Wesselingh and Krishna [11] can be used:

$$D_{i,j} = x_i D_{i,j}^{x_i \rightarrow 1} + x_j D_{i,j}^{x_j \rightarrow 1} + \sum_{k=1, k \neq i, j}^N x_k D_{i,j}^{x_k \rightarrow 1} \quad (5)$$

Here, $D_{i,j}^{x_i \rightarrow 1}$ and $D_{i,j}^{x_j \rightarrow 1}$ describe the diffusion between a diluted component and the solvent. The diffusion coefficient $D_{i,j}^{x_k \rightarrow 1}$ describes the diffusion between components i and j when both are infinitely diluted in a third component k . In the past, several empirical models were proposed for estimating this coefficient from binary diffusion data [12-15]. For instance the following equation published by Wesselingh and Krishna can be used [16].

$$D_{i,j}^{x_k \rightarrow 1} = \sqrt{D_{i,j}^{x_i \rightarrow 1} D_{i,j}^{x_j \rightarrow 1}} \quad (6)$$

As another approach calculating mutual diffusion coefficients the Free Volume Theory can be found in literature. Originally, this theory was developed for dense glassy polymeric membranes in contact with one solvent [17, 18]. Wesselingh and Bollen [19] extended this model to diffusion in multicomponent mixtures and rubbery polymers.

Using this theory the following basic assumption have to be accepted: A molecule can move through a mixture when a hole next to this molecule is large enough for the molecule to fit in. This free volume of a pure component $V_{i,FV}^0$ can be calculated with the molar volume V_i^0 and the minimal (compressed) volume V_i^* at 0 K as follows:

$$V_{i,FV}^0 = V_i^0 - V_i^* \quad (7)$$

A detail description calculating these volumes can be found in literature [19, 20].

In order to calculate the mutual diffusion coefficient, commonly the friction coefficient is used [21]. The Free Volume theory introduced effective friction forces ("eff") of tracer ("#"), so the mutual friction coefficient can be calculated using the following equation: [19]

$$\zeta_{ij} = \frac{\zeta_{i\#,eff} \cdot \zeta_{j\#,eff}}{\sum_{k=1}^n x_k \cdot \zeta_{k\#,eff}} \quad (8)$$

Calculating this effective friction force, the surface weighted free volume $V_{i,FV}$, the molecular diameter d_i , the maximum compressed density ρ^* , the Avogadro constant N_{av} , the Boltzmann constant k and the temperature T has to be known.

$$\zeta_{i\#,eff} = 2N_{av} \sqrt{3k \cdot T \cdot \rho^* \cdot d_i} \cdot \exp\left(0.7 \cdot \frac{V_i^*}{V_{i,FV}}\right) \quad (9)$$

In order to calculate the surface weighted free volume $V_{i,FV}$, the surface fraction of one component σ_i has to be determined using the compressed volume V_i^* :

$$V_{i,FV} = \frac{\sigma_i}{x_i} \cdot V_{FV} \quad (10)$$

$$\text{with } \sigma_i = \frac{x_i (v_i^*)^{2/3}}{\sum_{j=1}^n x_j (v_j^*)^{2/3}} \quad (11)$$

Using these four equations, the mutual diffusion coefficient can be calculated.

In general, these presented mathematical improvements will increase the complexity of the model but give a predictive approach without any use of experimental data. This increasing complexity can also increase convergence problems of the model. So building a model library is recommended in order to choose complexity of the model on the one hand but reduce fitting parameter on the other hand.

However, further developments are required especially regarding process modelling and modeling of hybrid processes. Developing a process simulation tool, the applicability of OSN can be evaluated in early process development. Furthermore, using such a tool will offer the possibility to compare OSN adequately with existing unit operation and make the real application potential accessible.

8.4 References

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