Three step modelling approach for the simulation of industrial scale pervaporation modules

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Abstract

The separation of aqueous and organic mixtures with thermal separation processes is an important and challenging task in the chemical industry. Rising prices for energy, stricter environmental regulations and the increasing demand for high purity chemicals are the main driving forces to find alternative solutions to common separation technologies such as distillation and absorption. These are mostly too energy consumptive and can show limited separation performance, especially when applied to close boiling or azeotropic mixtures. Pervaporation can overcome these thermodynamic limitations and requires less energy because only the separated components need to be evaporated. This separation technology is already well established for the production of anhydrous solvents, but not yet widely distributed in the chemical and petrochemical industry due to some crucial challenges, which are still to overcome.

Besides the need of high selective membranes, the development of membrane modules adapted to the specific requirements of organoselective pervaporation needs more research effort. Furthermore, only few modelling and simulation tools are available, which hinders the distribution of this process in industrial scale.

In this work, these issues are addressed in a combined approach. In close collaboration with our cooperation partners, a novel membrane module for organophilic pervaporation is developed. A novel technology to manufacture high selective polymeric pervaporation membranes is applied to produce a membrane for an industrially relevant organic-organic separation task. A three step modelling approach ranging from a shortcut and a discrete to a rigorous model is developed and implemented in a user interface. A hydrophilic and an organophilic membrane are characterised for the separation of a 2-butanol/water mixture in a wide range of feed temperature and feed concentration in order to establish a generally valid description of the membrane performances. This approach is implemented in the three developed models to simulate the novel membrane module in industrial scale. The simulations are compared to the results of pilot scale experiments conducted with the novel membrane module. Good agreement between simulated and experimental values is reached.
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Abbreviations

ABE  Acetone-Butanols-Ethanol
ACM  Aspen Custom Modeler
ECN  Energy Centre of the Netherlands
GP   Gas Permeation
HZG  Helmholtz-Zentrum-Geesthacht
MSE  Molecular Surface Engineering
MTBE Methanol-Tert-Butyl-Ether
NRTL Non Random Two Liquids
PAN  Poly-Acryl-Nitrile
PCS  Process Control System
PDMS Poly-Di-Methyl-Siloxan
POMS Poly-Octyl-Methyl-Siloxan
PV   Pervaporation
PVA  Poly-Vinyl-Alcohol
VOC  Volatile organic component
VP   Vapour Permeation

Dimensionless Numbers

Re  Reynolds number
Pe  Péclet number
Sc  Schmidt number
Sh  Sherwood number
### Greek Letters

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<tr>
<td>$\alpha$</td>
<td>Heat transfer coefficient</td>
<td>$W/(m^2K)$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Randomness parameter</td>
<td>–</td>
</tr>
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<td>$\tilde{\beta}$</td>
<td>Mass transfer coefficient</td>
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<td>$\Delta h^{\nu p}$</td>
<td>Enthalpy of vaporisation</td>
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<td>Difference</td>
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### Latin Letters

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<td>$a_{ij} - d_{ij}$</td>
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<td>–</td>
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<td>$a_i - g_i$</td>
<td>Antoine parameters</td>
<td>–</td>
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<tr>
<td>$b$</td>
<td>Mobility inside the membrane</td>
<td>$mol/(barsm)$</td>
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<tr>
<td>$b$</td>
<td>Width</td>
<td>$m$</td>
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<tr>
<td>$\tilde{c}$</td>
<td>Molar concentration</td>
<td>$mol/m^3$</td>
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<tr>
<td>$c_p$</td>
<td>Constant pressure heat capacity</td>
<td>$J/(molK)$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
<td>$m^2/s$</td>
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List of Symbols

\( \frac{d}{dz} \)  First derivation in spatial dimension \( z \)  \( 1/m \)
\( d_h \)  Hydraulic diameter  \( m \)
\( DF \)  Driving force  \( J/(molm) \)
\( E \)  Modulus of concentration polarisation –
\( E_o \)  Enrichment factor –
\( E_{Act} \)  Overall activation energy  \( J/mol \)
\( \dot{F} \)  Molar flow  \( mol/s \)
\( \dot{j} \)  Specific molar flux  \( mol/(sm^2) \)
\( G \)  Free enthalpy  \( J/mol \)
\( h \)  Molar enthalpy  \( J/mol \)
\( k \)  Thermal transmittance  \( W/(m^2K) \)
\( L \)  Permeance  \( mol/(m^2sbar) \)
\( N \)  Integer number –
\( p \)  Pressure  \( bar \)
\( p_r \)  Vapour pressure  \( bar \)
\( \dot{Q} \)  Heat flow  \( J/s \)
\( \dot{q} \)  Specific heat flux  \( J/(sm^2) \)
\( R \)  Ideal gas constant  \( J/(molK) \)
\( S \)  Sorption coefficient  \( mol/m^3 \)
\( T \)  Absolute temperature  \( K \)
\( T_o \)  Reference temperature  \( K, ^\circ C \)
\( v \)  Molar Volume  \( m^3/mol \)
\( w \)  Velocity  \( m/s \)
\( x \)  Molar fraction in the liquid phase  \( mol/mol \)
\( y \)  Molar fraction in the vapour phase  \( mol/mol \)
\( x, y, z \)  Spatial dimension –

Superscripts

cond  Conductive
conv  Convective
liq  Liquid state
°  Reference value
start  Starting point of the iteration
### List of Symbols

- $vap$  
  Vapourisation / Vapour state

#### Subscripts

- **BL**  
  Boundary layer
- **comp**  
  Compartment
- **crit**  
  Critical state
- **env**  
  Envelope
- **F**  
  Feed flow
- **FM**  
  Membrane surface layer on the feed side
- $i,j$  
  Component index
- **M**  
  Inside the membrane
- **Mem**  
  Membrane
- **Mod**  
  Module
- **MP**  
  Membrane surface layer on the permeate side
- $o$  
  Reference value
- **P**  
  Permeate flow
- **R**  
  Retentate flow
- **Sec**  
  Discrete section
- **TM**  
  Transmembrane flow
1. Motivation and thesis outline

Pervaporation (PV) is a thermal membrane separation process, in which the feed/retentate stream is in liquid state, whereas the permeate is withdrawn as a vapour from the system. In figure 1.1, a simplified illustration of the process with its main fluxes is depicted.

![Simplified sketch of a pervaporation module with condenser.](image)

**Fig. 1.1.:** Simplified sketch of a pervaporation module with condenser.

A feed stream consisting of two or more components is brought in contact with a dense membrane, which shows a preferential selectivity towards at least one of the feed components. The better permeating components adsorb at the membrane surface, pass through the membrane and desorb at the downstream side of the membrane. Due to the permeate conditions (e.g. low pressure), the components evaporate in the permeate chamber. This vapour is removed from the system and usually liquefied by means of a condenser.

This process is mainly used for the separation of close boiling and azeotrope mixtures ([Smitha et al. [1]]). Dehydration of organic solvents like ethanol by PV can already be considered as an established industrial application. Also the removal of volatile organic compounds (VOCs) from dilute aqueous solutions is an emergent application.
for pervaporation. A number of membranes for those applications are available and
described in literature (SHAO ET AL. [2]). The separation of organic/organic mixtures
by pervaporation (oPV) is the most awaited and least distributed application for this
technology (BRÜSCHKE [3], BAKER [4]).

Besides gas and vapour permeation (GP, VP), PV is considered as “developing indus-
trial membrane separation technologies” (BAKER [4]) being in the “growth” phase
(STRATHMANN [5]). In figure 1.2, the results of different search queries with the scientific
search engine sciencedirect are plotted over the time period between 1982 and 2012. It
clearly shows that most effort is made in “membrane” development and investigation
of “separation” tasks in laboratory scale pervaporation plants. Research in “process”
development for pervaporation is dominated by simulation of standalone and hybrid
applications using shortcut models. The combination with “modelling” and “modules”
results in the lowest number of publications.

![Fig. 1.2: Distribution of published journal articles with Pervaporation & Membrane, Separation, Process Module, Modeling in the title, abstract and keywords.](image)

Different reasons to explain this development can be identified. On the one hand,
research in polymer synthesis has rapidly developed in the last decade, which enables
the production of long lasting and high selective membranes. Furthermore, simulation of
pervaporation plants and hybrid processes with shortcut models becomes much easier
due to increasing computational capacity. On the other hand, development and testing

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3Chapter 1, page 7
of industrial scale modules as well as the construction of pilot plants for the investigation of entire separation processes are very cost intensive. The low availability of advanced but comprehensive modelling approaches additionally hinders the introduction of this process in industrial scale.

Therefore, this work focuses on the development of a modelling approach that includes membrane manufacturing and characterisation, simulation of the process as well as the design and construction of an industrial scale membrane module.

1.1. Problem definition

Despite the advantages of pervaporation (lower energy requirement, no additional entrainer), its propagation in industrial scale is still limited to individual applications. Considering the distribution of the research areas (see figure 1.2), and the requirements on R&D in membrane technology (SOMMER [6], JONQUIÈRES ET AL. [7]), different challenges are identified, which need to be overcome to promote the distribution of pervaporation in chemical industry. In this work, these are summarised to:

1. Insufficient understanding of the overall mass transfer effects in pervaporation membranes is one reason for its poor distribution, although membrane production has become more present in scientific research during the last decade. Besides the casting and the pre-/post- treatment of dense and porous membranes, especially the transfer of membrane characteristics from laboratory experiments to industrial scale pervaporation applications is of main interest.

2. Membrane modules have been originally developed and optimised for ultra filtration and reverse osmosis processes. As organophilic pervaporation poses high requirements on the materials used in the module, the known constructions cannot be easily adapted to pervaporation applications (BAKER [4]). Thus, the separation performance of the used membranes are not fully utilised.

3. Only few process models for the simulation of pervaporation applications are available, in which relevant process parameters and the occurring heat and mass

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transport phenomena are sufficiently implemented (González [8], Abetz et al. [9]). In most cases, the simulations are based on phenomenological relationships such as separation factors and stage cuts. These parameters are measured using the actual membrane module and process configuration, why these models are only valid in a small application range (Marriott [10], Daviou [11]).

Because of these drawbacks, the separation performance of large scale membrane modules is difficult to predict accurately, which slows down the implementation of this process in industrial applications. The necessary extensive experimental investigations in laboratory and pilot scale for each separation task makes the design of pervaporation applications time consuming and cost intensive.

1.2. Structure of the work

In this work, the challenges of membrane characterisation, module design and process modelling are addressed in an integral approach. Chapter 2 contains a short overview on the actual state of the art of pervaporation. Historical and recent developments in membrane and module technology as well as the current standards in process integration and the modelling of this technology are depicted. In chapter 3, the transport phenomena necessary for the description and modelling of this process are described. Besides the solution diffusion model for the description of the transmembrane fluxes, this includes mass transfer resistances like temperature and concentration polarisation as well as the pressure drops in the feed and the permeate.

Chapter 4 contains the design of a novel membrane module concept and the production of an organophilic membrane. Both have been developed within the framework of a joint research project with the PolyAn GmbH and the HZG Research Centre. For the industrial relevant separation of isoprene from a mixture with n-pentane, Molecular Surface Engineering (MSE) is applied to manufacture pervaporation membranes with enhanced separation performances. The membrane module, equipped with the novel membrane is investigated in pilot scale at the HZG Research Centre.

\footnote{Helmholtz-Zentrum Geesthacht}
1. Motivation and thesis outline

In chapter 5, a three step modelling approach ranging from a *shortcut* and a *discrete* to a *rigorous* model is developed. The geometrical design of the membrane module is included in the *discrete* and the *rigorous* models. The models are embedded in a user interface which facilitates the data management and the display of the results. With an intensive experimental investigation in chapter 6, the performances of two membranes are investigated for the separation of 2-butanol/water in a wide range of feed temperature and feed concentration. In chapter 7, the results of this investigation are used to identify a temperature and concentration dependent permeance approach for both membranes, which is integrated in the three models. With this modelling tool and the permeance approach, a more detailed simulation of the pervaporation process becomes possible, which will be shown on two industrial separation tasks in chapter 8. The simulations are compared to the experimental results gained from a pilot scale investigation.

At the end of this work, a conclusion of the achieved tasks and a short outlook for further research is resumed in chapter 9.

Part of the information and data in this thesis have been published as peer reviewed journal articles, a patent and in oral and poster presentations in national and international conferences and work shops. A list of these publications is included in appendix A.1.
2. Introduction and state of the art

The origin of the pervaporation process and its actual state of the art in the chemical industry are the topics of this chapter. After a short overview of the development of this technology, different membrane types used for pervaporation and their theoretical separation performance are described. Furthermore, the four major module types and their integration into industrial processes are also topics of this chapter. The two model applications treated in this work are outlined from a thermodynamic point of view. Finally, a general survey of the modelling and simulation of this process is given.

2.1. Historical development

The discovery of the separation capacity of natural membranes (pig’s bladder) and their use to separate ethanol/water mixtures dates back to the 18th century (BÖDDEKER [12]), but it was not until 1917 that the evaporation of water through dense collodion bags was investigated and the term “pervaporation” was introduced (KOBER [13]). The scientific interest for membrane separation processes was born, but because of missing applications, industrial research in this area did not start until the 1950ies and 1960ies. At the beginning, the work focused on the development of membrane materials for the separation of crude oil into different classes of hydrocarbons (BINNING ET AL. [14]). The insufficient separation capacities, high production costs, short life times and the poorly conceived membrane production at this time prevented the industrial propagation of this technology. In figure 2.1 major milestones of industrial pervaporation are illustrated.

The interest and research efforts were revived when the fabrication of defect-free membranes in large scale was advanced enough to produce membranes with industrially
2. Introduction and state of the art

1870 Breaking the azeotrope of ethanol with pig’s bladder
1917 Introduction of term “pervaporation”
1950 Research for applications in petroleum industry
1982 Dehydration plants for organic solvents
1988 Industrial bioethanol dehydration plant in Bethéniville
1994 Removal of water from reaction mixtures
1997 Separation of methanol from trimethylborate
1999 First industrial PV plant with ceramic membranes
2008 Separation of (VOCs) from aqueous mixtures

Fig. 2.1.: Milestones of pervaporation (BRÜSCHKE [3]a, BAKER [4]b).

aChapter 3, page 151
bChapter 9, page 357

relevant life times (BRÜSCHKE [3]6, BAKER [4]7). Finally, the development of hydrophilic membranes for the dehydration of organic solvents gave the technology a new boost in the late 1970ies and 1980ies (APTEL ET AL. [15]). In 1983, the first hydrophilic membrane producible in industrial scale was developed by GFT Membrane Systems (patent EP 0096 339 B1 [16]) and the first small scale commercial dehydration plant with a capacity of 1200 l/d pure ethanol was erected in Brazil. The ethanol dewatering facility in Bethéniville/France (built in 1988) was the first industrial scale pervaporation plant in Europe (2400 m² membrane area) with a capacity of 5000 kg/h of anhydrous ethanol (BAKER [4]8). Also the dewatering of an ester was achieved for the first time in 1988 (BRÜSCHKE [3]9). Today, the dehydration of organic solvents by pervaporation is considered as “state of the art” and is the most advanced separation task with this technology (FAHMY [17]). A pilot plant for the removal of methanol from a methanol-tert-butyl-ether (MTBE) reaction mixture was erected by SEPAREX (BAKER [4]10). Industrially, this process was introduced in 1991 at BASF SE (KUJAWSKI [18]). This application is the topic of numerous research projects, which mostly focus on the development of new, high selective membrane materials (SRIDHAR ET AL. [19], RAY AND RAY [20]).
Besides these hydrophilic applications, removing volatile organic components (VOCs) from aqueous streams is another promising application for pervaporation. But because of the lower permselectivity of the organic compounds in the membrane, relatively high feed concentrations are required to render this process more effective than e.g. adsorption processes (Shao and Huang [2]). Especially in the pharmaceutical and fine chemical industry, large waste-water streams with hazardous or high valuable products in small quantities are nowadays treated by stripping and absorption processes. Due to low product contents and large feed streams, a high amount of energy is required for these techniques (Lipnizki et al. [21]). Besides that, the recovery of heat sensitive aroma compounds in the food and fragrance industry is in the focus for pervaporation because it can be conducted at lower temperature levels than other thermal separation processes (Brazinha and Crespo [22]). The production of biofuels from fermentation broths also shows high potential for this application (Vane [23]). The ABE\textsuperscript{11}-fermentation is a good example where the use of distillation is not viable because of the low product content in the aqueous phase. Despite intensive research in this filed, only very few large scale industrial plants have been realised so far (Lipnizki et al. [21]). Low selectivity of organophilic membranes and thus large membrane areas are the limiting factors for a wide industrial distribution of this technology (Brüschke [24]\textsuperscript{12}).

The most challenging and most anticipated separation task for pervaporation is the target removal of single components from purely organic mixtures. Since the beginnings of pervaporation, the chemical and petrochemical industry look forward to alternative separation technologies for established processes like distillation or absorption. Growing market demands for high purity chemicals, stringent environmental regulations and increasing costs for energy and resources are promoting the research effort in this field (Smitha et al. [1], Shao et al. [2]). A review with examples of aromatics separation by pervaporation can be found in the literature (Smitha et al. [1]).

The separation of organic mixtures is divided into different classes and for some of them, pervaporation has already showed promising results. The separation of aromatics and alicyclic components (e.g. benzene and cyclohexane) is an important industrial separation task and has been successfully implemented with pervaporation membranes (Villaluenga and Tabe-Mohammadi [25], Chen et al. [26]). For aromatic/aliphatic separation tasks, some membranes have been developed. Especially the removal of sulphur

\textsuperscript{11}Acetone, Butanols, Ethanol
\textsuperscript{12}Chapter 11, page 337
containing aromatics from gasoline is of great interest (Lin et al. [27], Pasel [28]) and has been implemented industrially in the S-Brane process (Konietzny [29]). The separation of different isomer mixtures has been investigated for polymer and zeolite membranes in laboratory scale (Wessling et al. [30], Flanders et al. [31]). Removing organics from air and gas streams using vapour permeation and gas separation however has been present in industrial scale since 1989 (Ohlrogge et al. [32]).

2.2. Actual situation

Today, pervaporation is considered as a viable alternative in the chemical industry to established separation processes such as distillation and absorption (Jonquière et al. [7]). Using PV can contribute to a cleaner environment and a more sustainable chemical industry as the process can be conducted at lower temperatures and requires less energy compared to distillation. But despite its potential, the predicted large-scale breakthrough has never been achieved and pervaporation is still considered as a niche-technology. The actual number of pervaporation plants in the chemical industry is difficult to denominate. From 1984 to 1996, 63 industrial pervaporation plants were erected, where the majority serves as dehydration plants for organic solvents like ethanol, acetonitrile, isopropanol and butanols (Smitha et al. [1]). More than 100 pervaporation plants for azeotropic distillation were built from 1982 until 2004 (Baker [4]) and 110 plants have been sold by SULZER Chemtech and licensing companies until the year 2000 (Kujawski [18]). Extrapolating this trend to the present (2013) yields a number of around 160 industrial pervaporation plants worldwide.

2.3. Membrane materials

“In essence, a membrane is nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it.” (Baker [4]) Although this simple quote, membrane technology and its industrial competitiveness are strongly dependent on the separation performance and the membrane lifetime. Only with the development

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14Chapter 1, page 3
of the *Loeb-Sourirajan*-process in the 1960ies, membrane fabrication became feasible in commercially relevant scale (BAKER [4]15). Since then, a vast range of membranes have been developed and introduced more or less successfully in industrial applications. Depending on the focus of the separation task and the field of application, different methodologies can be used to classify these membranes (MELIN AND RAUTENBACH [33]16, BAKER [4]17). The most common examples are shown in figure 2.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Morphology</th>
<th>Target compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>Porous</td>
<td>Symmetric</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>Organic</td>
<td>Dense</td>
<td>Asymmetric</td>
<td>Hydrophobic/organophilic</td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td></td>
<td>organoselective</td>
</tr>
</tbody>
</table>

Fig. 2.2.: Different possibilities of membrane classification.

Considering the target compounds of the separation, hydrophilic membranes have very high selectivities towards water. Hydrophobic membranes reject water and let pass organic components more preferably. In this work, the term organophilic is used equally to hydrophobic. The third type are organoselective membranes, able to separate single organic components from mixtures of organic solvents. In pervaporation, porous inorganic (ceramic) membranes in tubular shape and dense polymer membranes as flat sheet material are the most prevalent types. Polymeric asymmetric membranes on the one hand are the most advanced membranes and available for a number of separation tasks ranging from dehydration of organic solvents to organoselective separation tasks (BACHMANN ET AL. [34], SHAO AND HUANG [2]). Inorganic membranes on the other hand, are well developed for hydrophilic applications (MORIGAMI ET AL. [35]) and the expansion to organophilic pervaporation is in progress (KITA ET AL. [36]). Which membrane to chose is a question of necessary fluxes and selectivities and the available types of membranes and modules types. Generally, flat sheet membranes can be integrated in plate & frame, spiral wound or envelope type modules, whereas tubular inorganic membranes can solely

15 Chapter 1, page 3
16 Chapter 2, page 20
17 Chapter 1, page 4
be found in tube bundle modules. In some applications, polymeric as well as inorganic membranes can be used (Gallego-Lizon et al. [37]).

### 2.3.1. Inorganic membranes

Almost all inorganic membranes are nowadays produced in tubular shape because of the limitations of the casting process and the higher mechanical stability compared to plates. Depending on the composition of the separating layer, they are divided into amorphous silica membranes and zeolite membranes. Their maximum operating temperature is above 250 °C, which makes them much more favourable in dewatering applications compared to organic membranes. For both types, a porous ceramic or metal support tube is coated with the selective material. Since the porous support has usually very large pores and to prevent defects in the active layer, multiple layers need to be coated on the tubes (Brüschke [3]). A principle sketch of such a membrane is shown in figure 2.3. This production procedure makes the tubular membranes much more expensive than the casting of polymer flat sheet membranes.

The separation effect is governed by molecular sieving through the defined pores and adsorption of small molecules at the outer membrane and the inner pore surface of the active layer (Bowen et al. [38]). The main applications of this membrane type are dewatering of organic solvents and removal of alcohols from reaction mixtures (Casado et al. [39], Sommer and Melin [40]).

![Principle structure of an inorganic tubular membrane](image)

**Fig. 2.3.** Principle structure of an inorganic tubular membrane.
2. Introduction and state of the art

Amorphous silica

Amorphous silica membranes are very selective towards polar liquids like water and the lower alcohols methanol or ethanol. One major advantage compared to the zeolites is the resistance against acids (Van Veen [41]). Compared to polymeric membranes, the fluxes are much higher (Gallego-Lizon et al. [37]). The long term stability and separation performance is not yet fully understood and investigated (Brüschke [3]\(^{19}\)).

Crystalline zeolites

By changing their aluminium to silicon ratio, zeolites can be produced with defined pore sizes and a specific affinity to different molecule sizes and structures. At high aluminium contents, the pores become very narrow and thus show a higher selectivity for water and small alcohols. Experimental studies showed that by elevating the silicon content in the active layer, zeolites are also suitable for the removal of VOCs from aqueous streams and the separation of organic mixtures by vapour permeation (Sommer and Melin [42]). One major technical challenge is that zeolites are very prone to acid conditions, which reduces their possible field of applications (Voigt and Tudyka [24]\(^{20}\)). The mass transfer through the pores of zeolites is governed by adsorption and diffusion phenomena. This effects as well as the driving force have been thoroughly investigated (Bowen et al. [43, 38]).

2.3.2. Polymeric membranes

Polymeric membranes are produced as symmetric membranes with a single polymer layer or in asymmetric multilayer structure. The latter shows higher mechanical stability and is thus the preferred membrane for industrial applications (Brüschke [24]\(^{21}\)). A principle sketch of such a composite membrane is shown in figure 2.4. Their main advantage is that the support layer and the selective layer can be composed of different polymer mixtures with specific properties (selectivity, chemical resistance). The disadvantage of

\(^{19}\)Chater 3, page 179  
\(^{20}\)Chapter 5, page 119  
\(^{21}\)Chapter 11, page 354
this combination however is that different polymers show different degrees of swelling when they are in contact with organic solvents. This can lead to internal stresses and in worst case to the destruction of the membrane structure. To enhance their stability, different methods like cross-linking of the top layer, casting of multiple layers on the porous support and the “integrally skinned structure approach” are applied (Shao and Huang [2]). The upper dense layer is the selective part of the membrane with a thickness of about 1 \( \mu m \). To minimise transport resistance, it should be as thin as possible. It is cast on a porous asymmetric support layer of the same material. Its pore size is in the range of 100 \( \mu m \) and the pores get larger to the bottom of the membrane. To further increase the mechanical stability of the membrane, this microporous support membrane is usually cast on a fabric fleece. In some cases, an additional thin layer of a non-selective polymer is added between or on top of the structure to increase the chemical stability of the membrane (Brüschke [24][22]). For the porous support and the selective layer, a wide range of polymer and polymer blends is available and continuously developed further. With reference to the preferentially solved components in the active layer, polymeric membranes are usually subdivided in hydrophilic and organophilic membranes (Shao and Huang [2]). In this work, both types are characterised experimentally in a wide range of feed temperature and concentration.

Fig. 2.4.: Principle structure of a polymer composite membrane.

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Hydrophilic membranes

The most developed polymer membrane consists of a hydrophilic Poly-Vinyl-Alcohol (PVA) active layer on a porous Poly-Acryl-Nitrile (PAN) support. This type of membrane is very well developed and shows high fluxes and selectivities for polar molecules such as water and methanol. Besides the dehydration of organic solvents, this type can also be used for the separation of lower alcohols from hydrocarbon mixtures. It is very resistant to acid conditions and temperature stable up to 130 °C (Melin and Rautenbach [33]). The separation of methanol from mixtures of organic solvents (Toluene, THF, Methylacetate, Acetone) can also be achieved with commercially available hydrophilic membranes (Bachmann et al. [34]). A detailed review about this membrane type can be found in literature (Semenova et al. [44]). In the present work, a PVA/PAN membrane, provided by the HZG Research Centre is used (patent DE 102 004053402 B3 [45]). Its separation capacity and performance data are investigated for a wide range of feed temperatures and compositions.

Organophilic membranes

The second widespread type of polymeric membranes is the organophilic membrane, including hydrophobic and organoselective membranes. They are often called silicon-rubber composite membranes (Brazinha and Crespo [22]) and are usually formed of a dense layer of Poly-Di-Methyl-Siloxane (PDMS) or Poly-Octyl-Methyl-Siloxane (POMS), which is cast on a porous support of e.g. Poly-Ether-Imide (PEI) (Luo et al. [46]). This type of membrane is more soluble for organic components and is thus used for the separation of organic mixtures or VOCs from aqueous solutions (Shao and Huang [2]). Their second field of application is the recovery of organic vapours from gaseous streams (Brinkmann et al. [47]). In this work, a POMS membrane provided by the HZG Research Centre is used (patent WO 932 0930 A1 [48]).
2.3.3. Hybrid membranes

Polymer membranes show very high long term stability in acid or aggressive conditions. The casting process is well developed and thus the production costs are already low compared to ceramic membranes. Using zeolites on the other hand, much higher selectivities and fluxes can be reached at high temperatures. The combination of these two advantages into one membrane is the goal of different research groups. At the Energy Research Centre of the Netherlands (ECN), the Hybsi membrane\(^{24}\) has been developed. Thin layers of high performance polymers are fixed upon and inside the pores of rigid ceramic support tubes, which combines the mechanical and the thermal stability of ceramic membranes with the specific selectivities of polymers materials (Kreiter et al. [49], Castricum et al. [50], Veen et al. [51], Paradis et al. [52]).

Another approach is the inclusion of zeolite particles inside the polymeric structure of organic membranes, which results in mixed matrix membranes (Shao and Huang [2], Mosleh et al. [53], Mushardt et al. [54]). In this case, the additional pores of the zeolites facilitate the transport of the preferred components without decreasing the selectivity. Furthermore, the preparation of facilitated transport membranes is another possibility to produce membranes with enhanced performances (Abetz et al. [9]).

2.3.4. Membrane performance

Fluxes and separation factors of different membranes and for different component mixtures are described in literature (Bachmann et al. [34], Wesslein et al. [55], Guo et al. [56]). In most cases, mass fluxes and permeate composition or separation factors are plotted over the feed temperature and the feed concentration. In figure 2.5, the general trends of the transmembrane flux (\(\cdot\cdot\cdot\)) and the permeate composition (\(\ldots\)) in dependency of the feed temperature (figure 2.5(a)) and the feed composition (figure 2.5(b)) are shown for polymeric membranes. The transmembrane flux is usually exponentially increasing with the feed temperature. Higher temperatures elevate the mobility of the polymer molecules in the active separation layer and thus facilitate the diffusive transport of the feed components through the membrane (Chen et al. [26]). Additionally, the sorption of the components at the membrane surface is ameliorated. A negative

\(^{24}\)http://www.hybsi.com/
2. Introduction and state of the art

Fig. 2.5.: Qualitative trends of the temperature dependency at different feed compositions (a) and concentration dependency at different feed temperatures (b) of the transmembrane flux (---) and the permeate content (-----) of the preferred permeating component for pervaporation membranes.

Effect is that the enhanced mobility also elevates the flux of the retained component, which considerably reduces the membrane selectivity. More than that, a higher feed concentration of the preferred permeating component favours a higher total flux through the membrane. This relation is mainly due to swelling effects of the polymer material, which enhance the diffusive transport. With a higher feed content of the preferred permeating component, its permeate composition rises. The overall selectivity of the membrane can be considerably reduced by this effects (Bachmann et al. [34], Guo et al. [56], Huang et al. [57], Bettens et al. [58]).

2.4. Membrane modules

Different types of membrane modules have been developed in the last decades and are very well suited for different membrane processes. The choice which membrane module to use is depending on the application and the available membrane material for the separation. In this section, the membrane modules which are nowadays used for pervaporation are described. These are tubular, hollow fibre, frame & plate, spiral wound and envelope type modules. Capillary modules are also mentioned in literature but usually used synonymously for hollow fibre modules (Melin and Rautenbach [33]). To the best
of my knowledge, no industrial PV application with capillary modules has been realised until today, why it will not be described separately in this work (Smitha et al. [1]).

2.4.1. Tubular membrane modules

Tubular modules are used for inorganic membranes. The tubes are fitted and sealed individually in metal end caps like in tube bundle heat exchangers. This is the most common technology as the membranes can be cast and tested separately and in case of a damage, replaced individually or sealed with a dummy socket. Alternatively, the membrane can be moulded as monolithic zeolite blocks which are put under a vacuum dome (Morigami et al. [35]). Figure 2.6 shows the Pervap SMS module from SULZER Chemtech, which is one of the most widespread tubular membrane modules. If the feed is directed inside the tubes and the permeate is withdrawn from the shell side, the pressure drop of the permeate can be kept very small. To compensate the temperature drop (section 3.2) in the module, a heat integration system needs to be included. One possibility is to insert additional tubes inside the membranes through which a heating fluid flows. In hybrid applications with distillation, this could be the top product of the column, withdrawn as a vapour and condensed in the inner tube. Afterwards, it is directed in the annular gap as feed for the membrane (Del Pozo et al. [59, 60]). Another possibility is a module, in which the membrane tubes are interconnected in the end caps of the membrane module, and a heating fluid provides the necessary energy (Patent DE 103 23440 B4 [61]). The module in figure 2.6 shows the opposite approach. Membrane tubes are put inside the tubes of a heat exchanger.
shell side of the module is loaded with heating fluid and the feed is conducted through the annular gap. The permeate is withdrawn at the end caps of the module (Melin and Rautenbach [33]).

A major challenge for inorganic membranes is the assembling of the membrane tubes in the modules and the fixation of the ceramic membrane with the stainless steel module. In high temperature applications, the membrane material, the metal of the module and the material of the sealing gasket have different heat expansion rates which can damage the membranes or displace the sealing gaskets. Additionally, if the feed consists of strongly aggressive and/or organic components, the capital cost of the modules rises because of the need of special sealing materials (Brüschke [24]).

2.4.2. Hollow fibre modules

Already well developed for the membrane processes ultra- and microfiltration are hollow fibre membranes. Using spinning techniques, the polymer is formed in long filaments with inner diameters between 100 and 500 µm. These fibres are combined in bundles which are potted at the ends in an impermeable material as shown in figure 2.7 (Melin and Rautenbach [33]). For pervaporation, the pressure drop inside the fibres would be too high when used as permeate channel. Therefore, only the inside out configuration,
in which the feed flows through the fibres and the permeate is removed from the shell side, is applied. Another major challenge of this module type is the reheating of the feed. Because of the large membrane area in such a module, the permeate flux is very high and a large temperature drop occurs (section 3.2). As the heat supply is provided outside of the module, the maximum membrane length would be small and the overall installation costs increase. These pressure drops reduce the maximum fibre length (BRÜSCHKE [24]).

2.4.3. Frame & plate modules

Flat sheet membranes in plate and frame modules (figure 2.8), were the first industrial membrane modules for pervaporation (BAKER [4], PATENT DE 352 9175 A1 [62]). The membrane sheets are arranged between metal frames and gaskets, forming alternating feed/retentate and permeate chambers. The feed channels are interconnected and sealed from the exterior. The permeate channels are open to the environment and the modules are put under a vacuum dome. Although this module type is installed in a number of industrial scale pervaporation plants, it shows some essential constructive difficulties. Because of the high number of large sealing gaskets, the assembling of the module is complex and equal contact pressure on each sealing difficult to achieve (MELIN AND RAUTENBACH [33]).

Fig. 2.8.: Assembling and flows in a frame and plate module (GOMEZ ET AL. [63]).
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2.4.4. Spiral wound modules

The spiral wound module is the most common membrane module for filtration processes (Schwinge et al. [64]). The rapid expansion of the desalination industry by reverse osmosis boosted the development and production of this module type. Very high packing density and easy installation of the spirals made this membrane the most economic solution for many applications (Melin and Rautenbach [33]). In figure 2.9, the principle of the spiral wound module is shown. Two membrane sheets are glued together on three sides to form membrane pockets. To prevent them from collapsing, one or more layers of membrane spacer are placed between the membranes. Spacer material is also placed on the feed side of the membrane between the pockets to ensure a defined feed channel height. Additionally, this enhances mixing effects and thus counteracts mass transfer resistance like concentration polarisation. The open side of the envelope is fixed on a perforated central permeate removal tube and the envelope is wound around this tube. The feed flows along the membrane envelopes and the permeate passes through the envelopes into the collector. Despite this module type is perfectly suited for pressure driven filtering applications, only few applications for pervaporation exist (Cao et al. [65]). The pressure drop inside the envelopes is very high because of the length of the spacer filled channel. Because the joint between the membranes needs to be flexible for the coiling process, welding is not an option and the membranes need to be glued together. As pervaporation and vapour permeation are mainly considered for the separation of organic solvents and aggressive media, the glue could be affected or even dissolved (Lipnizki et al. [24]). To the best of my knowledge, Membrane Technology

Fig. 2.9.: Assembling and flows in a spiral wound module.
and Research Inc.\textsuperscript{34} and Pervatech BV\textsuperscript{35} are the only companies, producing spiral wound membrane modules for the removal of VOCs by pervaporation and vapour permeation in industrial scale.

### 2.4.5. Envelope type modules

A well developed type of membrane module available for a multitude of dense membrane processes is the GS envelope type module of the HZG Research Centre (Abetz et al. \textsuperscript{[9]}, Brinkmann \textsuperscript{[24]}\textsuperscript{36}). This module is introduced in industrial scale and very well suited for the recovery of VOCs from fuel tanks and vent gases at gas stations and tank farms. The arrangement of the membrane envelopes on the central permeate tube and the membrane/spacer configuration are shown in figure 2.10. In this module type, spacer

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{envelope_type_module.png}
\caption{Design of the HZG GS envelope module (Brinkmann [24]).}
\end{figure}

\textsuperscript{34}http://www.mtrinc.com
\textsuperscript{35}http://www.pervaporation-membranes.com
\textsuperscript{36}Chapter 10, page 307
material at the feed side of the membranes is not necessary for stability reasons but mostly installed for mixing purposes. The membrane stack is put inside a pressure vessel. Baffle plates divide the module in compartments which can be equipped with variable numbers of membrane envelopes. Thus, the free cross section of the feed channel can be varied in order to maintain high feed velocities and thus reduce concentration polarisation. The major advantage compared to plate and frame modules is that less sealing gaskets are needed and no additional vacuum dome is required. The relative low packing density compared to spiral wound and hollow fibre modules is a major drawback of this module type, but since membrane materials become more selective and have higher fluxes, this is not anymore the main criteria for pervaporation modules.

The described membrane modules are more or less suited for different applications, and their is no universal module for all applications. In the present work, a membrane module optimised for the separation of organic-organic mixtures is developed and constructed. The requirements on the module design are identified by considering two industrial relevant organophilic separation tasks.

### 2.5. Process integration

Pervaporation modules can be integrated in different locations in chemical processes. One possibility is to use pervaporation for the dehydration of organic solvents close to the azeotrope point, instead of using additional columns for entrainer recovery in extractive distillation (BAKER [4]37). An example of such a process is shown in figure 2.11. The organic solvent/water mixture is separated into water at the bottom and an azeotrope mixture at the top of the first column. In figure 2.11(a) this stream is mixed with an entrainer and separated in the second column. This yields a pure organic phase with trace components of the entrainer at the bottom of the column and an entrainer/water/solvent mixture at the top. The entrainer is then concentrated in the top of the third column and the water leaves the third column at the bottom. In figure 2.11(b), the setup of the process using pervaporation is shown. The azeotropic product of the distillation column is treated with a hydrophilic membrane module which removes water with a high purity of around 95-99 wt%. This permeate can be removed from the system or recycled to the

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**Fig. 2.11.:** Two examples for the separation of an organic solvent and water.

The retentate of the pervaporation module is concentrated up to 99.9 wt% solvent without trace components of the entrainer.

Another common application is the removal of single components from reaction mixtures to enhance the reaction. In figure 2.12, a pervaporation membrane module is connected to a continuously stirred tank reactor. In the reactor, a mixture of educts A and B is transformed to the desired product C and the unwanted by-product D in an equilibrium reaction. With a membrane selective for the side product D, the concentration of the educts A and B and the wanted product C can be elevated, which causes an equilibrium shift to the wanted product C. Such membrane assisted hybrid processes and the prove of

**Fig. 2.12.:** Example of a hybrid reactor-pervaporation system.

Their advantage over a common reaction-separation process are topics of many research projects (Huang et al. [57], Kreis and Gorak [66], Koch et al. [67]). These
processes show an essential economic advantage (Lipnizki et al. [68]), especially when high purities are required (Hömmerich and Rautenbach [69]).

In some small scale applications, pervaporation-only processes can also represent a reasonable solution. The decentralised bioethanol recovery from fermentation broths is one example where pervaporation with hydrophobic membranes competes with distillation (Vane [70], Huang and Vane [71]).

2.6. Applications

As mentioned before, pervaporation is well developed for the dehydration of organic solvents. The removal of organic components is the second application, for which pervaporation shows high potential. The separation of purely organic mixtures is the most anticipated and challenging task.

One goal of this work is the design of a membrane module optimised for the separation of organic components and the development of a modelling approach for the simulation of the module and the process. Therefore, two model binary mixtures are chosen, which represent the removal of organics from water (2-butanol/water) and the separation of organic components from purely organic mixtures (isoprene/n-pentane).

2.6.1. 2-butanol/water

The separation of 2-butanol/water is a model application for hydrophobic pervaporation. One possibility to produce 2-butanol is the ABE fermentation processes in which 2-butanol is formed together with acetone and ethanol. Butanols are widely used in the resin production and as cleaning fluids or in reactions to produce esters (Guo et al. [56]). A major challenge is that 2-butanol and water form a miscibility gap from 13 to 80 wt% 2-butanol at atmospheric pressure as shown in figure 2.13 with an azeotrope point at 72 wt% 2-butanol (Aspen Properties [72]). The separation of 2-butanol from the fermentation broth is achieved nowadays by pressure swing distillation, which is an
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energy and cost intensive process (DÜSSEL [73]). Pervaporation represents a viable alternative, especially when applied in small scale fermentation plants (VANE [70]).

![Figure 2.13](image-url)  
(a) T-xy diagram

![Figure 2.13](image-url)  
(b) xy-diagram

**Fig. 2.13.** T-xy and xy diagram for 2-butanol/water at atmospheric pressure (ASPID [72]).

In this work, a hydrophilic and an organophilic membrane are characterised with the binary mixture of 2-butanol/water over a wide range of feed temperatures and concentrations. The feed concentration is varied through the miscibility gap. If this process is applied as stand alone unit operation in the mentioned fermentation process, it is possible that the feed composition changes during the process in a magnitude that phase separation occurs.

### 2.6.2. Isoprene/n-pentane

As second industrial application, the separation of isoprene from a mixture with n-pentane is chosen. This oleine/paraffine separation is challenging as the components have very similar boiling points of 34 and 36 °C respectively. Additionally, they form an azeotrope at an isoprene content of approximately 73.5 wt% (ASPID [72]). Conventional thermal separation processes such as extractive distillation are energy intensive and use additional entrainers which requires additional purification steps. Pervaporation could achieve the separation without entrainer and thus increase the purity of the products.

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The separation performance of pervaporation membranes or this mixture is investigated by our cooperation partner PolyAn GmbH in laboratory scale.

![Graph](image)

(a) T-xy diagram  
(b) xy-diagram

**Fig. 2.14.** T-xy and xy diagram for isoprene/n-pentane at atmospheric pressure (ASPEX PROPERTIES [72]).

### 2.7. Modelling and simulation of PV

For the design and planning of industrial processes in chemical engineering, simulation studies are an essential and important tool. The necessary models for these simulations and their development are a vast field in industrial and academic research. Although the computational performance is increasing continuously, a reasonable and consolidated modelling of the process and the occurring transport phenomena are of major interest in chemical engineering. The main task of the modelling is the prediction of the separation performance of the process. In this work, the following requirements on the models are defined:

- Description of relevant transport phenomena
- Fast and stable computational behaviour
- Detailed results which are easy to revise
2. Introduction and state of the art

The priority of these requirements depends on the available information about the system to describe, the numerical complexity of the established system of equations and the envisaged results. In some cases, the requirements are even contradictory and a compromise is needed.

For many established unit operations like distillation, different modelling approaches ranging from shortcut methods to rigorous heat and mass transfer equations have been developed (Goedecke [73]). These models have been validated with numerous experimental investigations and for a multitude of component mixtures. Thus, distillation processes can be simulated in software tools like Aspen Plus™ or ChemCAD™. A recent literature survey revealed that membrane processes and especially pervaporation are not yet implemented in these commercial packages as standard unit operations. The trend of publications dealing with “Pervaporation & Modelling”, shown in figure 1.2 also illustrates that this topic is poorly represented in research and development. In consequence, potential users of this technology need to implement self-programmed models and subroutines to perform simulation studies. Thus, most of the modelling concepts of pervaporation are restricted to the considered application or component mixture and only valid in a very narrow range of process parameters (Marriott et al. [10]). A possible reason for this situation is the lack of a general and comprehensive process understanding, which makes it difficult to establish a generally valid model for pervaporation.

Depending on the planning progress in chemical engineering, different modelling and simulation strategies are commonly used. For a first assessment of possible process parameters, fast and robust shortcut models are essential, but rigorous and reliable simulation tools become necessary in detailed process engineering (Bausa and Marquardt [74]). Also dynamic simulations or the introduction in a flowsheeting environment requires appropriate and target oriented modelling approaches (Kreis and Gorak [75], Koczka et al. [76]).

There are general and detailed model concepts for pervaporation published in literature (Marriott and Sørensen [77, 78], Marriott [79], Bausa [80], Mafi [81]). A dynamic, but not general model of the pervaporation process for the modelling software Aspen Custom Modeler™ (ACM) has been published recently (Luyben et al. [82]). Also the simulation using computational fluid dynamics are used for modelling mass, heat and momentum transport (Mafi [83]). For the simulation of gas and vapour permeation
processes, a comprehensive modelling tool based on the GS membrane module has been developed at the HZG for implementation in ACM. This model and an extensive review about modelling pervaporation and gas/vapour permeation can be found in literature (Brinkmann [24]).

A detailed modelling is especially important the for scale-up of separation processes from laboratory experiments to industrial scale applications. Such a scale-up procedure for the removal of aroma components using hydrophobic pervaporation is described in literature (Lipnizki [84, 85]).

One of the reasons for the slow distribution of pervaporation in the chemical industry, is the lack of suitable software tools for the simulation of the module and the process. Other state-of-the-art separation technologies like distillation are implemented in professional design tools like Aspen Plus™ or ChemCAD™. Simulation and correct dimensioning of distillation columns, additional equipment or the calculation of necessary utilities becomes much easier with such software tools. Even though pervaporation has been introduced in industrial applications about 30 years ago, a standard modelling and simulation procedure does not yet exists.

In this work, the available models from literature are investigated in this work and a three step modelling approach including a shortcut, a discrete and a rigorous model developed. The degree of detail of the three models is derived from the three stages of engineering, which allows a stepwise simulation of the process.

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3. Transport phenomena in pervaporation

In pervaporation, the feed/retentate flow is liquid, whereas the permeate is vaporous. Thus it shows common elements of reverse osmosis and gas separation (FENG AND HUANG [86]). The advantage of pervaporation is that only the permeating components need to be evaporated. Although, this is also the reason for some challenges considering the design and operation of this process.

The permeation of the components through the membrane is hindered by different transport resistances, which occur more or less strong in pervaporation. Temperature and concentration polarisation as well as pressure drops are the most important of these effects and need to be considered when designing the process. Detailed descriptions of these and more effects are published in literature (BRÜSCHKE [3]40, BRINKMANN [24]41, MELIN AND RAUTENBACH [33]42). In this work, the mass and heat transfer through the membrane as well as the momentum transfer at the feed and the permeate sides of the membrane are described.

3.1. Mass transfer

The transmembrane fluxes of the components $\dot{j}_i$ in membrane processes can generally be described by the product of their molar concentrations $\tilde{c}_i$ and mobility $b_i$ inside

\[^{40}\text{Chapter 3, page 166}\]
\[^{41}\text{Chapter 10, page 291}\]
\[^{42}\text{Chapter 12, page 424}\]
the membrane material and their overall driving force $DF_i$ between the two membrane interfaces:

$$\dot{f}_{i,TM} = \tilde{c}_i \times b_i \times DF_i \quad (3.1)$$

One disadvantage of this description is that the concentrations and mobility inside the membrane are difficult to access. As the membrane is a multilayer structure with different layer thicknesses and transport characteristics, additional sorption effects occur at the different membrane/fluid and membrane/membrane interfaces. Therefore, a definition of the membrane performance depending on the process parameters feed temperature and composition is more useful. Assuming an asymmetric polymer membrane with permeate side spacer support, a typical molar concentration profile from the feed to the permeate side of the preferentially permeating component is shown in figure 3.1. The resulting

**Fig. 3.1.:** Different mass transfer steps in dense polymer membranes during the pervaporation process, according to the Solution-Diffusion Model.

overall mass transfer process of this component from the feed side to the permeate side of the membrane can be divided in six major steps:

**Step I - Feed side boundary layer:** Depletion of the permeating components in the feed causes a concentration gradient from the feed bulk phase to the membrane surface. High feed velocities or feed spacers can be used to enhance mixing between the bulk and the boundary layer and reduce this concentration polarisation (section 3.1.5).
Step II - Sorption at the feed side: Sorption of molecules in the membrane on the feed side can be described with sorption isotherms. If more than two components are present, effects like preferential sorption need to be implemented. In general, the sorption step is usually fast compared to the diffusive transport through the membrane (Wijmans and Baker [87]43).

Step III - Diffusion through the membrane: The molecular transport of the molecules through the dense layer of the polymer membrane can be described basically with Fick’s law of diffusion or the Maxwell Stefan diffusive transport equation. In this work, the former is used as it is the more practical method and thus more suited for industrial applications (Wijmans and Baker [87]44).

Step IV - Permeate side desorption: The components passing through the membrane evaporate at the permeate side. The desorption step at this interface from the active layer is also very fast and has therefore only small influence on the overall transport rate.

Step V - Porous support layer: In asymmetric membranes, the active membrane layer is cast on a porous support, which can be made form the same polymer as the active layer (figure 2.4). As the numerous pores in this layer are very large compared to the voids in the dense separation layer, this step does not contribute to the mass transfer resistance and is therefore usually combined in the diffusion step through the membrane. In detailed membrane investigation, this transport step can also be described with the Maxwell Stefan diffusive transport equation (Krishna and Wesseling [88]) or the Dusty Gas Model (Brinkmann [24]45).

Step VI - Permeate side spacer: On the permeate side, the membrane is supported by different layers of spacer material to provide mechanical stability. Due to the pressure difference between the feed and the permeate side, the membrane would collapse without this support. In long permeate channels like in spiral wound modules, high pressure drops can occur in these channels and considerably reduce the separation capacity of the membrane.

As the dissolved species in the membrane and in the fluid can be assumed to be in thermodynamic equilibrium, sorption relationships are used to calculate the concentration

43 Chapter 5, page 161
44 Chapter 5, page 168
45 Chapter 10, page 286
in the membrane depending on the composition of the feed side bulk phase. The mobility of the components in the respective layers can be described using diffusion coefficients in the polymer material. The combination of these two effects results in the Solution-diffusion model which is well described in literature (Wijmans [89], Heintz and Stephan [90, 91]).

### 3.1.1. Solution Diffusion Model

Resuming the approach from equation 3.1, the flux of a component \( i \) through the active layer of the membrane \( \dot{f}_{i,TM} \) can be described with the extended diffusion equation where the gradient of the chemical potential \( d\mu_i(z)/dz \) is introduced as general driving force and described later in detail (Melin and Rautenbach [33]46):

\[
\dot{f}_{i,TM}(z) = -\tilde{c}_{i,M}(z) \cdot b_{i,M}(z) \cdot \frac{d\mu_i(z)}{dz} \tag{3.2}
\]

\( \tilde{c}_{i,M} \) is the molar concentration in the membrane and \( b_{i,M} \) the mobility of the component \( i \) in the membrane polymer. \( z \) represents the spatial dimension orthogonal through the membrane.

#### Concentration and mobility

The concentration of the component \( i \) inside the membrane can be calculated from the activity of the component \( a_{i,FM} \) at the membrane interface in the liquid feed by using sorption relationships \( S_i(T,x_i) \) which depend on the process conditions temperature and molar composition. For moderate pressures, as it is the case in this work, the influence of the pressure can be neglected.

\[
\tilde{c}_{i,M} = a_{i,FM} \cdot S_i(T,x_i) \tag{3.3}
\]

In this equation, \( T \) is the absolute thermodynamic temperature and \( x_i \) the molar composition of the bulk stream in the feed. The mobility coefficient is replaced by the

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thermodynamic diffusion coefficient \( D_{i,j} (T) \), which is independent from the concentrations of the components (Melin and Rautenbach [33]).

\[
b_{i,M} = \frac{D_{i,j} (T)}{RT}
\]

By combining equations 3.2 - 3.4, the partial flux through the membrane becomes:

\[
\dot{f}_{i,TM} = -a_{i,FM} \cdot \frac{S_i (T, x_i) \times D_{i,j} (T)}{RT} \cdot \frac{d\mu_{i,M} (z)}{dz}
\]

**Driving force**

The overall driving force in membrane separation processes can be described by the gradient of the chemical potential of the component \( i \) over the membrane thickness, which can be derived from the Gibbs free energy (Melin and Rautenbach [33]). A detailed description of the thermodynamic principles can be found in literature (Baehr and Kabelac [92], Gmehling and Kolbe [93]). With the assumption that the membrane is treated as an incompressible liquid, the chemical potential inside the membrane is defined as:

\[
\mu_{i,M} = \mu^o_i + v_i (p - p^o_i) + RT \ln (a_i)
\]

where \( \mu^o_i \) is the chemical potential at reference conditions and \( v_i \) the molar volume of the component \( i \). \( p \) is the total pressure and \( p^o_i \) the pure component vapour pressure, which is chosen as reference pressure. As the chemical potential is not a process variable, the following assumptions and simplifications are taken into account to yield a more convenient description:

- Thermodynamic equilibrium between fluid and membrane at the interface
- The gradient of the chemical potential inside the membrane is linear
- Pressure and temperature in the membrane are identical to the feed side values
• The permeate vapour is at low pressure and can be considered as ideal gas.

With these assumptions, the driving force for the component $i$ can be written as:

$$\frac{d\mu_{i,M}}{dz} = \frac{d\mu_r^i}{dz} + \frac{d(v_i(p - p_r^i))}{dz} + RT\frac{d\ln(a_{i,M})}{dz} \quad (3.7)$$

The reference chemical potential is constant and its derivation therefore becomes zero. The pressure in the membrane is equal to the pressure in the feed. The vapour pressure of the components is in the same order of magnitude as the total pressure and the molar volume of the components small compared to the molar volume of the polymer. Following, the second term of the right side becomes negligible compared to the last one and the gradient of the chemical potential can be expressed as:

$$\frac{d\mu_{i,M}}{dz} = RT\frac{d\ln(a_{i,M})}{dz} \quad (3.8)$$

The derivation of the logarithmic function can also be expressed as:

$$\frac{d\ln a_{i,M}}{dz} = \frac{1}{a_{i,M}} \frac{da_{i,M}}{dz} \quad (3.9)$$

Assuming a linear gradient, the derivative becomes a difference over the membrane thickness $\delta_{Mem}$:

$$\left.\frac{d\mu_{i,M}}{dz}\right|_{z=0} = \frac{RT}{a_{i,M}} \left( a_{i,FM} - a_{i,MP} \right) \quad (3.10)$$

Thus, the driving force of a component $i$ can be expressed as difference of its activity between both sides of the membrane (MELIN AND RAUTENBACH [33]). In a second step, a hypothetical vapour phase in equilibrium with the liquid feed is assumed. The permeate vapour is at very low overall pressure and can be treated like an ideal gas. Thus, the activities in the feed and the permeate side can be replaced by the partial

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pressures at the interfaces, which results in the following expression for the driving force for pervaporation:

\[
\frac{d\mu_{i,M}}{dz} = RT \frac{1}{p_{i,M}} \left( p_{i,MF} - p_{i,MP} \right)
\]

\[
= \frac{RT}{p_{i,M} \cdot \delta_{Mem}} \cdot \left( p_i^o(T_F) \cdot x_{i,MF} \cdot \gamma_i(x_{i,FM}) - p_P \cdot y_{i,MP} \right)
\]

\(\gamma_i\) is the activity coefficient, \(x_{i,FM}\) and \(y_{i,MP}\) the mole fractions of the component \(i\) at the feed and the permeate side of the membrane and \(p_P\) the permeate pressure. As in all separation processes, a high driving force is advantageous for an efficient separation. On the liquid feed side, the maximum partial pressure is given by the temperature and the composition of the mixture. On the permeate side, a low partial pressure is reached by applying a vacuum, condensing at low temperatures or by flushing the permeate side with a sweep gas (Brüschke [3], Jonquières et al. [7], Vallières [94]). Here, a combination of low temperature condensation and a vacuum pump to evacuate incondensable gases is applied.

**Permeance**

Combining equations 3.5 and 3.12 yields the following expression for the transmembrane flux of a component \(i\):

\[
\dot{j}_{i,TM} = S_i(T, x_{i,FM}) \times D_{i,j}(T) \frac{RT}{p_{i,M} \cdot \delta_{Mem}} \cdot \left( p_i^o(T_F) \cdot x_{i,MF} \gamma_i(x_{i,FM}) - p_P \cdot y_{i,MP} \right)
\]

Although the differentiated evaluation of the sorption and diffusion effects is of great interest in academic research, it is mostly not feasible for industrial applications. One reason is that the thicknesses of the different membrane layers are often not exactly known. Thus it is more convenient to combine the sorption and diffusion effects and the membrane thickness in the membrane specific parameter permeance \(L_i\), which is assumed to be dependent on the temperature and the molar composition in the feed.

\[
\frac{S_i(T, x_{i,FM}) \times D_{i,j}(T)}{p_{i,M} \cdot \delta_{Mem}} = L_i(T, x_{i,FM})
\]

\(^{52}\text{Chapter 3 page 165}\)
This description for the mass transfer is called solution-diffusion model and is widely accepted to describe the flux through dense polymer membranes (Wijmans and Baker [87]).

The major advantage of using the permeance is that it represents the flux normalised with its driving force, which makes it easier to compare different experimental investigations conducted under changing operating conditions (Baker et al. [95]). Thus, the permeance is calculated from experimental data with the following equation:

\[ L_i (T, x_i) = \frac{\dot{f}_{i,TM} (T,x_i)}{(p_o (T_F) x_i \gamma_i (x_i) - p_p y_i)} \]  (3.15)

### 3.1.2. Temperature dependency

The temperature dependency of the sorption and the diffusion coefficients can be described with Arrhenius-type relationships (Matteuci et al. [87]), which are calculated from a reference value at an arbitrary chosen reference temperature. In this work, the same approach is applied to the permeance:

\[ L_i (T) = L_i^o \exp \left[-\frac{E_{Act,i}}{R} \left( \frac{1}{T_o} - \frac{1}{T} \right) \right] \]  (3.16)

The overall activation energy \( E_{Act,i} \) combines the sorption energy \( E_{Ads,i} \) and the diffusive activation energy \( E_{D,i} \) of the components. Thus, only the reference permeance at reference temperature \( L_i^o (T_o) \) and the overall activation energy \( E_{Act,i} \) need to be identified in dependency of the temperature and relative to a reference temperature. For most applications of hydrophilic pervaporation, this procedure is sufficient for the description of the mass transfer. In applications where the vapour pressure and the activities of the components cannot be calculated as easily, the Arrhenius approach is applied immediately to the partial flux equation:

\[ \dot{f}_{i,TM} (T) = \dot{f}_{i,TM}^o \cdot \exp \left[-\frac{E_{Act,i}}{R} \left( \frac{1}{T_o} - \frac{1}{T} \right) \right] \]  (3.17)
3. Transport phenomena in pervaporation

3.1.3. Concentration dependency

When using membranes with high transmembrane fluxes, substantial concentration changes can occur over the length of the membrane module. In such cases, the influence of the feed concentration on the separation performance needs to be considered and concentration dependent membrane parameters have to be identified. Additionally, the solubility of the feed components in the membrane material and the degree of membrane swelling of the different membrane layers can be very high, which also influences the mass transport through the membrane. If large differences of swelling rates in these layers exist, the composite structure can even be disintegrated (Shao et al. [2]). One approach to include these effects is the introduction of activation energies, which are dependent of the feed content of the better permeating component (Ohlrogge [24]).

A selection of further approaches can be found in literature (Kreis and Gorak [75] and Gorak et al. [96]). The general equation for the permeance then becomes:

\[
L_i(T, x_{i,FM}) = L_{o,i}(x_{i,FM}, T_o) \cdot \exp \left[ \frac{E_{act,i}(x_{i,FM})}{R} \cdot \left( \frac{1}{T_o} - \frac{1}{T} \right) \right]
\] (3.18)

In this work, an extensive experimental investigation of the permeance in a wide range of feed temperature and composition is carried out. For a mixture of 2-butanol and water the concentration dependency of the permeance and is identified for a hydrophilic and a hydrophobic membrane in order to describe the membrane performance.

3.1.4. Multicomponent mixtures

In many industrial pervaporation applications, multicomponent mixtures need to be separated. Considering the permeance of each component individually is often not practical, either due to unknown components or because of unknown interactions between the components and the membrane. A common simplification is therefore to assume the mixture to be composed of a better permeating and a retained fraction. This approach is especially than acceptable, if the influence of the minor components is negligible. In organophilic and organoselective pervaporation although, this simplification is not always valid as the selectivities and permeances of the membrane can be strongly affected by the components. In has been shown that the presence of small quantities of 2-propanol in a

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water-ethanol mixture influences the mass transfer of ethanol more than the mass transfer of water (Lovasz et al. [97]). One effect is that an additional component of the feed mixture, which is not able to pass through the membrane, will accumulate on the surface and thus reduce the concentration of the other components which reduces the driving forces and the fluxes. If the membrane is selective to the additional component, it will be adsorbed on the surface and thus block the available active sites of the membrane. Inside the membrane, coupled diffusion can also have counteracting effects on the mass transfer. Additional components can cause structural changes of the membrane, such as swelling, which enlarges the diameter of the voids inside the polymer and elevates the diffusion coefficients of all components. This results in higher fluxes and lower selectivities of the membrane. Another possibility is that the additional component blocks the other components because it is larger anddiffuses much slower through the membrane. On the downstream side of the membrane, the driving force in pervaporation is ruled by the partial pressures of the components. At constant permeate pressure, the presence of an additional component reduces the partial pressures of all the other components and thus increases their driving forces. But if the additional component increases the total pressure, because it is not quickly enough withdrawn from the feed-side, the partial pressures increase and the driving forces decrease (Lipnizki and Field [98]).

Finding a suitable membrane is thus a challenging task and the subject of many research projects. One possibility to manufacture such membranes is molecular surface engineering, which is applied by PolyAn GmbH to produce organoselective membranes with specific selectivities. In this work, the separation performance of such a membrane is used to simulate an industrial scale pervaporation module and compare the results to an experimental investigation in pilot scale. To reduce the number of parameters which influence the process, purely binary mixtures are used in this work.

### 3.1.5. Concentration Polarisation

Low feed concentrations of the preferred permeating components and high selectivities of modern membranes are two major reasons for concentration polarisation, which represents a challenge in hydrophobic pervaporation, especially for the construction of pervaporation membrane modules (Shao and Huang [2]).
Due to the removal of the preferred permeating component from the feed, a concentration profile orthogonal to the membrane surface will develop. This causes a concentration rise of the rejected components at the membrane surface and hence, a diffusive flow of this component back to the bulk flow. This affects the transmembrane flux as well as the composition of the permeate negatively. In figure 3.2, the concentration profiles of the preferred permeating and the retained components in the feed side boundary layer are shown. High turbulence in the feed flow assured by high feed velocities and/or feed spacers minimise this effect. In most pervaporation applications, the feed velocities are usually very high, why concentration polarisation does not pose a serious problem. It mainly occurs in the separation of VOCs from water (Baker et al. [99]). For membranes with high fluxes and selectivities, this effect becomes more important and needs to be considered. As the aim of this work is the design of a novel membrane module suitable for organophilic pervaporation in wide application range and the development of a general valid simulation tool, two different approaches for the calculation of concentration polarisation are included in the rigorous model.

**Stagnant film theory**

In the first approach, the mass transfer coefficient $\tilde{\beta}$ is used to calculate the concentration at the membrane surface (Brinkmann [24]56). Therefore, the following assumptions are made:

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- All transport resistances are considered to be in serial
- The thickness of the boundary layer is not considered

Numerical values of this coefficient are determined from experiments and empirical correlations. The partial flux equation from the bulk of the feed to the membrane surface through the boundary layer becomes:

\[
\dot{f}_{i,TM} = x_{i,FM} \cdot \dot{f}_{TM} + \tilde{c}_F \cdot \tilde{\beta}_i \cdot (x_{i,F} - x_{i,FM})
\]  \hspace{1cm} (3.19)

Where the molar mass transfer coefficient \( \tilde{\beta} \) is defined with the Sherwood number \( Sh \), the molar diffusion coefficient and a specific length \( L_o \):

\[
\tilde{\beta} = Sh \cdot \frac{D_{i,j}}{L_o}
\]  \hspace{1cm} (3.20)

In this case, the Sherwood number \( Sh \) is calculated from Reynolds and Schmidt relationships using an empirical approach (BRINKMANN [24]57):

\[
Sh = \frac{\beta \cdot L_o}{D_{i,j}} = a \cdot Re_F^b \cdot Sc^c \left( \frac{\delta_F}{L_o} \right)^d
\]  \hspace{1cm} (3.21)

\( a, b, c \) and \( d \) represent fitting parameters, and the \( Re \)- and \( Sc \) numbers are defined as follows:

\[
Re = \frac{w \cdot L_o}{\nu}
\]  \hspace{1cm} (3.22)

\[
Sc = \frac{\nu}{D_{i,j}}
\]  \hspace{1cm} (3.23)

Where \( w \) is the velocity and \( \nu \) the kinematic viscosity of the liquid feed flow. The specific length in this relationships is the hydraulic diameter, which is generally defined by the following equation:

\[
L_o = d_h = 4 \times \frac{\text{cross sectional area}}{\text{wetted perimeter}}
\]  \hspace{1cm} (3.24)

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In the case of the developed membrane module (chapter 4), the form of the gap between two membrane envelopes is approximated as a flat channel as depicted in figure 3.3:

\[ d_h = 4 \cdot \frac{b_{Mem} \cdot \delta_F}{2 \cdot (\delta_F + b_{Mem})} \approx 2 \cdot \delta_F \]  

(3.25) (3.26)

In this design, it is assumed that the channel height \( \delta_F \) between two membranes is much smaller (1-10 mm) compared to the membrane width \( b_{Mem} \) (100 - 1000 mm), and can be neglected in the sum of the denominator.

These correlations have been investigated for different flow regimes and geometric structures. Values for the parameters \( a, b, c \) and \( d \) can be found in literature (Lipnizki et al. [98], Kraume [100]) and are tabulated in table 3.1 for plate and frame modules:

<table>
<thead>
<tr>
<th>Flow regime</th>
<th>Parameter</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>laminar</td>
<td></td>
<td>1.615</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>turbulent</td>
<td></td>
<td>0.026</td>
<td>0.80</td>
<td>0.30</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3.3.: Sketch of the feed channel geometry between two membrane envelopes.

Tab. 3.1.: Parameters of the Sherwood correlation for plate and frame modules (Lipnizki et al. [98]).
Laminar boundary layer

In the second approach, a polarisation modulus is calculated for the minor component to evaluate the intensity of the concentration polarisation (Baker [4][59], Wijmans et al. [101]). In this case, the following simplifications and assumptions are considered:

- Stagnant mass transfer boundary layer
- Concentration gradient only in the boundary layer
- Ideally mixed feed bulk phase
- Simplification of module fluid dynamics
- Velocity boundary layer assumed

The strength of the polarisation can be deduced from the following mass transport balance of the convective and the diffusive flow in the boundary layer (figure 3.2).

\[
\dot{f}_{TM} \cdot x_i - D_{i,j} \cdot \frac{\partial x_i}{\partial z} = \dot{f}_{TM} \cdot y_{i,p}
\]  
(3.27)

After integration over the boundary layer thickness \( \delta_{BL} \), equation 3.27 becomes:

\[
\frac{(x_{i,FM} - y_{i,p})}{(x_{i,F} - y_{i,p})} = \exp \left( \frac{\dot{f}_{TM} \cdot \delta_{BL}}{D_{i,j} \cdot \bar{\rho}} \right)
\]  
(3.28)

The ratio in the exponential term compares the convective and the diffusive flow and is called Péclet number, which is the product of the Re- and the Sc-number:

\[
Pec = Re \cdot Sc = \frac{w \cdot L_o}{D_{i,j}} = \frac{\dot{f}_{TM} \cdot \bar{\rho} \cdot \delta_{BL}}{D_{i,j}}
\]  
(3.29)

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The enrichment factor $E$ is then defined as the ratio of the permeate and the feed bulk flow mole fractions. $E_0$ is the intrinsic enrichment factor between the feed membrane concentration and the permeate (no boundary layer):

$$E = \frac{y_i, P}{x_i, F}$$

$$E_0 = \frac{y_i, P}{x_i, FM}$$

Inserted into equation 3.28 yields the following equation:

$$\frac{1}{E_0} - 1 = \exp(Pe)$$

The concentration polarisation modulus is defined as the ratio between the enrichment factor $E$ and the intrinsic enrichment factor $E_0$:

$$\frac{E}{E_0} = \frac{x_{i, FM}}{x_{i, F}}$$

In figure 3.4, the concentration polarisation modulus is plotted as a function of the Péclet number and the intrinsic enrichment factor $E_0$. If the ratio $x_{i, FM}/x_{i, F}$ is one, no polarisation effect occurs. The larger the difference from unity is, the stronger become the polarisation effects. For pervaporation, mainly the lower part of the diagram

Fig. 3.4.: Dimensionless description of concentration polarisation with the concentration polarisation modulus for different Péclet numbers (adopted from Baker et al. [99] and Wijmans et al. [101] and adapted to mole fractions).
(concentration polarisation modulus smaller than 1) is of interest, as this represents the case where the minor component of the feed mixture is enriched in the permeate. This is for example the case in ethanol dehydration by pervaporation. In practice, this means that for a specific polarisation modulus (i.e. \( x_{i,FM}/x_{i,F} = 0,1 \)), the Péclet number needs to be increase tenfold to reduce the intrinsic enrichment in the permeate from 1000 to 100. Figure 3.4 shows that concentration polarisation is larger under comparable process conditions if the minor component is depleted in the feed and enriched in the permeate.

### 3.2. Heat transfer

In a pervaporation module, the heat transfer is a combination of different effects. The molecules permeating through the membrane carry convective heat. Additionally, they evaporate on the permeate side (BRINKMANN [24][60]). The necessary energy for the phase transition is provided by the latent heat of the feed stream. This reduces the retentate temperature and in consequence, the transmembrane fluxes. Furthermore, the selectivities of the membrane change as sorption and diffusion are also temperature dependent effects. The resulting temperature difference between the feed and the permeate side induces a conductive heat transfer. On top of that, heat losses occur at the outer surface of the module. In figure 3.5, a hypothetical membrane module is shown with indicated heat streams of the feed \( \dot{Q}_F \), the retentate \( \dot{Q}_R \), the permeate \( \dot{Q}_P \), the transmembrane fluxes \( \dot{Q}_{TM} \) and the module heat loss \( \dot{Q}_{Mod} \). In the module construction designed in this work (chapter 4), a part of the feed is led around the membrane stack to reduce the temperature drop of the module. In industrial applications, additional insulation of the module reduces this heat loss to a minimum.

The overall energy balance for such a membrane module can be written as:

\[
\dot{Q}_F - \dot{Q}_R - \dot{Q}_P - \dot{Q}_{Mod} = 0
\]  

(3.34)

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3. Transport phenomena in pervaporation

To calculate the temperature profile along the module, the energy balances are established for discrete elements on both sides of the membrane. On the feed/retentate side, this balance is:

$$\dot{Q}_R(x) - \dot{Q}_R(x + dx) - \dot{Q}_{TM}(x) - \dot{Q}_{Mod}(x) = 0$$  \hspace{1cm} (3.35)

As the permeate chambers of the membrane envelopes are surrounded by liquid feed, the heat loss over the outer surface can be neglected and the balance becomes:

$$\dot{Q}_P(x) - \dot{Q}_P(x + dx) + \dot{Q}_{TM}(x) = 0$$  \hspace{1cm} (3.36)

The latent heat transported by the retentate flow $\dot{F}_R(x)$ is defined by its enthalpy:

$$\dot{Q}_R(x) = \dot{F}_R(x) \cdot h_R(x) = \dot{F}_R(x) \cdot c_{p,R}(x) \cdot (T_R(x) - T_0)$$  \hspace{1cm} (3.37)

where $h_R(x)$ is the local enthalpy of the retentate and $c_{p,R}(x)$ the constant pressure heat capacity. The transmembrane heat flow $\dot{Q}_{TM}(x)$ is composed of three parts:

$$\dot{Q}_{TM}(x) = \dot{Q}^{\text{vap}}_{TM}(x) + \dot{Q}^{\text{conv}}_{TM}(x) + \dot{Q}^{\text{cond}}_{TM}(x)$$  \hspace{1cm} (3.38)

The molecules passing through the membrane cause a convective heat flow $\dot{Q}^{\text{conv}}_{TM}(x)$:

$$\dot{Q}^{\text{conv}}_{TM}(x) = \dot{F}_{TM}(x) \cdot h_{TM}(x)$$  \hspace{1cm} (3.39)
To evaporate the molecules at the permeate side, the enthalpy of vaporisation $\Delta h^{\text{vap}}(x)$ is withdrawn from the retentate.

$$\dot{Q}^{\text{vap}}_{TM}(x) = \dot{F}_{TM}(x) \cdot \Delta h^{\text{vap}}(x)$$  \hspace{1cm} (3.40)

If a temperature gradient is present across the membrane, a conductive heat flow $\dot{Q}^{\text{cond}}_{TM}(x)$ between feed and permeate needs to be considered.

$$\dot{Q}^{\text{cond}}_{TM}(x) = k \cdot A_{\text{Sec}} \cdot (T_R(x) - T_P(x))$$  \hspace{1cm} (3.41)

### 3.2.1. Temperature Polarisation

Temperature polarisation describes the effect that the necessary enthalpy of vaporisation, the convective and conductive heat fluxes are withdrawn from the latent heat of the feed, which decreases its temperature over the membrane length. As the permeance and mass transfer coefficients are temperature dependent, the transmembrane flux will also decrease and reduce the separation capacity of the membrane. Additionally to the axial temperature drop along the membrane length, an orthogonal temperature profile from the bulk of the feed flow and the membrane surface can develop, as depicted in figure 3.6.

![Temperature profiles](image)

**Fig. 3.6:** Temperature profiles over the membrane length and in the boundary layer at the feed side of the membrane.

The conductive heat transfer through the membrane is calculated with the following approach.

$$\dot{Q}^{\text{cond}}_{TM} = k \cdot A_{\text{Mem}} \cdot (T_R - T_P)$$  \hspace{1cm} (3.42)
Where the thermal transmittance $k$ is defined as:

$$\frac{1}{k} = \frac{1}{\alpha_R} + \frac{\delta_{Mem}}{\lambda_{Mem}} + \frac{1}{\alpha_P}$$

The values for the heat transfer coefficients $\alpha_R$ and $\alpha_P$ and the heat conduction coefficient $\lambda$ have to be evaluated experimentally or estimated from similar module constructions using Nusselt and Reynolds correlations. Examples for different applications and further information on this topic are described in literature (Brinkmann [24]).

As the permeance is exponentially depending on the temperature, a large temperature drop between feed and retentate can severely reduce the transmembrane fluxes. This implies a larger membrane area which elevates the capital costs of the pervaporation plant. Neglecting or bad integration of this temperature drop often results in a severe overestimation of the product purity and thus an underestimation of the membrane area (Marriott et al. [10]). In industrial applications, the temperature drop is usually counteracted by reheating the feed between two membrane modules. In recent research, other strategies, like direct heat integrating systems have been investigated (Del Pozo Gomez et al. [59]). At SULZER Chemtech, a tubular membrane module with ceramic membranes inside of heat exchanger tubes has been developed. A heating fluid (e.g. steam) flows through the inner lumen of the tubes and the feed passes through the annular gap. The permeate is withdrawn at the shell side (Sommer et al. [102]). A different approach is the reduction of temperature polarisation by introducing a two-phase (liquid-vapour) feed flow. The vapour condenses and provides its condensation energy to the liquid feed (Fontalvo et al. [103], Alzate [104]).

### 3.3. Momentum transfer

In pervaporation, the feed pressure needs to be higher than the vapour pressures of the components in the feed. To prevent the creation of a vapour phase, the pressure drop in the feed should not be too high. The pressure drop is depending on the feed velocity. To reduce concentration polarisation, the feed velocity is considerably high in pervaporation modules which can result in large pressure drops between the feed and the retentate.

\[^61\text{Chapter 10, page 300}\]
3. Transport phenomena in pervaporation

On the permeate side, the pressure plays a more important role. Since it directly influences the driving forces and thus the partial transmembrane fluxes of the components (equation 3.13). This influence is well described in literature (Olsson et al. [105, 106], Vallieres et al. [107]). One goal in the design of pervaporation modules is thus the minimisation of the permeate side pressure drop. In applications with large permeate streams or when using a sweep stream to remove the permeate, the velocity and therefore pressure drop at the permeate side of the membrane can be of importance as an increase of the pressure reduces the driving force considerably. Especially in relative long spiral wound modules, when the permeating components are removed by co-current or counter-current flows, the influence of the pressure drop on the membrane needs to be considered. As suggested in literature (Marriott and Sørensen [77], Lipnizki et al. [98]), the pressure drop is calculated from the momentum balance, which results in the pressure drop equation of Bernoulli. The derivation of the equation is performed for the permeate side, but a similar procedure can be carried out for the feed side. In figure 3.7, the simplified geometrical design of a permeate channel is shown.

\[ \frac{dp_p(x, y)}{dy} = -\zeta(x, y) \cdot \rho_p(x, y) \cdot \frac{w^2(x, y)}{2} \frac{d}{d_{n, p}} \]  \hspace{1cm} (3.44)

Fig. 3.7.: Sketch of the permeate channel for the calculation of the pressure drop.

The pressure drop of a discrete element is calculated with the exiting permeate stream at the spatial position \( y \). The equation for the centre element in the figure for example becomes:

\[ \frac{dp_p(x, y)}{dy} = -\zeta(x, y) \cdot \rho_p(x, y) \cdot \frac{w^2(x, y)}{2} \frac{d}{d_{n, p}} \]  \hspace{1cm} (3.44)
3. Transport phenomena in pervaporation

The friction coefficient \( \zeta(x, y) \) is a function of the Reynolds number and can be described with empirical relationships (Lipnizki and Field [98], VDI Wärmeatlas [108]). Assuming a laminar flow in the permeate, \( \zeta(x, y) \) can be calculated as follows:

\[
\zeta(x, y) = \frac{38}{Re(x, y)} \tag{3.45}
\]

or for the turbulent regime in the permeate:

\[
\zeta(x, y) = \frac{1.22}{Re(x, y)^{0.252}} \tag{3.46}
\]

The Reynolds number is defined as:

\[
Re(x, y) = \frac{w_p(x, y) \cdot d_{h,P}}{\nu_p(x, y)} \tag{3.47}
\]

where the hydraulic diameter is defined similar as before as four times the fraction between the cross sectional area and its circumference:

\[
d_{h,P} = 4 \cdot \frac{\delta_p \cdot dx}{2 \cdot (\delta_p + dx)} \tag{3.48}
\]

The permeate channel height is in the range of 1-10 mm and the width of a discrete element in the range of 1-10 cm. Thus the hydraulic diameter can be simplified to:

\[
d_{h,P} = 2 \cdot \delta_p \tag{3.49}
\]

As the permeate is considered as an ideal gas, its velocity can be calculated from the molar vapour flow \( \dot{F}_p(x, y) \) through the sectional cross area in y-direction \( A_{sec,y} \):

\[
w_p(x, y) = \frac{R \cdot T_p(x, y) \cdot \dot{F}_p(x, y)}{A_{sec,y} \cdot p_p(x, y)} \tag{3.50}
\]

Substituting \( w_p(x, y) \) from equation 3.50, \( \zeta(x, y) \) from equation 3.45 and the \( Re \)-number from equation 3.47 in equation 3.44 yields:

\[
\frac{dp(x, y)}{dy} = -4.75 \cdot R \cdot \nu_p(x, y) \cdot \rho_P(x, y) \cdot \frac{T_p(x, y)}{p_p(x, y)} \cdot \dot{F}_p(x, y) \frac{1}{\delta_p^3} \cdot \frac{dx}{dx} \tag{3.51}
\]
Rearrangement and integration between the spatial positions $y - dy$ and $y$ gives:

$$\int_{y - dy}^{y} p_p(x, y) dp(x, y) = -4.75 \nu_p(x, y) \rho_p(x, y) RT_p(x, y) \dot{F}_p(x, y) \int_{y - dy}^{y} y$$ (3.52)

The describing equation for the pressure in an element $y$ then becomes:

$$p_p(x, y) = \sqrt{p_p^2(x, y - dy) - 9.5 \frac{R \cdot T(x, y) \cdot \dot{F}_p(x, y) \cdot \eta_p \cdot dy}{\delta_p^3 \cdot dx}}$$ (3.53)

For the laminar case, the pressure drop can be solved analytically. In a turbulent flow regime, the $Re$-correlation is usually a non-linear function of the type:

$$\zeta(x, y) = a + \frac{b}{Re(x, y)^c}$$ (3.54)

Different values for the parameters $a$-$c$ can be found in literature (Lipnizki and Field [98]). Substituting this equation in the pressure drop relationship 3.44 yields an equation which needs to be solved numerically. Therefore, the pressure drops in the shortcut and the discrete models of this work are calculated assuming a laminar flow. In the rigorous model however, the equations are solved iteratively and the pressure drop calculation for turbulent flows is possible.
4. Design of a novel pervaporation membrane and module

Membrane modules used nowadays in pervaporation, such as the frame and plate module are modules originally developed for filtration processes (BAKER [4]). As pervaporation shows similarities of reverse osmosis and gas separation, the specific requirements of the pervaporation process are often not sufficiently met with these modules. In this work, a novel pervaporation membrane module for the separation of aqueous and organic mixtures is described, which has been developed in a collaborative research project with the PolyAn GmbH and the HZG Research Centre (patent WO 2013 013785 A1 [109]). The project was funded by the Federal Ministry of Economics and Technology in the framework of the Central Innovation Program SME (Zentrales Innovationsprogramm Mittelstand – ZIM).

To identify the requirements on the design of the membrane module, two representative industrial separation tasks are considered:

- The separation of 2-butanol/water is a typical aqueous-organic separation task. This non-ideal system forms a liquid-liquid miscibility gap from 13 to 80 wt% 2-butanol content and has an azeotrope point at 72 wt% 2-butanol at 25 °C (Aspen Properties™ [72]).

- The separation of isoprene/n-pentane is a challenging organic/organic separation task for conventional technologies such as distillation. Isoprene and n-pentane have very similar boiling points of 34 and 36 °C respectively and form an azeotrope at an isoprene content of approximately 73,5 wt% at 25 °C (Aspen Properties™ [72]).

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Membranes for these separation tasks are provided by the HZG Research Centre, respectively manufactured by PolyAn GmbH. The novel module is constructed and tested experimentally in pilot scale in the technical centre of the HZG Research Centre.

**4.1. Membrane functionalisation**

A novel technology for the production of high selective membranes, *Molecular Surface Engineering (MSE)* has been developed by PolyAn GmbH. A functional polymer matrix is covalently fixed on the surface of commercial ultrafiltration membranes. The technology can be applied on the inner and outer surface of the pores to produce porous membranes for filtration applications or the pores can be filled with the functional polymer to produce dense membranes for pervaporation or gas and vapour permeation applications (PASEL ET AL. [28], MATUSCHEWSKI AND SCHEDLER [110]). In figure 4.1, both alternatives are depicted. With this technology, membranes with very specific membrane characteristics can be manufactured. For this work, an organoselective membrane for the separation of isoprene/n-pentane is produced.

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*Fig. 4.1.*: Functionalisation of membranes by *Molecular Surface Engineering* (MATUSCHEWSKI AND SCHEDLER [110]).
4.2. Identification of the optimal module type

As in all separation processes, also in pervaporation, a low resistance to the mass transfer is crucial for the success of the process. Especially for the separation of organic mixtures, such as isoprene/n-pentane, driving forces and selectivities are small. Thus, module packing density is not the primary selection factor for a membrane module any more (Shao et al. [2]).

To identify the best suitable module construction for the separation tasks considered in this work, the four module types described in section 2.4 are evaluated with regard to the properties of both component mixtures. The main requirements on the membrane and the module design are identified with a parameter matrix (table 4.1). The symbols at the intersections indicate if the modules are suitable (+) or not suitable (-) or if the requirement does not apply to the module type (o). The module type with the most positive elements is used in the further investigation.

Tab. 4.1.: Parameter matrix of the membrane module requirements (+: positive, -: negative, o: not applicable).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Plate &amp; frame</th>
<th>Tubular</th>
<th>Spiral wound</th>
<th>Envelope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate pressure drop</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Feed side turbulence</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Flat sheet membrane</td>
<td>o</td>
<td>o</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Welding of membrane</td>
<td>o</td>
<td>o</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Leaking feed/permeate</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

- To maintain a high driving force, a low pressure drop in the permeate channel is essential. In frame and plate, tubular and envelope type modules, such a low pressure drop can be easily realised. Only spiral wound modules show higher pressure drops, because the envelopes are usually very long, which results in narrow and long permeate channels (Melin and Rautenbach [33]).

- To achieve good mixing conditions and fully developed turbulence on the feed side of the membrane, spacers and redirection of the flow using feed baffles can easily be applied to all four module types.

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4. Design of a novel pervaporation membrane and module

- The membranes used in this work need to be made of polymeric material, because MSE-technology can only be applied to this membrane type so far. Therefore the use of tubular membranes is not possible at this point.

- The membrane envelopes for the spiral wound and the envelope type module need to be fixed together at their circumference. To compensate the inevitable membrane shifting during coiling of the membrane in spiral wound modules, flexible glues need to be used. As the membrane module is conceived for the separation of purely organic mixtures, all parts and materials inside the module need to be resistant against organic solvents which is difficult to guarantee for glues. Therefore, the spiral wound module is not an option for these applications.

- In frame and plate modules, the sealing gaskets between the membrane and the frames are located at the circumference of the membrane sheets. This results in a relative large sealing area compared to the total membrane area and increases the risks of leaks between the feed and the permeate side of the module (BAKER [4]). This is particularly fatal in the separation of organic mixtures where fluxes and selectivities are low.

Consequently, the envelope type module is found to represent the most favourable module type for the considered applications in this work. A well known variant of this module is the GS-module, developed at the HZG Research Centre for gas and vapour permeation applications (section 2.4.5).

4.3. Envelope and module design

Based on the design of the GS membrane envelope module (figure 4.2) and with inclusion of the expertise at the HZG Research Centre, a novel envelope shape (figure 4.3) and module construction (figure 4.5) are developed in order to meet the specific requirements of organophilic pervaporation.

The main disadvantage of the GS-module with respect to the considered applications is the circular shape of the envelopes. Due to this design, a uniform flow pattern at the

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4. Design of a novel pervaporation membrane and module

Fig. 4.2.: Standard membrane envelope as top view (a) and sectional view (b) with indicated feed (→) and permeate (←) stream flows.

Feed side is not guaranteed (figure 4.2(a)). Additional flow baffles and feed spacers are installed between the membrane envelopes to guide the feed into the wanted flow pattern. This reduces the packing density and increases the installation costs of the module. On the permeate side, the circular shape of the envelope design causes a reduction of free cross sectional area of the permeate channel in radial direction to the central permeate collection tube (figure 4.2(b)). In consequence, the velocity of the permeate vapour increases in radial direction and with it the pressure drop in the channel. The pressure in the permeate collection tube is predefined by the vacuum system and thus the permeate pressure in the membrane envelope increases. With a rectangular envelope shape, both challenges can be assessed at once. In figure 4.3, the design of the membrane envelope from the top view (figure 4.3(a)) and the sectional view (figure 4.3(b)) are shown. Due to

Fig. 4.3.: Novel membrane envelope as top view (a) and sectional view (b) with indicated feed (→) and permeate (←) stream flows.

the rectangular shape, the feed and the permeate streams can flow in a straight direction. The location of the long permeate collection channel causes a cross flow configuration between feed and permeate. The length of the permeate pathway is kept very short,
4. Design of a novel pervaporation membrane and module

which in combination with the straight flow pattern considerably reduces the permeate pressure drop of the new envelope compared to the GS-envelope. A simulation of the pressure drop in both envelope designs is performed at the HZG Research Centre. For this calculation, both membrane envelopes are implemented with the same membrane area. The height of the permeate channel and the spacer material is also chosen identical to yield the same hydraulic diameter. A permeate flux of 10 kg/m²h is assumed and the component properties are calculated locally. The pressure drop is calculated by solving the mass balances and the pressure drop correlations numerically. The results are shown in figure 4.4, where can be seen that the novel membrane envelope has a much smaller permeate pressure drop than the GS envelope (MATUSCHEWSKI ET AL. [111]).

![Fig. 4.4.: Comparison of the calculated permeate side pressure drop in the standard circular (●) and the novel rectangular (■) membrane envelopes (MATUSCHEWSKI ET AL. [111]).](image)

In figure 4.5, a three dimensional view of the cut-open membrane module and the envelope arrangement inside the inner housing case are shown. The envelopes, sealing rings, optional spacer material and feed baffle plates are mounted to a membrane stack, which is housed in an inner casing. A variable number of membrane envelopes is enclosed between two feed baffle plates and form a compartment. Successive compartments are equipped with decreasing number of envelopes in order to reduce the free cross sectional area of the feed channel and to increase the feed velocity. This way, the turbulence of the feed flow can be kept at a high level to counteract concentration polarisation. The feed inlet and the retentate outlet are located at the front side of the module. The permeating molecules pass through the membrane and the permeate stream is collected in a central permeate collecting tube from which it is removed by means of a deep temperature condenser or a vacuum pump. The total maximum number of membrane envelopes in the module shown in this case (figure 4.5) is 24, which results in a total membrane area of approximately 3 m². Additionally to the mentioned benefits of the rectangular envelope...
described above, the shape of the membrane envelope is advantageous for the modelling of the geometry. As the rectangular shape ensures a straight flow of the feed and the permeate, a uniform velocity field can be assumed. Thus, the effects of cross mixing are neglected in the modelling approach.

4.4. Experimental setup of the pilot plant

The pilot plant used for the experimental investigation of the process is designed and constructed at the HZG Research Centre (MATUSCHEWSKI ET AL. [111]). In figure 4.6 and table 4.2, the flowchart and the essential process parameters of the pilot plant are shown respectively.

**Tab. 4.2.:** Process data of pervaporation pilot plant and module.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow</td>
<td>500 kg/h</td>
</tr>
<tr>
<td>Feed pressure</td>
<td>2.5-3.8 bar</td>
</tr>
<tr>
<td>Feed Temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Permeate pressure</td>
<td>8 mbar</td>
</tr>
</tbody>
</table>
4. Design of a novel pervaporation membrane and module

Fig. 4.6.: Flowchart of the pervaporation pilot plant (Matuschewski et al. [111]).

The feed is circulated with the pump P2 from the feed vessel B3. The feed stream can be set to a maximum of 500 kg/h to minimise concentration polarisation effects. In a plate and frame heat exchanger W1, the feed is heated before entering the pervaporation module M1. The permeate is removed with a liquid ring vacuum pump P1 supported by an ejector pump P3. The ring liquid and permeate mixture is collected in the vessel B2 and separated with a phase separator B4. Cooling of the ring liquid is performed with a second plate heat exchanger before the liquid is recycled to the vacuum pump. The permeate is recycled to the feed/retentate vessel with the membrane pump P4. With the retentate valve VR1, the feed flow is controlled automatically. Permeate samples are taken with cooling traps at B1. As coolant, liquid nitrogen is used to ensure a total condensation of the permeate. The membrane module is equipped with five membrane envelopes in five compartments, which yields a membrane area of 0.63 m². As the feed/retentate vessel is large compared to the membrane area, and the withdrawn permeate is recycled to the feed vessel, it can be assumed that the feed composition does not change during one experiment. Furthermore, the feed flow is high compared to the membrane area and the expected permeate streams. Therefore, a negligible temperature drop can be assumed.
5. Development of a three step modelling approach

As mentioned in chapter 1, pervaporation is not yet available as unit operation model in commercial process simulation software such as Aspen Plus™ or ChemCAD™. Only a model for ultrafiltration is for example available in Aspen Plus™ since 2011. Thus for the simulation of membrane processes, self-programmed models and subroutines need to be implemented. Such models are mostly written for a specific case study and process configuration. As a consequence, they are only valid in a very narrow application range (MARRIOTT [10]). Membrane process simulators as stand-alone software tools only exist for reverse osmosis or filtration processes and are mainly distributed by companies selling membrane systems (i.e. Winflows™ by GE, Rosa™ by DOW). This development can be traced back to the high market share of reverse osmosis in membrane applications and the advanced understanding of this process.

A similar development for pervaporation is not yet to be observed, although a large number of computational models have been described and published in literature. Only few have been implemented in industrial scale applications. An extensive review about modelling of membrane processes can be found in literature (BRINKMANN [24]65). As mentioned in section 2.7, the availability of models for commercial process simulators and standalone software programs for the simulation of pervaporation would increase the acceptance and distribution of this process in the chemical industry.

In this work, a set of three models with increasing simulation detail is developed and implemented in the widely distributed software MS Excel™ and in the process simulator Aspen Custom Modeler™. Additionally, a user interface to facilitate the data management of the models is programmed in MS Visual Studio™.

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5. Development of a three step modelling approach

5.1. Modelling approach

For the simulation of chemical processes, different modelling approaches can be identified. Applied to pervaporation, these approaches can generally be:

**Shortcut:** With shortcut models, a fast and robust assessment of the pervaporation process is possible, e.g. the calculation of the approximate membrane area and the order of magnitude of the permeate flow. Such models are well suited for a quick comparison of different module configurations and a rough estimation of energy demand and installation costs (Bausa [74]).

**Rigorous:** With the detailed modelling of mass, energy and momentum balances in rigorous models, the concentration and temperature profiles in the membrane module can be calculated. This allows the simulation of overall process configurations including interconnections of the pervaporation module with other unit operations such as distillation columns and reaction vessels, as well as the transient behaviour of the pervaporation module in the entire chemical process (Bausa et al. [80]).

The main disadvantage of shortcut models is that they can predict the behaviour of a process only in a very narrow range of validity. This limitation is mainly due to the large number of simplifying assumptions. Rigorous models however are mostly not applicable in early stage engineering because of the high computational requirements and unknown process parameters. Additionally, rigorous modelling is only possible in professional modelling software, which is difficult to use and often not available for example in small and medium-sized enterprises. In this work, this two step modelling methodology is extended to a third approach, the **discrete** model, which incorporates elements of a rigorous model, but is implemented in *MS Excel™*. This results in the development of three consecutive steps for the simulation of the pervaporation process, which are arranged according to the three engineering design phases (see table 5.1). With such a modelling structure, the necessary trade-off between the accuracy of the results and the robustness of the models can be achieved. The models are successive, which means that the calculated results of the shortcut model can be used as starting values for the discrete model and the results of the discrete model as starting values for the rigorous model. The shortcut and the discrete models are implemented in the widely distributed *MS Excel™*, which facilitates the understanding and the possibility to extend the model. The rigorous
A shortcut model is realised in the equation orientated process simulator *Aspen Custom Modeler*™ (ACM). The ACM-model can be exported to *Aspen Plus*™ or *Aspen Dynamics*™ and with the add-in *Simulation Workbook* accessed from *MS Excel*™.

**Tab. 5.1.:** Modelling structure of the implemented models according to the three engineering design phases.

<table>
<thead>
<tr>
<th>Design phase</th>
<th>Model</th>
<th>Possible results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concept planning</td>
<td>Shortcut</td>
<td>Approximation of total membrane area based on average values of retentate temperature and concentration</td>
</tr>
<tr>
<td>Basic engineering</td>
<td>Discrete</td>
<td>First geometrical design of membrane and module, concentration and temperature profile over the module length</td>
</tr>
<tr>
<td>Detail engineering</td>
<td>Rigorous</td>
<td>Detailed design of the membrane module geometry, number of compartments and envelopes, pressure drops and driving forces, dynamic behaviour</td>
</tr>
</tbody>
</table>

### 5.1.1. *Shortcut Model*

The *shortcut* model describes the pervaporation module as a single stage module. At this point, only binary mixtures are implemented in the model and multicomponent separation tasks need to be divided into a pseudo-binary mixture consisting of a permeating and a retained fraction (section 3.1.4). Necessary input data for the model are the process parameters of the feed, the component properties and the membrane performance data, which are the reference permeances $L_o^i$ and activation energies $E_{Act,i}$ of the components. A simplified flow chart of the *shortcut* model is shown in figure 5.1.

For the model configuration described in this section, the following simplifications and assumptions are considered:

- Single integral membrane area in the module
5. Development of a three step modelling approach

Fig. 5.1.: Simplified flowchart of the shortcut model with the relevant variables and parameters.

- Average value of feed/retentate composition
- Ideally mixed condition in the feed (no boundary layer)
- Direct permeate removal perpendicular to the membrane
- Neglecting pressure drops in feed and permeate
- Integral energy balance for temperature drop estimation
- Binary or pseudo-binary mixtures

The resulting equations for the mass and heat transfer are implemented in MS Excel™. The “cells” in which the variables are used for the first time, are defined as “names” to make them easily accessible in the whole spreadsheet.

**Mass transfer**

In the shortcut model, the permeate flow \( \dot{F}_p \) is calculated from the partial fluxes \( \dot{f}_{i,TM} \) through the integral membrane area in the module \( A_{Mem} \):

\[
\dot{F}_p = \sum_{i=1}^{2} \dot{F}_{i,TM} = A_{Mem} \cdot \sum_{i=1}^{2} \dot{f}_{i,TM}
\]  

(5.1)
A described in chapter 3, each component’s partial flux is defined by the product of its permeance $L_i(T_{FR}, \bar{x}_{i,FR})$ and the driving force, which is expressed as difference of the partial pressure $\Delta p_i$ between both sides of the membrane:

$$\dot{f}_{TM,i} = L_i(T_{FR}, \bar{x}_{i,FR}) \cdot \Delta p_i = L_i(T_{FR}, \bar{x}_{i,FR}) \cdot (\bar{x}_{i,FR} \cdot p_i(\bar{T}_{FR}) \cdot \gamma_i(\bar{T}_{FR}, \bar{x}_{i,FR}) - y_{i,P} \cdot p_P) \tag{5.2}$$

$x_{i,F}$, $x_{i,R}$ and $y_{i,P}$ are the molar compositions of the components in the feed, the retentate and the permeate respectively. $\gamma_i$ is the activity coefficient and $p_i^o$ the pure component vapour pressure. Permeances, activity coefficients and vapour pressures are calculated using the arithmetic mean value of the molar composition $\bar{x}_{FR,i}$ and temperature $\bar{T}_{FR}$ between the feed and the retentate:

$$L_i(T_{FR}, \bar{x}_{i,FR}) = L_i^o(\bar{x}_{i,FR}) \cdot \exp\left[-\frac{E_{Act,i}(\bar{x}_{i,FR})}{R} \cdot \left(\frac{1}{T_o} - \frac{1}{\bar{T}_{FR}}\right)\right] \tag{5.3}$$

This equation has a circular reference in MS Excel™ because the retentate and permeate compositions, necessary for the calculation of the driving forces and the permeances, are depending on the transmembrane fluxes. These are again depending on the molar composition in the retentate and the permeate (figure 5.2).

![Fig. 5.2.: Visualisation of the circular reference in MS Excel™ between transmembrane fluxes, permeate composition and driving forces.](image)

This numerical problem is solved by using the SOLVER routine, which is included in MS Excel™. This solver is capable to solve linear and non linear equation systems numerically. The freely available version is limited in its functionality and restricted to 100 variables.
To calculate the solution, a macro is programmed which solves one of the component balances by variation of the retentate and permeate compositions:

\[
\dot{F}_F \cdot x_{1,F} - \dot{F}_R \cdot x_{1,R} - \dot{F}_P \cdot y_{1,P} = 0
\]  

(5.4)

As constraint, the permeate composition has to be smaller or equal to 1.

\[
y_{1,P} \leq 1
\]  

(5.5)

Sum conventions are used for the calculation of the remaining molar compositions:

\[
x_{2,R} = 1 - x_{1,R}
\]  

(5.6)

\[
y_{2,P} = 1 - y_{1,P}
\]  

(5.7)

Considering the total membrane area as fixed parameter, this system of equations has in the case of a binary mixture a total number of eight equations and eleven variables. As the feed flow and its composition represent design variables, the degree of freedom becomes zero and the system of equations can be solved numerically.

To ensure that not only local solutions are found, a starting point close to the assumed target value is introduced. In this case, it is assumed that the permeate composition can be calculated from the ratio of the partial transmembrane fluxes:

\[
y_{1,P}^{\text{Start}} = \frac{\dot{f}_{1,TM}}{\dot{f}_{1,TM} + \dot{f}_{2,TM}}
\]  

(5.8)

Inserting equation 5.2 for each component yields:

\[
y_{1,P}^{\text{Start}} = \frac{L_1 \cdot (\bar{x}_{1,F} \cdot p_{1,F} \cdot \gamma_1 - y_{1,P} \cdot p_F)}{L_1 \cdot (\bar{x}_{1,F} \cdot p_{1,F} \cdot \gamma_1 - y_{1,P} \cdot p_F) + L_2 \cdot (\bar{x}_{2,F} \cdot p_{2,F} \cdot \gamma_2 - y_{2,P} \cdot p_F)}
\]  

(5.9)

As the retentate composition is not yet known in this preliminary calculation, it is omitted at this point. A further simplification is that the retentate composition is identical to the feed composition. Additionally, due to the generally low permeate pressure, it is assumed that the partial pressures in the permeate are small compared to the values in the feed.
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Thus, this equation can be reduced to a function depending on feed parameters and be written as:

\[ y_{1,p}^{\text{Start}} = \frac{1}{1 + \frac{\Delta h_{\text{vap}}^1 y_{1,P}}{L_1 x_{1,F} P_{1,P} \gamma_1}} \]  

(5.10)

**Heat transfer**

The component properties, such as vapour pressure, activity coefficient and permeances are dependent of the average feed/retentate temperature. As the temperature in the module will decrease because of the vaporisation of the permeate, especially the permeances and thus the driving forces and the transmembrane fluxes will decrease. In equation 5.3 can be seen that the calculation of the temperature also leads to a circular reference. In this case the iterative solution of this equation is avoided by calculating an average temperature drop with a method similar to one suggested in literature (BAUSA [74]). With this preliminary temperature drop, the component properties and permeances can be calculated. In this equation, only the thermodynamic data of the mixture and the flows of the feed and permeate are required:

\[ \Delta T \approx \frac{\dot{F}_P}{\dot{F}_F} \cdot \frac{\sum_{i=1}^{2} \Delta h_{i,\text{vap}} y_{i,P}}{\sum_{i=1}^{2} c_{p,i,F} \cdot x_{i,F}} \]  

(5.11)

The permeate flow \( \dot{F}_P \) is substituted by equations 5.1 and 5.2. As simplifications for the calculation of the permeate flow, it is assumed that the permeate partial pressure is small compared to the values of the feed side and can be neglected. Additionally, the transmembrane flux is calculated with the feed temperature, which yields the maximum possible value. Furthermore, for the calculation of the heat of vaporisation, it is assumed that the permeate only consists of the preferred permeating component. Thus, the equation can be written as:

\[ \Delta T \approx A_{\text{Mem}} \left( L_1 (T_F, x_{1,F}) \cdot (x_{1,F} P_{1,P} \gamma_1) + L_2 (T_F, x_{2,F}) \cdot (x_{2,F} P_{2,P} \gamma_2) \right) \]  

\[ \cdot \frac{\Delta h_{1,\text{vap}}}{(c_{p,F} \cdot x_{1,F} + c_{p,F} \cdot x_{2,F})} \]  

(5.12)
After the calculation of the preliminary temperature drop and the resulting transmembrane fluxes, a more accurate value of the retentate temperature is calculated using the overall energy balance of the module.

\[ \dot{Q}_F = \dot{Q}_R + \dot{Q}_P \]  (5.13)

Replacing the heat flows of the feed and the retentate by their heat capacities and the heat flow of the permeate by the enthalpy of vaporisation yields:

\[
\hat{F}_F(x_{1,F}c_{p_{1,F}} + x_{2,F}c_{p_{2,F}}) \cdot (T_F - T_o) = \hat{F}_R(x_{1,R}c_{p_{1,R}} + x_{2,R}c_{p_{2,R}}) \cdot (T_R - T_o) \\
+ \hat{F}_P(y_{1,P}\Delta h_{vap}^1 + y_{2,P}\Delta h_{vap}^2)
\]  (5.14)

Rearrangement of this equation yields:

\[
T_R = T_o + \frac{\hat{F}_F(x_{1,F}c_{p_{1,F}} + x_{2,F}c_{p_{2,F}}) \cdot (T_F - T_o) - \hat{F}_P(y_{1,P}\Delta h_{vap}^1 + y_{2,P}\Delta h_{vap}^2)}{\hat{F}_R(x_{1,R}c_{p_{1,R}} + x_{2,R}c_{p_{2,R}})}
\]  (5.15)

With this shortcut model, approximated values of the permeate and retentate flows as well as their compositions and the temperature of the retentate can be calculated for a preset membrane surface in the module. These results can be used for a first assessment of the size of a pervaporation plant.

**5.1.2. Discrete Model**

In the discrete model, the total membrane area is divided into distinct elements (figure 5.3). This way, the concentration change in the retentate stream is considered by solving the set of mass transfer equations in each cell. Furthermore, the heat transfer is included in each element and therefore a temperature profile can be calculated. The discrete model is also realised in MS Excel™.

The simplifying assumptions for this model are:

- Uniform feed flow profile over the membrane width
- Ideally mixed flow in each element at the feed side
5. Development of a three step modelling approach

Fig. 5.3.: Simplified flowchart of the discrete model with the relevant variables and parameters.

- Accumulation of the permeate in consecutive cells
- Co-current configuration between feed and permeate
- Equal distribution of membranes in the compartments

Contrary to the shortcut model, in this case the SOLVER routine is not necessary to solve the resulting equations. To avoid circular references between two adjacent cells, a straight forward method is implemented. The transmembrane flux of a discrete element and the composition of the permeate and the retentate are computed with the concentrations of the preceding discrete element. The higher the number of discretisation cells, the smaller becomes the difference of the feed/retentate composition between two neighbouring cells and thus, the consequential error.

In modelling, it is of great advantage to use symmetry conditions in the geometry. This reduces the number of discrete elements considerably and thus the number of equations to solve, which saves computational resources. In figure 5.4, six membrane envelopes, each consisting of two membrane sheets are depicted. The envelopes are arranged in two compartments. In the module, these can be equipped with different number of membrane envelopes. As simplification in the discrete model, it is assumed that all compartments contain identical number of envelopes. Additionally, the membrane envelopes are symmetric with respect to the lower and upper membrane.

**Mass transfer**

The identified symmetry conditions of the membrane are used to calculate the feed flow for a single membrane sheet. The feed stream entering in the first membrane compartment
5. Development of a three step modelling approach

![Image: Discretisation of the membrane envelopes in the discrete model.](image)

Fig. 5.4.: Discretisation of the membrane envelopes in the discrete model.

\( \dot{F}_F \) is divided by two for each membrane sheet of an envelope and the ratio of membrane envelopes per compartment \( N_{env}/N_{comp} \) (figure 5.4). This yields the following equation for the initial feed stream \( \dot{F}_R(k=0) \) of the first row of discrete elements:

\[
\dot{F}_R(0) = \frac{\dot{F}_F}{2 \cdot \left( \frac{N_{env}}{N_{comp}} \right)}
\]

(5.16)

where \( N_{comp} \) is the number of compartments and \( N_{env} \) the total number of membrane envelopes in the module. The feed/retentate stream in the following element \( (k) \) is calculated from total molar and component balances between this element and the preceding element \( (k - 1) \):

\[
\dot{F}_R(k) = \dot{F}_R(k - 1) - \dot{F}_{TM}(k)
\]

(5.17)

\[
\dot{F}_R(k) \cdot x_{1,R}(k) = \dot{F}_R(k - 1) \cdot x_{1,R}(k - 1) - \dot{F}_{TM}(k) \cdot y_{1,TM}(k)
\]

\( \Leftrightarrow x_{1,R}(k) = \frac{\dot{F}_R(k - 1) \cdot x_{1,R}(k - 1) - \dot{F}_{TM}(k) \cdot y_{1,TM}(k)}{\dot{F}_R(k)} \)

(5.18)

The transmembrane flux from each discrete element is withdrawn from the downstream side of the membrane and added to the permeate stream in this element. Due to this co-current accumulation, the permeate flow and composition changes over the membrane.
length. The molar flow and composition of this stream are calculated with the following equations:

\[ \dot{F}_P(k) = \dot{F}_P(k-1) + \dot{F}_{TM}(k) \]  
\[ \dot{F}_P(k) \cdot x_{1,P}(k) = \dot{F}_P(k-1) \cdot x_{1,P}(k-1) + \dot{F}_{TM}(k) \cdot y_{1,TM}(k) \]
\[ \iff x_{1,P}(k) = \frac{\dot{F}_P(k-1) \cdot x_{1,P}(k-1) + \dot{F}_{TM}(k) \cdot y_{1,TM}(k)}{\dot{F}_P(k)} \]

(5.19)  
(5.20)

The permeate flow of the first element \( \dot{F}_P(0) \) is set to zero and the discretisation starts at \( k = 1 \). The transmembrane flux of an element \( k \) is calculated with the following equation:

\[ \dot{F}_{TM}(k) = A_{sec} \cdot \sum_{i=1}^{2} \dot{f}_{i,TM}(k) = A_{sec} \cdot \sum_{i=1}^{2} L_i(T(k-1),x_{i,R}(k-1)) \cdot \Delta p_i(k-1) \]  
\[ = A_{sec} \cdot \sum_{i=1}^{2} [L_i(T(k-1),x_{i,R}(k-1)) \cdot (x_{i,R}(k-1)p^*_i(k-1)\gamma_i(k-1) - y_{i,P}(k-1)p_P(k-1))] \]

(5.21)  
(5.22)

As this model is not implemented as a linear dependent system of equations, no degree of freedom can be calculated.

**Heat transfer**

With the discrete model, not only the concentration profile but also the temperature drop over the membrane length can be calculated. Because of this temperature drop, the separation performance of the membrane decreases over the module length and thus the transmembrane fluxes decrease. To calculate the local permeances of the components, the energy balance is included in the model. Also in this case, only the heat transfer by vaporisation is considered. The overall energy balance of a discrete element is defined as the difference between its latent heat of the entering feed and exiting retentate flow and the enthalpy of vaporisation withdrawn from the discrete element by the transmembrane flux:

\[ 0 = \dot{Q}_n(k) - \dot{Q}_n(k-1) - \dot{Q}_{TM}(k) \]

(5.23)
The energy of the entering flow is calculated with the molar heat capacities:

\[ \dot{Q}_R(k-1) = \dot{F}_R(k-1) \cdot \sum_{i=1}^{2} (x_{i,R}(k-1)c_{pi,R}(k-1)) \cdot (T_R(k-1) - T_o) \]  

(5.24)

as well as the energy of the exiting flow of a discrete element:

\[ \dot{Q}_R(k) = \dot{F}_R(k) \cdot \sum_{i=1}^{2} (x_{i,R}(k)c_{pi,R}(k)) \cdot (T_R(k) - T_o) \]  

(5.25)

The energy content of the transmembrane flux is equal to the vaporisation enthalpy:

\[ \dot{Q}_{TM}(k) = A_{sec} \cdot \sum_{i=1}^{2} \left( j_{i,TM}(k) \Delta h_{vap}^i(k) \right) \]  

(5.26)

Rearranging equation 5.25:

\[ T_R(k) = \frac{\dot{Q}_R(k)}{\dot{F}_R(k) \cdot (x_{1,R}(k-1)c_{pi,R} + (1 - x_{1,R}(k-1))c_{pi,R})} + T_o \]  

(5.27)

and introduction of equations 5.23, 5.24 and 5.26 yields the equation for the retentate temperature of a discrete element \( k \):

\[ T_R(k) = \frac{\dot{F}_R(k-1) \cdot \sum_{i=1}^{2} (x_{i,R}(k-1)c_{pi,R}(k-1)) \cdot (T_R(k-1) - T_o)}{\sum_{i=1}^{2} (x_{i,R}(k)c_{pi,R}(k)) \cdot (T_R(k) - T_o)} \]

\[ - A_{sec} \cdot \sum_{i=1}^{2} \left( j_{i,TM}(k) \Delta h_{vap}^i(k) \right) \]  

(5.28)

### 5.1.3. Rigorous Model

The rigorous model is implemented in Aspen Custom Modeler™ (ACM). The mass and energy balances are solved simultaneously. Similar to the construction of the novel membrane module (figure 4.5), the model structure in ACM is divided into a main model called Module which is composed of a variable number of sub models called Compartment. The sub models are interconnected in ACM with the command connect and linked with the main model using the command link as depicted in figure 5.5.

As the geometrical design of the model is adapted to the construction of the membrane module, only few simplifying assumptions considering the geometry need to be made:
5. Development of a three step modelling approach

**Fig. 5.5.:** Structure of the rigorous model in *Aspen Plus™* using the commands *connect* and *link*.

- Ideal cross flow configuration between feed and permeate
- Concentration polarisation only in feed/retentate considered
- Permeate accumulation in in direction of the permeate collector
- Neglecting heat losses over the membrane module surface

The number of membrane envelopes in the different compartments is variable. As cross flow between feed and permeate is considered in this model, the membrane width also needs to be divided in discrete elements. The discretisation is applied from the edge of the membrane to the permeate channel (y-direction, discretisation variable l) and over the whole membrane length (x-direction, discretisation variable k). Each of these elements of the feed side comprises one entering and one exiting feed/retentate stream as well as one exiting transmembrane flux. Each element at the permeate side comprises one entering and one exiting permeate and the entering transmembrane flux. The permeate flow in the first elements on the permeate side are set to zero. In figure 5.6, a sketch of the first four discrete cells of a membrane is depicted.

The permeate accumulates on the way to the withdrawal channel, which causes mass accumulation and a concentration change on the downstream side of the membrane in y-direction. Because of the depletion of the feed, the total molar flow and the composition change also in every element at this side of the membrane in x-direction. Following, the driving forces and the transmembrane fluxes are different in each discrete element. This two dimensional profile will also develop for the temperature and the pressure, which will also influence the driving forces and thus the separation performance of the membrane. These changes are the main reason for the development of the *rigorous model*. The equations of the model are based on the mass, energy and momentum balances.
Mass transfer

The component balance on the retentate side in a discrete element different from the membrane edge is:

\[
\dot{F}_R(k-1, l)x_{i,RM}(k-1, l) - \dot{F}_R(k, l)x_{i,RM}(k, l) - \dot{F}_{TM}(k, l)x_{i,TM}(k, l) = 0 \quad (5.29)
\]

where \(x_{i,RM}\) and \(x_{i,TM}\) are the liquid mole fractions of the component \(i\) at the membrane interface and of the transmembrane flux respectively and \(\dot{F}_R\) and \(\dot{F}_{TM}\) the molar flows of the feed/retentate stream and the transmembrane flow. Due to concentration polarisation effects, this concentration is different from the concentration in the bulk flow of the feed. At the permeate side, concentration polarisation is neglected and the balance can be written as:

\[
\dot{F}_P(k, l-1)y_{i,P}(k, l-1) - \dot{F}_P(k, l)y_{i,P}(k, l) + \dot{F}_{TM}(k, l)x_{i,TM}(k, l) = 0 \quad (5.30)
\]
Where \( \dot{F}_p \) and \( y_{i,p} \) are the permeate flow and molar composition. Similar to the shortcut and the discrete model, the transmembrane flow \( \dot{F}_{TM} \) is defined by the product of the permeance \( L_i \) and the driving force for each element.

\[
\dot{F}_{TM}(k,l) x_{i,TM}(k,l) = A_{sec} L_i(k,l) \cdot (x_{i,RM}(k,l)p_i(k,l)\gamma_{i,RM}(k,l) - y_{i,p}(k,l)p_p(k,l))
\] (5.31)

The index \( RM \) indicates the molar composition in the retentate flow at the membrane surface. In the rigorous model, component properties are calculated with subroutines implemented in Aspen Properties\textsuperscript{TM}, which allows a more detailed calculation of the mass transfer resistance. The mentioned concentration polarisation occur at the feed side of the membrane and are considered by implementing e.g. the calculation of the mole fraction at the membrane interface by using the mass transfer coefficient \( \tilde{\beta}_i \):

\[
\dot{f}_{i,TM}(k,l) = x_{i,RM}(k,l) \cdot \dot{f}_{TM}(k,l) + \tilde{c}_{i,R}(k,l) \cdot \tilde{\beta}_i(k,l) \cdot (x_{i,R}(k,l) - x_{i,RM}(k,l))
\] (5.32)

where the mass transfer coefficient is calculated from Sherwood relationships described in section 3.1.5:

\[
\tilde{\beta}(k,l) = Sh(k,l) \cdot \frac{D_{i,j}(k,l)}{L_o}
\] (5.33)

The diffusion coefficients of the components are retrieved from the Aspen Properties data base. The specific length in this case is equal to the double of the feed channel.

**Heat transfer**

Energy balances are introduced to calculate the temperature in each cell at the feed and the permeate side of the membrane:

\[
\dot{Q}_{R}(k-1,l) - \dot{Q}_{R}(k,l) - \dot{Q}_{TM}(k) = 0 
\] (5.34)

\[
\dot{Q}_{P}(k,l-1) - \dot{Q}_{P}(k,l) + \dot{Q}_{TM}(k) = 0 
\] (5.35)

The heat streams are described with the enthalpies of the flows. The heat transfer from the feed to the permeate side is composed of the convective heat transported by the molecules permeating through the membrane, the enthalpy of vaporisation of the permeating components, and the additional heat transfer caused by the temperature
difference between the feed and the permeate. Additional heat losses over the outer module surface and over the metal parts of the module from the feed to the permeate are neglected in this work as they are small compared to the other terms if the module is appropriately insulated. The heat balances for feed and permeate can be written as:

\[
\dot{F}_R(k-1,l) \cdot h_R(k-1,l) - \dot{F}_R(k,l) \cdot h_R(k,l) - \dot{F}_{TM}(k,l) \cdot h_{TM}(k,l) - \dot{F}_{TM}(k) \cdot \Delta h_{vap}(k) - A_{sec} \cdot \dot{q}_{TM}(k) = 0
\]  
(5.36)

\[
\dot{F}_P(k,l-1) \cdot h_P(k,l-1) - \dot{F}_P(k,l) \cdot h_P(k,l) + \dot{F}_{TM}(k) \cdot h_{TM}(k) + \dot{F}_{TM}(k) \cdot \Delta h_{vap}(k) + A_{sec} \cdot \dot{q}_{TM}(k) = 0
\]  
(5.37)

In Aspen Custom Modeler™, the enthalpy of vaporisation is implemented as the difference of enthalpies of the permeating stream in the liquid and vapour state:

\[
\Delta h(k,l)_{vap} = h_{vap}^{TM}(k,l) - h_{liq}^{TM}(k,l)
\]  
(5.38)

The conductive heat transfer between the feed and the permeate is considered with an overall heat transfer coefficient:

\[
\dot{q}_{TM}(k,l) = k_{TM} \cdot (T_R(k,l) - T_p(k,l))
\]  
(5.39)

**Momentum transfer**

In the rigorous model, momentum balances are introduced to calculate the pressure drops in the feed and the permeate channels. In this section, the procedure is shown on the example of the retentate channel. The pressure drop \(\Delta p\) in a flat channel can be calculated by the equation of Bernoulli (Subramani et al. [112]):

\[
\Delta p = \frac{1}{2} \rho w_R^2 \cdot \zeta_R \cdot \frac{x_R}{d_h}
\]  
(5.40)

where \(w_R\) is the mean velocity of the retentate, \(x_R\) the length in flow direction and \(d_h\) the hydraulic diameter. After rearrangement and formulation in discrete form, the equation for the calculation of the pressure in an element \((k,l)\) in the retentate stream becomes:

\[
p_R(k,l) = p_R(k-1,l) - \zeta_R(k,l) \cdot \rho_R(k,l) \cdot \frac{1}{2} \cdot v_R^2(k,l) \cdot \left( \frac{x_R}{d_{h,R}} \right)
\]  
(5.41)
The friction coefficient can be calculated with empirical *Reynolds* correlations, available in literature (VDI Wärmeatlas [108]):

\[
\zeta_R(k,l) = 1.25 \cdot \frac{64}{Re_R(k,l)}
\]  
(5.42)

The *Reynolds* number is calculated using the double height of the feed channel as hydraulic diameter (section 3.1.5):

\[
Re_R(k,l) = \frac{w_R(k,l) \cdot \rho_R(k,l) \cdot d_{h,R}}{\eta_R(k,l)}
\]  
(5.43)

The velocity of the retentate flow in a discrete element \(w_R(k,l)\) is defined by the volumetric flow rate \(\dot{V}_R(k,l)\) through the free cross sectional area of the retentate channel \(A_{sq,x}\). The flow rate is thus calculated from the molar flux \(\dot{f}_R(k,l)\) and the molar density \(\tilde{\rho}_R(k,l)\):

\[
w_R(k,l) = \frac{\dot{V}_R(k,l)}{A_{sq,x}} = \frac{\dot{f}_R(k,l)}{\tilde{\rho}_R(k,l) \cdot A_{sq,x}}
\]  
(5.44)

As the retentate fluxes, their composition and temperature change in each discrete element (in \(x\)- and \(y\)-direction), also the pressure drops and thus the pressures in adjacent elements will have different values. As these differences are very small compared to the overall pressure and pressure drop, the arithmetic average of the pressure is calculated for each row of elements in \(x\)-direction:

\[
p_{R,av}(k) = \frac{\sum_{i=1}^{N_{sec,b}/2} p_R(k,l)}{N_{sec,b}/2}
\]  
(5.45)

In the *rigorous* model, the component properties such as density and viscosity are retrieved from the *Aspen Properties*™ database.

### 5.2. Calculation of component properties

The *rigorous* model is implemented in *Aspen Custom Modeler*™, which is an equation orientated simulation software. Additionally to the numerical algorithms to solve the system of equations, the component’s physical properties can be calculated with integrated subroutines. The pure component liquid vapour pressure and the activity coefficients are
calculated with the extended * Antoine* equation and the NRTL model respectively. The heat of vaporisation and the liquid heat capacity at constant pressure are also dependent of the temperature and calculated with *DIPPR* equations.

Neither in the *shortcut*, nor in the *discrete* model, these advanced calculations are available as subroutines. The * Antoine* equation and the *NRTL* model are implemented and the parameters are retrieved from the *Aspen Properties™* database. The liquid heat capacity and the heat of vaporisation are assessed using correlations which are fitted to data calculated with *Aspen Properties™*. In the following description, the components of the first separation task (2-butanol/water) are used as model system. The parameters for isoprene and n-pentane are listed in the appendix A.2.

### 5.2.1. Vapour pressure

The liquid pure component vapour pressure is calculated with the extended * Antoine* equation ([Aspen Properties][72]):

\[
\ln p_i^o = a_i + \frac{b_i}{c_i + T} + d_i \cdot T + e_i \cdot \ln T + f_i \cdot T^g
\]  

(5.46)

The temperature in the equation is the absolute temperature and the equation is valid for a temperature range between -114.7 and 262.75 °C for 2-butanol and between 0.01 and 373.95 °C for water. The respective parameters for 2-butanol and water are listed in table 5.2 and are retrieved from the *Aspen Properties™* database, in order to guarantee similar values in the three models. The Antoine parameters for the mixture of isoprene/n-pentane are listed in the appendix A.2.

<table>
<thead>
<tr>
<th>Tab. 5.2.</th>
<th>Aspen Properties parameters for the extended * Antoine* equation for 2-butanol and water ([Aspen Properties][72]).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>a&lt;sub&gt;i&lt;/sub&gt;</td>
</tr>
<tr>
<td>2-butanol</td>
<td>122,550</td>
</tr>
<tr>
<td>water</td>
<td>73,649</td>
</tr>
</tbody>
</table>
5. Development of a three step modelling approach

5.2.2. Binary activity coefficients

In this work, the Non Random Two Liquid (NRTL) model is used for the calculation of the binary activity coefficients \( \gamma_{ij} \) of the components. This model is suitable for highly non ideal systems and for mixtures showing liquid/liquid miscibility gaps. The general equations described for example in the literature (Lüdecke [113]) are shown for the binary case:

\[
\ln \gamma_1 = x_2^2 \left[ \frac{\tau_{21}}{x_1 + x_2 G_{21}} \right] + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \]
\[
\ln \gamma_2 = x_1^2 \left[ \frac{\tau_{12}}{x_2 + x_1 G_{12}} \right] + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \]
\]

(5.47)

(5.48)

The free enthalpy of the components is calculated with:

\[
\ln G_{12} = -\alpha_{12} \tau_{12} \]
\[
\ln G_{21} = -\alpha_{21} \tau_{21} \]
\]

(5.49)

(5.50)

The interaction parameters \( \tau_{ij} \) can be described with the following relationship:

\[
\tau_{ij} = a_{ij} + b_{ij} \frac{T}{T} + c_{ij} \ln T + f_{ij} T \]
\]

(5.51)

The parameter \( \alpha \) describes the non-randomness of the liquid system and becomes 0 in the case when the local composition equals the overall composition. It can also be described with the following temperature dependent empirical relationship:

\[
\alpha_{ij} = c_{ij} + d_{ij} \cdot (T - 273, 15K) \]
\]

(5.52)

In this case, \( \alpha \) is assumed to be independent of the temperature \( (d_{ij} = 0) \) and is thus equal to \( c_{ij} \). In Aspen Properties™, this parameter is set to the default value 0.3 for mixtures with small deviations from ideal behaviour. As most of the experimental investigations are performed outside of the miscibility gap, this parameter is adopted for the evaluation. The binary parameters in this equation are listed in table 5.3 for 2-butanol and water and in the appendix A.2 for isoprene and n-pentane. In MS Excel™, the total molar composition of the mixture is used for the calculation of the activity coefficient instead of the compositions of the two liquid phases. A comparison of both approaches shows
5. Development of a three step modelling approach

Tab. 5.3: NRTL parameters for activity coefficients of 2-butanol/water (2-butanol: 1, water: 2).

<table>
<thead>
<tr>
<th></th>
<th>$a_{12}$</th>
<th>$a_{21}$</th>
<th>$b_{12}$</th>
<th>$b_{21}$</th>
<th>$c_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0.99</td>
<td>3.5447</td>
<td>-385.3</td>
<td>21.2734</td>
<td>0.3</td>
</tr>
</tbody>
</table>

only small deviations in the relevant range of feed concentrations, why this simplification is considered valid for the model mixture used in this work.

5.2.3. Heat of vaporisation

The heat of vaporisation for the pure components is calculated with the DIPPR 106 (Aspen Properties [72]):

$$\Delta h_{vap}^i = a_i \cdot \left(1 - \frac{T}{T_{cr,i}}\right)^{b_i + \sqrt{c_i + d_i T_{cr,i}} + \frac{e_i}{T_{cr,i}}}$$ (5.53)

The parameters for this equation are retrieved from Aspen Properties and listed in table 5.4 for 2-butanol/water and in the appendix A.2 for isoprene/n-pentane.

Tab. 5.4: Parameters of the DIPPR equation for 2-butanol/water.

<table>
<thead>
<tr>
<th>Component</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
<th>$T_{cr,i}$ (in K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butanol</td>
<td>75,007</td>
<td>0.09616</td>
<td>1.1444</td>
<td>-0.78448</td>
<td>535.9</td>
</tr>
<tr>
<td>water</td>
<td>51,546</td>
<td>0.28402</td>
<td>-1.5843</td>
<td>0.2375</td>
<td>647,096</td>
</tr>
</tbody>
</table>

5.2.4. Liquid heat capacity

The correlation for the calculation of the liquid heat capacity is fitted to data retrieved from Aspen Properties™. For a temperature range between 20 and 100 °C, a linear equation can be assumed:

$$c_{p,i} = a_i + b_i \cdot T_F$$ (5.54)

The parameters for this equation are listed in table 5.5 for 2-butanol/water and in the appendix A.2 for isoprene/n-pentane (table A.4).
5. Development of a three step modelling approach

Tab. 5.5.: Parameters for the calculation of liquid heat capacity of 2-butanol/water.

<table>
<thead>
<tr>
<th>Component</th>
<th>$a_i$</th>
<th>$b_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butanol</td>
<td>229.01</td>
<td>0.3204</td>
</tr>
<tr>
<td>water</td>
<td>66.087</td>
<td>0.1257</td>
</tr>
</tbody>
</table>

5.3. Development of the software tool

Besides the development of the three step modelling approach for the pervaporation process, a user interface is programmed in this work. The main objective is to facilitate the data management of the models and to enhance its usability. The three modelling approaches in this work need to be initialised with different input data and also provide results containing different types of information. Especially the SOLVER subroutine in MS Excel™ and the rigorous model in Aspen Custom Modeler™ are difficult to control if the user is not familiar with these programs.

Generally, the usability of such a tool can be defined by five major tasks, which should be achieved by the software (Golubovskyi [114]):

- **Task-Adequacy**: The focus of the software is the minimisation of interactions.
- **Self-explaining**: The user should see all the time its actual position in the program
- **Expectations-compliance**: The software should meet the expectations of the user
- **Fault-tolerance**: Operating errors of the user should be recognized and corrected
- **Instructiveness**: The software should help the user to understand the process

A simplified diagram of the virtual interface and the communication pathways between the user interface and MS Excel™, respectively ACM is shown in figure 5.7. It assists the user navigating through the different modelling steps and checks the consistency of the data. Model calculations are made within dedicated applications running in the background. The program itself is responsible only for sending and obtaining data from the interfaces. The interface is arranged in a simple way, keeping the user from making mistakes and simplifying the simulation procedure.
5. Development of a three step modelling approach

Fig. 5.7.: Program structure and data transfer of the user interface.

5.3.1. User interface

The user interface is programmed in the object orientated Microsoft Visual Studio™ using the programming language Visual Basic, which is based on the Microsoft .NET Framework. In the following figures 5.8 - 5.10, screen shots of the user interface are shown. In the start up window of the software (figure 5.8(a)) the data input for the simulation of a separation task is managed. The components property data can be entered manually or chosen from a list of default values if the mixture already exists in the internal data base (figure 5.8(b)). During the navigation in the program, the user can always return to the start up window and change or adjust the input data. A Standard button allows
5. Development of a three step modelling approach

the user to load the first component mixture in the data base with all the properties and the process parameters of a model simulation. The \textit{Clear} button can be used to delete all values at once. All input fields are defined with delimiters for the number format and minimum/maximum values. These values and additional information for the user are displayed as text in a status bar in the lower right corner of the window.

When all necessary values are entered correctly, the buttons for the different models are activated and the user can proceed to the \textit{shortcut} model (figure 5.9(a)). The calculation of the model is performed by activating the button \textit{Calculate Model 1}. The molar fluxes, compositions, temperatures and pressures of the retentate and the permeate streams are displayed at the right side of the panel. In the next step, the \textit{discrete} model can be chosen from the tab in the upper part of the window. The calculation is again performed by activating the \textit{Calculate} button (figure 5.9(b)). To check the consistency of the results,

the residuum of the total molar and component balances is calculated. If a specific threshold of these equations is below a fixed value of $10^{-4}$, the text “Balance is solved” and a green signal are displayed. The results of the retentate and permeate streams are shown at the right side of the panel. The resulting flow and concentration profiles can be displayed in a separate window by activating the button “Show charts” (figure 5.9(b)).

After completion of the \textit{discrete} model, the \textit{rigorous} model can be chosen from the tab in the upper part in the window (figure 5.11(b)). This model is linked with an \textit{Aspen Custom Modeler™} program file. Process conditions, such as temperature, feed flow and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5_9.png}
\caption{Screenshots of the shortcut (a) and the discrete (b) models.}
\end{figure}
5. Development of a three step modelling approach

![Fig. 5.10.](image)

Plotted results of the discrete model.

Composition as well as variables and fixed parameters in the ACM simulation like number of membranes and compartments and discretisation steps can be changed by the user. For each component system in the data base of the user interface, a separate ACM model is necessary. One major advantage of the software tool is that Aspen Custom Modeler™ is running in the background. After execution of the simulation and if the simulation in

![Fig. 5.11.](image)

(a) Results window of the rigorous model  
(b) Results overview of the three models

ACM is converging, the results of the retentate and the permeate stream are displayed in the respective fields. In the last panel of the user interface (figure 5.10), a summary of the results can be displayed in diagrams and saved in an external MS Excel™ file, which contains all the data.
6. Experimental investigation of polymer membranes

To identify the influence of the feed concentration and temperature on the permeance, a systematic and detailed experimental investigation is carried out. In this work, a hydrophilic and an organophilic membrane are used for the separation of a 2-butanol/water mixture. This binary system represents a model mixture for industrial aqueous/organic separations. To characterise the membrane performance in a wide range of process parameters, the feed concentration is varied across the miscibility gap (see chapter 2). For each value of the feed concentration, the feed temperature is varied in a temperature range between 25 °C and 85 °C. The total feed concentration ranges from 0-85 wt% 2-butanol. For the experimental investigation, 2-butanol of analytical grade and deionised water are used.

6.1. Laboratory test cell

A laboratory scale pervaporation plant is designed and constructed in the technical centre of the Institute of Thermal, Environmental and Natural Products Process Engineering at TU Bergakademie Freiberg. In figures 6.1 and 6.2, the flow sheet and a picture of the test device are shown respectively. Inside a 5-l feed vessel B-1, a heat exchanger W-1 is connected to a water circulated heating bath. The feed is pumped in a cycle stream from the vessel through a micro filter F-1. The latter is placed in front of the gear pump P-1 to guard the pumping head from solid particles. The membrane test cell and an upstream finned tube heat exchanger W-2 are placed in an electrical oven to ensure isothermal conditions at the feed and the retentate side of the membrane. The inside of the oven is tightly sealed from the heating coils W-3 and equipped with an exhaust
fan. A sensor for organic vapours and an emergency shut-down makes it possible to use the oven with organic components in the planned temperature range. In the feed line

![Flowchart of the laboratory pervaporation plant.](image)

after the feed vessel, a connection to a nitrogen supply V-10 is placed to purge and to create inert conditions in the feed system. By closing valve V-9 and opening valve V-6, the feed can be removed from the system. The permeate side of the system can be shut from the membrane module with the butterfly vacuum valve V-1. The permeate side of the system is connected to a high power vacuum pump P-2 to evacuate inert gases from leaks in the system. The cooling traps CT-1 and CT-2 for the condensation of the permeate are set up in parallel configuration and the circuit can be changed between both traps by opening the vacuum valves V-2, V-4 and closing V-3, V-5 or vice versa. The permeate withdrawal channels are 25 mm wide to minimize the pressure drop from the permeate side of the test cell to the cooling traps. With the needle valve V-8, the vacuum can be adjusted. As cooling liquid, a frigorific mixture of solid carbon dioxide and isopropanol is used.

A process control system (PCS) is programmed in Labview™. The communication of the temperature sensors and pressure gauges with the PCS is realised with a Datatranslation DT9802 module. The set point of the oven temperature is calculated with a feedback control system in Labview™ from the measured temperatures T-1 and T-2 in the feed and permeate chamber of the test cell. Also the feed pump is controlled.
6. Experimental investigation of polymer membranes

6.1.1. Membrane test cell

The pervaporation test cell is a circular stainless steel test module for polymeric flat sheet membrane material with an effective membrane area of 0.0049 m². The test cell is composed of a feed and a permeate chamber separated by the membrane, which is placed on a perforated metal plate and permeate side spacers. The feed enters the cell at the top and flows in radial direction from the centre to the border of the membrane. The retentate is lead through an annular gap around the feed tube. The feed and retentate tubes are equipped with quick connectors, which enable a fast (de-)installation of the test cell and to create a bypass for the operation of the PV-device without the test cell. The permeate is withdrawn from the downstream side of the membrane by a vacuum pump and condensed in the cooling traps.

6.1.2. Experimental procedure

The experimental investigation in this work is divided in several experimental runs during which the feed concentration is kept constant. This is guaranteed by the large amount of feed mixture compared to the removed permeate. In each run, the temperature is varied from 25 °C to 85 °C in steps of 15 °C. At the beginning of each experimental investigation, the test device is prepared by carrying out the following eleven steps:
6. Experimental investigation of polymer membranes

![Principle sketch of the test cell with indicated feed, permeate and retentate flows.](image)

**Fig. 6.3.:** Principle sketch of the test cell with indicated feed, permeate and retentate flows.

1. Disconnection of the test module from the system and bypassing feed and retentate
2. Flushing the system with deionised water and purging with nitrogen
3. Installation of the membrane sheet and reassembling of the test cell
4. Preparation of the feed mixture and loading the feed vessel
5. Connection of membrane module to the feed and retentate lines
6. Starting of the gear pump and setting to predefined value
7. Input of temperature set points of the heating bath and oven (25 °C)
8. Checking the system for leaks at the feed, retentate and permeate connections
9. Connection of the module to the permeate system
10. Installation of the cooling traps and starting the vacuum pump
11. Preparation of the frigorific mixture and filling the dewar vessels

During the preparation steps 7 - 11, the feed content is preheated to the first temperature setpoint of the experimental run (25 °C). One of the cooling traps is connected to the membrane module and permeate is condensed in the cooling trap. When the temperatures of the feed, retentate and permeate are constant for a minimum of 10 minutes after the temperatures of the feed, the retentate and the feed vessel are at a constant level, the system is considered to have reached steady state, which is the starting point of the experimental run. The following steps are performed for each temperature value.
13. Collecting permeate for 10-50 minutes, depending of the expected permeate flux
14. Taking a sample of the feed content
15. Preparation, installation and evacuation of new cooling trap
16. Switching vacuum valves to new and removal of loaded cooling trap
17. Weighing of content of loaded cooling trap and taking sample of permeate
18. Repeating steps 12-17
19. Input of new temperature set point

If the permeate consists of two liquid phases, water respectively 2-butanol is added to the permeate in the cooling trap until the phase separation disappears. At each temperature, at least two repeat experiments are conducted with different time periods. If the deviation of the first two measured results is obviously to large, a third experiment is performed. The samples taken during the experimental runs are collected in sealable glass vials. The water content is determined by refractometry. The refractive index is measured for both single phase regions to generate a calibration curve. As shown in figure 6.4, a polynomial trend line of second degree can be used for the description of the water content over the whole concentration range. Additionally, the 2-phase region is indicated.

Fig. 6.4.: Water mass content in dependency of the refractive index for 2-butanol/water at 20 °C.
6. Experimental investigation of polymer membranes

6.2. Experimental results

In this work, one hydrophilic and one hydrophobic membrane\(^{66}\) are characterised. The transmembrane mass fluxes and the permeate mass fractions are plotted in dependency of the feed temperature and the feed composition in figure 6.5 for the hydrophilic and in figure 6.6 for the hydrophobic membrane. The dashed lines in the figures indicate which data points belong to an experimental run. The data points marked with grey circles are values which deviate considerably from the overall trends. These values are discussed in the following section 6.3. The transmembrane flux of the hydrophilic membrane (figure 6.5(a)) increases with increasing temperature and the permeate water content (figure 6.5(b)) decreases for increasing feed temperatures. A higher water content in the feed also causes a higher water content in the permeate.

![Transmembrane flux](attachment://transmembrane_flux.png)

![Permeate water content](attachment://permeate_water_content.png)

**Fig. 6.5.:** Experimental values of the total transmembrane mass flux (a) and the permeate mass water content (b) in dependency of the feed temperature and the feed mass water content for the hydrophilic membrane (--- Values of one experimental run, ○ deviating values).

The transmembrane flux (figure 6.6(a)) and the permeate 2-butanol content (figure 6.6(b)) of the hydrophobic membrane are shown in dependency of the feed temperature and the feed 2-butanol content. Similar to the hydrophilic membrane, the fluxes increase with increasing temperatures and feed concentrations. With this investigation, a large data basis for fluxes and permeate compositions is established for a wide range of feed temperatures including feed concentrations inside the miscibility gap.

\(^{66}\)Kindly provided by the HZG Research Centre
6. Experimental investigation of polymer membranes

Fig. 6.6.: Experimental values of the total transmembrane mass flux (a) and the permeate 2-butanol content (b) in dependency of the feed temperature and the feed 2-butanol content of the hydrophobic membrane (— — — Values of one experimental run, ○ deviating values).

6.3. Evaluation of the experimental results

As illustrated in figures 6.5 and 6.6, the majority of the measured fluxes and permeate compositions show the same trend. Nevertheless, some values seem to be outlying from these trends. These values are checked for reliability and possible sources for experimental errors are identified. Following, the measured values of the transmembrane flux and the permeate composition are compared to the theoretical trends described in chapter 2.3.4 and a qualitative comparison between the two membranes is performed.

6.3.1. Determination of erroneous data values

During the experimental work, different errors can occur, which need to be considered for the data validation and the model development as they can have a severe impact on the calculated membrane performance (Wijmans [115]). For this examination, some preliminary assumptions concerning the expected trends are taken into account:

- The feed vessel is large compared to the amount of permeate removed during one experimental run. Therefore, a negligible decrease of the feed water content can be expected.
6. Experimental investigation of polymer membranes

- Considering the theoretical membrane performance of polymeric membranes, the transmembrane flux is expected to rise with higher temperatures and with higher molar feed content of the preferred permeating component.

- The molar content of the preferred permeating component rises with higher molar feed content of this component, but it declines with rising temperatures.

As can be seen in the figures 6.5 and 6.6, some data points of the transmembrane flux and the permeate composition show large deviations from the overall trend or a different trend compared to the other data of the respective experimental run (marked with circles). Besides measurement errors during the determination of the water content by refractometry and reading errors during weighting of the permeate mass in the cooling traps, two main reasons for these deviations are probable:

- If the permeate side is not completely sealed against the environment, humid air of the surrounding is sucked into the vacuum system and the condensed water from changes the amount of water and thus the apparent permeate composition.

- If the feed is not mixed properly by the circulation of the feed pump, phase separation can occur in the feed channel and at the feed side of the membrane.

The respective data points are identified and omitted from the further evaluation and modelling. A detailed discussion of these values can be found in the appendix A.3.

6.3.2. Qualitative analysis of membrane performance

The theoretical behaviour of polymeric membranes in dependency of process temperature and feed concentration has been described in section 2.3.4. The results obtained in the experimental investigation are compared to these theoretical values. For better visualisation of the data, trend lines are generated with MS Excel™. Additionally, the variations of the measurements, calculated from repeat determination are included.
Hydrophilic membrane

Some experimental data of the transmembrane flux and the permeate water mass fraction in dependency of the feed temperature are shown in figure 6.7 for two different feed water contents ($\diamond = 23.8\ \text{wt\%};\ \Box = 90.7\ \text{wt\%}$). The transmembrane flux in figure 6.7(a) shows the expected exponential behaviour. The permeate water fraction decreases with increasing feed temperatures. For a higher feed water content, the transmembrane flux and the permeate water content are also higher (figure 6.7(b)). This behaviour is in accordance with the expected trends described in chapter 2.

In figure 6.8, the transmembrane fluxes and the permeate water content are plotted over the feed water content for two different temperatures ($\diamond = 25^\circ\text{C};\ \Box = 70^\circ\text{C}$). Both increase with increasing feed water content. The transmembrane flux increases for increasing feed temperatures figure 6.8(a)) whereas the permeate water content shows lower values at 70 °C than at 25 °C (figure 6.8(b)). This decrease is due to the reduced selectivity of the membrane at higher temperatures described in section 2.3.4. The flux and the permeate water content show constant values for feed water contents ranging from approximately 25 to 85 wt\%. These values are concordant with the liquid/liquid miscibility gap. This effect has also been described in literature (WESSLEIN ET AL. [55]).
6. Experimental investigation of polymer membranes

Fig. 6.8.: Concentration dependent transmembrane flux (a) and permeate water content (b) of the hydrophilic membrane (\(\bigodot\): 25 °C; \(\square\): 70 °C; ---: MS Excel™ trend lines; ---: boundaries of miscibility gap).

Hydrophobic membrane

In figure 6.9, the transmembrane flux and the permeate 2-butanol content in dependency of the feed temperature are shown for the hydrophobic membrane. The transmembrane

Fig. 6.9.: Temperature dependent flux (a) and permeate water content (b) for a hydrophobic membrane (\(\bigodot\): 6,1 wt%; \(\square\): 74,9 wt% ---: MS Excel™ trend lines).

fluxes show a clear exponential trend in dependency of the feed temperature (figure 6.9(a)) and increase for increasing 2-butanol contents in the feed. This behaviour is similar to the trend of the hydrophilic membrane (figure 6.7(a)). But for the hydrophobic membrane, the permeate 2-butanol content is nearly constant over the whole temperature range.
and shows similar values for both feed 2-butanol contents, which is a different behaviour observed with the hydrophilic membrane (figure 6.7(b)).

In figure 6.10, the transmembrane flux and the permeate composition in dependency of the feed 2-butanol content are shown for two different process temperatures (\(\Diamond = 40\, ^\circ\text{C};\, \Box = 55\, ^\circ\text{C}\)). Both values increase for increasing feed 2-butanol contents. Similar to the hydrophilic membrane (figure 6.8(b)), also the fluxes of the hydrophilic membrane increase for increasing temperatures (figure 6.10(a)). For the permeate 2-butanol contents, no evident difference can be seen in figure 6.10(b). Using \textit{MS ExcelTM}, a cubic trend line, as used for the other plots is not possible and a logarithmic trend line is used.

In this work, an extensive data set of fluxes and permeate concentrations in dependency of the feed temperature and the composition of the feed mixture is established for two different membranes. Both membranes show high transmembrane fluxes and good permeate compositions. The qualitative trends of the membrane separation characteristics are comparable to the behaviour described in literature. The feed concentration is varied in a wide range across the miscibility gap of 2-butanol and water and the results indicate that the fluxes and permeate compositions are constant inside the miscibility gap. But as the phase distribution and rate of dispersion at the feed/membrane interface is not exactly known, no reliable conclusions on the influence of the two phases feed can be made at this point.
7. Temperature and concentration dependent permeance

Molar permeances are one of the preferred parameters for the characterisation of pervaporation membranes (Baker et al. [95]). This approach is also followed in this work, and the permeance for each experimentally measured flux is calculated with the following equation:

\[
L_i(x_{i,F}, T) = \frac{\dot{J}_{i, TM}}{(p^o_i(T_F) x_{i,F} \gamma_i(x_{i,F}) - p_F y_{i,F})}
\] (7.1)

The experimental investigation from the previous chapter shows that the flux and the permeate composition is strongly dependent on the feed concentration. Therefore, a temperature and concentration dependent permeance approach for both membranes is established in this chapter. The influences of both process parameters on the permeance are analysed individually. The permeances are plotted over the inverse of the absolute temperature difference \(1/T_o - 1/T_F\) (similar to the Arrhenius approach) at constant feed concentration and over the feed mole fraction of the preferred permeating component at constant feed temperatures. Afterwards, a combined equation including both dependencies is fitted to experimental data. Trend lines are introduced using MS Excel\textsuperscript{TM} to identify the equation type describing these trends. Following, the approach is validated for the hydrophilic membrane with data from further laboratory experiments and for the hydrophobic membrane with experiments conducted in pilot scale using the novel pervaporation module.
7. Temperature and concentration dependent permeance

7.1. Hydrophilic membrane

The temperature and concentration dependent permeances of water and 2-butanol are shown in figures 7.1 and 7.2 for the hydrophilic membrane. The feed concentration is varied from 25.3 to 99.0 mol% water content and the feed temperature from 25 to 85 °C. In figure 7.1, the dependency of the feed temperature is shown exemplarily for molar feed water contents 25.3 and 96.4 mol%. The permeances decrease for both components with increasing feed temperatures. Higher feed water content causes a higher water permeance (figure 7.1(a)) and a reduced 2-butanol permeance (figure 7.1(b)). In accordance with Arrhenius type equations from literature, the dependency of both components can be described with exponential trend lines (---). Only, for the lowest feed temperature of 25 °C ($1/T_o - 1/T_F = 0$), a deviation can be identified. In figure 7.2, the permeances of water (7.2(a)) and 2-butanol (7.2(b)) in dependency of the molar feed water content is plotted for feed temperatures of 40 and 70 °C. Analysis of the complete set of calculated water permeances shows strong dispersion of the values at the right side of the miscibility gap. A plot with all permeance data of water for a feed temperature of 40 °C is included in appendix A.4/figure A.4, with indication which values are used for modelling and which for validation. One reason for these scattered data are swelling effects at high feed concentrations and feed temperatures. As such effects are not investigated in this work, a detailed analysis of these data points is not performed. Furthermore, hydrophilic pervaporation is usually not applied in this concentration range. Nevertheless, to establish a concentration dependent permeance approach, these data are included in the evaluation.
The identified concentration dependency of the water permeance shows a positive trend (figure 7.2(a)), whereas the 2-butanol permeance shows a concentration independent behaviour (figure 7.2(b)). Although the concentration dependency of the water permeance can also be described with a polynomial function, an exponential trend line is used in this work, in order to reduce the number of fitting parameters and thus to keep the approach as simple as possible. In this case, the exponential factor is neglected.

Combining both dependencies in one approach yields the following equation for the permeances of water and 2-butanol in dependency of the molar feed water content:

\[
L_i(x_{H_2O,F}, T) = a_i \cdot \exp\left( b_i \cdot \left( \frac{1}{T_o} - \frac{1}{T_F} \right) \right) + c_i \cdot x_{H_2O,F}
\]

(7.2)

**7.1.1. Parameter Fitting**

The fitting parameters \( a_i, b_i \) and \( c_i \) are identified by minimising the sum of the squared differences between the measured and the calculated permeance for each experimental value. In figure 7.3, the comparison between the measured and the calculated values of the permeance are shown for water (figure 7.3(a)) and for 2-butanol (figure 7.3(b)). Most simulated values show a deviation less than \( \pm 20 \% \). For both components, most of the values outside this boundary occur at feed water contents larger than 96 mol\% and at high feed temperatures. In this concentration and temperature ranges, strong
swelling effects occur and membrane performance becomes hard to predict. The resulting parameters of equation 7.2 for both components are listed in table 7.1. The average absolute deviations are 0.375 kmol/hm² for the water permeance, which equals 4.1 % of the maximum permeance and 0.098 kmol/hm² for the 2-butanol permeance (6.9 % of the maximum permeance), which is in an acceptable range.

<table>
<thead>
<tr>
<th></th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.474</td>
<td>2809</td>
<td>1.72</td>
</tr>
<tr>
<td>2-butanol</td>
<td>1.216</td>
<td>2171</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**7.1.2. Validation of the approach**

For the validation of this permeance approach, the transmembrane fluxes and the permeate compositions are calculated for six feed concentrations (from 42.1 to 97.1 mol% water) and at a feed temperature range between 20 and 90 °C. The calculations are performed at the average feed concentration of the respective experimental run. The following figures 7.4 - 7.6 show the experimental values of the total transmembrane flux $\Delta$ and
the permeate molar water content compared to the values calculated with equation 7.2. For a feed water content of 42.1 mol% (figure 7.4(a)) the exponentially increasing flux is predicted with good accuracy. The measured permeate water content is nearly constant, whereas the simulation shows a decreasing trend. The experimental values at 25 and 85 °C are omitted for this evaluation as they have been identified as erroneous data points in chapter 6. At 56.3 mol% feed water content (figure 7.4(b)), the transmembrane flux and the permeate composition can be well described for the entire temperature range. Except at 85 °C, the simulation does not reach the experimental value. For a molar feed water content of 71.3 mol% (figure 7.5(a)), the transmembrane fluxes and the permeate water contents can be described with high accuracy. Also in this experimental run, one temperature value (85 °C) has been omitted from the evaluation (chapter 6). At a feed water content of 88.1 mol% water, the transmembrane flux is overestimated for feed temperatures between 25 and 80 °C. The permeate water content
can be described with high accuracy (figure 7.5(b)). For 96.1 mol% water in the feed
(figure 7.6(a)), the calculated transmembrane flux is overestimated for temperatures above 60 °C. The permeate composition shows negligible deviations between the simulated and the experimental values. At 97.1 mol% feed water (figure 7.6(b)), the transmembrane flux and the permeate composition show negligible deviations from the experiments.

This evaluation shows that the temperature and concentration dependent permeance approach is suited for the prediction of transmembrane fluxes and permeate compositions of the hydrophilic membrane in wide feed temperature and concentration ranges.

7.2. Hydrophobic membrane

The temperature and concentration dependencies of the hydrophobic membrane are shown in figures 7.7 - 7.9. The permeances are gained from experiments at molar 2-butanol feed contents ranging from 0.5 to 85.8 mol % and for feed temperatures between 25 and 85 °C (SCHIFFMANN AND REPKE [116]). In figure 7.7, the temperature dependency of 2-butanol (figure 7.7(a)) and water (figure 7.7(b)) are exemplarily plotted over the inverse absolute temperature difference \(1/T_o - 1/T_F\) for two molar feed 2-butanol contents (3.5 ♦ and 85.8 ☐ mol%). Although all curves could be fitted with different trend lines, an exponential approach for all permeances is chosen in order to describe the permeance of both components and for the whole temperature range with one type of equation. The 2-butanol permeance is decreasing exponentially for increasing feed temperatures.
7. Temperature and concentration dependent permeance

![Graph showing temperature and concentration dependent permeance](image)

Fig. 7.7.: Temperature dependency of the 2-butanol (a) water (b) permeance of the hydrophobic membrane for feed 2-butanol contents ($\chi_0 = 3.5$ mol%; $\chi_0 = 85.8$ mol%; trend lines) (SCHIFFMANN AND REPKE [116]).

and increasing for increasing 2-butanol feed contents (figure 7.7(a)). Comparing the water permeances for low (3.5 mol%) and high (85.8 mol%) feed 2-butanol contents shows that the trend is close to a constant value over the whole temperature range for low concentrations but exponentially dependent from the feed concentration for a high value of feed 2-butanol content (figure 7.7(b)). This indicates that swelling effects in this hydrophobic membrane occur at high feed concentrations of the preferred permeating component and influence the permeance of the preferably retained component.

In figure 7.8, the concentration dependency of 2-butanol for two different feed temperatures (40 °C and 70 °C) is shown. Over the whole concentration range, the trend can be well

![Graph showing concentration dependency of 2-butanol permeance](image)

Fig. 7.8.: Concentration dependency of 2-butanol permeance (a) and detail view (b) for the hydrophobic membrane ($\chi_0 = 40$ °C; $\chi_0 = 70$ °C; trend lines; miscibility gap at 40 °C - - - miscibility gap at 70 °C)(SCHIFFMANN AND REPKE [116]).
described with a logarithmic approach (figure 7.8(a)). A detailed view of the values at the left boundary of the miscibility gap is shown in figure 7.8(b). The data points in this concentration range show larger scattering but can still be described using the logarithmic function.

In figure 7.9, the concentration dependency of water for different feed temperatures is shown. Also in this case, a logarithmic approach is assumed to describe the concentration dependency over the complete concentration range (figure 7.9(a)). This way, an identical equation can be used for both components. The permeance values at low feed 2-butanol contents show large deviations but nevertheless, the overall trend can be described with the logarithmic function (figure 7.9(b)).

Thus, the resulting equation combining the exponential temperature and the logarithmic concentration dependencies becomes:

\[
L_i(x_{2-buOH,F}, T) = (a_i \cdot \ln(x_{2-buOH,F}) + b_i) \exp\left[c_i \cdot \left(\frac{1}{T_o} - \frac{1}{T_F}\right)\right]
\]  

(7.3)

### 7.2.1. Parameter fitting

The parameters \(a_i, b_i,\) and \(c_i\) of equation 7.3 are fitted to minimise the difference of the square errors between the measured and the calculated permeances. In figure 7.10, the
simulated values of the permeance are plotted over the measured values for 2-butanol (figure 7.10(a)) and water (figure 7.10(b)). During this evaluation, it appears that one

![Graphs showing calculated and measured permeances for 2-butanol and water](image)

Fig. 7.10.: Comparison of measured and calculated permeances for 2-butanol (a) and water (b) through a hydrophobic membrane (--- 0 %, —— 10 %, - - - 20 % deviation)(Schiffmann and Repke [116]).

single value of the water permeance showed a very large deviation of about 60 % (● in figure 7.11). The 2-butanol permeance for this experiment sows a much smaller deviation (figure 7.10(a)). Although it is not identified as an erroneous data point in section 6.3.1, parameter fitting including this data point only reaches an overall deviation of more than 10%. Therefore, this data point is excluded from this evaluation. The permeances for

![Graph showing measured and calculated permeances for water](image)

Fig. 7.11.: Comparison of measured and calculated permeances for water through the hydrophobic membrane (--- 0 %, —— 10 %, - - - 20 % deviation; ● deviating value).

both components can be described with good accuracy using this approach. Most of the calculated values show a deviation of less than 20 %. The overall average deviation for 2-butanol is 0.031 kmol/hm² (4.8 % of the maximum value). For water, the average
absolute deviation of the model is 0,016 kmol/hm² (6,1 % of the maximum value). In table 7.2, the resulting values for the fitting parameters are listed.

**Tab. 7.2.:** Parameters of the permeance approach for the hydrophobic membrane (SCHIFFMANN AND REPKE [116]).

<table>
<thead>
<tr>
<th></th>
<th>2-butanol</th>
<th>water</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_i)</td>
<td>0.082</td>
<td>0.025</td>
</tr>
<tr>
<td>(b_i)</td>
<td>1.00</td>
<td>0.23</td>
</tr>
<tr>
<td>(c_i)</td>
<td>1830</td>
<td>794</td>
</tr>
</tbody>
</table>

This evaluation demonstrates that the temperature and concentration dependent approach proposed in this work, is well suited for the simulation and prediction of the transmembrane flux and the permeate composition for the hydrophilic and the hydrophobic membrane in a wide range of feed temperatures and feed concentrations. Only three fitting parameters are necessary to establish this approach. Furthermore, it could be shown that only a small number of membrane characterisation experiments over the total concentration range are necessary to describe the membrane performance. For this feed mixture (water/2-butanol), no influence on the separation performance for feed concentrations inside the miscibility gap could be identified. As the laboratory scale membrane test cell used for this experimental investigation is small, a concentration change over the membrane length can be neglected. But if larger membrane areas in industrial applications are applied, the concentration and temperature change inside the membrane module can be significant and the formation of a two phase feed flow could eventually have an unpredictable influence on the membrane performance.

Furthermore, it shows that the evaluation of erroneous data in experimental values is crucial for the determination of the model parameters. Single data points with large deviations have a strong influence on these parameters. This is especially the case when a small number of experimental results are available for the parameter determination.
8. Simulation of the pilot scale pervaporation module

In this chapter, simulation studies with the shortcut, discrete and rigorous models described in section 5.1 are performed. First, the three models are compared amongst each other for the separation task 2-butanol/water without discretisation of the membrane area. Following, a discretisation study is performed with the discrete and the rigorous models. After this, the simulation results of the three models are compared again including discretisation. In the last part, simulations of the membrane module, described in section 4 are compared to experimental investigations performed at the HZG Research Centre in the scope of a joint research cooperation. Therefore, two model separation tasks are considered:

2-butanol/water: The temperature and concentration dependent permeance approach of the hydrophobic membrane, identified in chapter 7, is used for this simulation. Commercial hydrophobic membranes are provided by the HZG Research Centre.

isoprene/n-pentane: The membranes for this application are treated using molecular surface engineering by PolyAn GmbH. The characterisation of the membranes is performed at their laboratory and the data have been kindly provided for this study.

8.1. Model comparison

The comparison of the shortcut, discrete and rigorous models and their comparability amongst each other are performed considering two cases:
Single envelope without discretization: The discrete and the rigorous models are set up without discretisation. The process parameters are chosen in order that no changes of the transmembrane fluxes, compositions and temperature over the membrane length are expected.

Five envelopes with discretisation: Discretisation is included in the discrete and the rigorous model. The process parameters are chosen in order to yield considerable differences in the transmembrane fluxes, compositions and the retentate temperature, to identify the differences between the models.

8.1.1. Single envelope without discretisation

For this simulation, the feed flow is set to 250 kg/h and the feed composition is varied from 1 to 100 mol% 2-butanol content. The feed temperature is set to 70 °C and the temperature drop is calculated with each model. The permeate pressure is set to 10 mbar. Concentration polarisation is turned off in the rigorous model to guarantee the same set-up of the three models. The results of this study are shown in figures 8.1 - 8.3. The transmembrane flux is nearly identical for all three models (figure 8.1(a)). It increases with increasing feed 2-butanol content and reaches a maximum of about 110 mol/hm². In figure 8.1(b), a detailed view of the transmembrane fluxes for feed 2-butanol contents

![Graph](image-url)
between 20 and 100 mol% is shown. The *shortcut* and the *discrete* models yield identical results whereas the *rigorous* model shows lower transmembrane fluxes.

The values of the permeate 2-butanol content (figure 8.2(a)) show similar trends as the transmembrane fluxes. As 2-butanol is the preferred component, it also represents the major part of the transmembrane flux, why its composition follows the trend of its partial flux. The calculated values of the permeate 2-butanol content are very similar for the three models. Only the *shortcut* model yields slightly higher permeate 2-butanol contents (figure 8.2(b)) than the *discrete* and the *rigorous* models.

In figure 8.3, the retentate temperature calculated with the three models is shown. Regarding figure 8.3(a), the retentate temperature does not seem to be different in the three models. Magnifying the plot to a smaller temperature range (figure 8.3(b)) reveals that, the *shortcut* model yields minimal higher results than the other two models.

Also the temperature dependent fluxes and permeate compositions are calculated with the three models. For this investigation, the feed flow is set to 500 kg/h and the mole fraction of butanol to 0.057. The results are shown in figure 8.4.

All models yield identical results for the transmembrane flux (figure 8.4(a)). For the permeate 2-butanol content (figure 8.4(b)), the values of the *shortcut* model are nearly identical over the whole temperature range, whereas the values of the *discrete* and the
8. Simulation of the pilot scale pervaporation module

Fig. 8.3.: Overall (a) and detail view (b) of the retentate temperature simulated with the *shortcut* ◇, *discrete* □, and the *rigorous* △ models (F_{Feed} = 250 kg/h, T_{Feed} = 70 °C, A_{Mem} = 0.1274 m² - single envelope, no discretisation).

The main reason for the variations between the models is the different calculation of the temperature drop. In the *shortcut* model, a lumped approach is used before the calculation of the transmembrane fluxes. This causes a higher temperature drop in this model and thus reduced permeances. The resulting transmembrane fluxes are lower in the *shortcut* model and following, a higher selectivity causes a higher permeate content of the preferred permeating component, which is in this case 2-butanol.

This study shows that the three models yield very similar results if no discretisation is applied and the retentate concentration does not deviate much from the feed concentration. This is especially then the case, when the feed flow is large compared to the permeate flow and the permeate pressure is low. For example if the permeate is the wanted product and extracted in low quantity but with high purity from a large feed stream. Industrial applications can be flavour extraction or the removal of pharmaceutical active components from aqueous streams.
8. Simulation of the pilot scale pervaporation module

(a) Transmembrane fluxes
(b) Permeate 2-butanol content

Fig. 8.4.: Transmembrane fluxes (a) and permeate 2-butanol content (b) in dependency of the feed temperature simulated with the shortcut ◊, discrete □, and the rigorous △ models (\(F_{\text{Feed}} = 500 \text{ kg/h}, x_{\text{Feed}} = 0.057 \text{ mol/mol 2-butanol}, A_{\text{Mem}} = 0.1274 \text{ m}^2\)- single envelope, no discretisation).

8.1.2. Discretisation study

To identify the necessary number of discrete elements for the discrete and the rigorous models, a discretisation study with five membrane envelopes in one compartment is performed. The feed flow is set to 25 kg/h at 70 °C. The 2-butanol content in the feed is 0.3 mol/mol. As reference value, the first simulation is calculated without discretisation. The number of discrete elements is increased step by step and the absolute value of the relative difference of the transmembrane flux, the permeate composition and the retentate temperature between two consecutive steps is calculated. If this difference is smaller than the absolute threshold of 1\% (---), the resolution is considered to be high enough.

In figure 8.5, these differences are plotted over the number of discrete steps for the transmembrane flux (◊) and the retentate temperature (△). The permeate composition does not differ considerably for all calculations in both models and is therefore excluded from the plots. Figure 8.5(a) shows the results for the discrete model. The retentate temperature (△) reaches the threshold with seven and the transmembrane flux (◊) with nine discrete elements. Due to the set-up of this model, simulations with one and two discrete elements yield the same results and the first data point in the plot is the value with three steps. In the rigorous model (figure 8.5(b)), the retentate temperature (△) reaches the threshold with four and the transmembrane flux (◊) with six discrete elements. As the discrete and the rigorous models are set up with the same discretisation in the developed user interface, a number of nine elements is used in both models.
8. Simulation of the pilot scale pervaporation module

The discretisation of the permeate side in the rigorous model is also analysed and all differences between a single and two discretisation elements are smaller than 0.1 %.

Subsequently, discretisation plays a minor role for this application and is not further discussed in this work.

8.1.3. Five envelopes with discretisation

For the third part of the study, five membrane envelopes in five compartments are implemented in the discrete and the rigorous models. The feed flow is set to 25 kg/h at 70 °C and the 2-butanol content is varied from 1 to 100 mol%. The permeate pressure is 10 mbar. The results of these simulations are shown in figures 8.6 - 8.8. In figure 8.6(a), the difference between the shortcut, the discrete and the rigorous models becomes visible. The transmembrane flux is much higher in the shortcut model. The trend is similar to the results shown in figure 8.1(a). The simulated values of the discrete model are nearly identical with those of the rigorous model. The lower fluxes are caused by concentration polarisation, which reduces the 2-butanol content at the membrane surface and thus lowers the driving force and the transmembrane flux.

The comparison of the simulated permeate 2-butanol content is shown in figure 8.7. Considerable differences between the shortcut and the other two models occur at small 2-butanol feed contents (below 10 mol %), which is shown in the enlargement in figure 8.7(b). The shortcut model predicts the highest, whereas the discrete model shows smaller
8. Simulation of the pilot scale pervaporation module

Fig. 8.6.: Overall (a) and detailed view (b) of the transmembrane flux simulated with the shortcut \( \Diamond \), discrete \( \Box \), and the rigorous \( \triangle \) models (\( F_{\text{Feed}} = 25 \) kg/h, \( T_{\text{Feed}} = 70 \) °C, \( A_{\text{Mem}} = 0.637 \) m\(^2\) - five envelopes, with discretisation).

and the rigorous model the smallest values for the permeate composition. The reason is that the driving force does not decrease over the membrane length in the shortcut model. In the discrete and the rigorous models, this drop of the driving force is calculated, which leads to a decreasing selectivity and thus a lower permeate content of the preferred permeating component. In the rigorous model, additional concentration polarisation is considered, which causes the difference compared to the discrete model.

In figure 8.8(a), the retentate temperatures in dependency of the feed 2-butanol content are shown for the three models. The shortcut model yields the highest temperature drop. One obvious reason for this effect is the fact that the transmembrane fluxes are higher in this model which leads to higher heat transfer rates through the membrane. Between the discrete and the rigorous model, no considerable difference can be recognised. As the same heat transfer effects are implemented in both models, and also the transmembrane fluxes are similar, this behaviour is in accordance with the expectations.

The temperature dependency of the fluxes and the permeate composition is also analysed with the three models including discretisation. In this case, the feed flow is set to 50 kg/h and the feed mole fraction of 2-butanol is set to 0.057 mol/mol. Concentration polarisation is calculated in the rigorous model. The plots of the transmembrane flux and the permeate 2-butanol content over the feed temperature are shown in figure 8.9. In this case, the differences between the three models is larger. The transmembrane fluxes are the highest for the shortcut model and decrease for the discrete and the rigorous
models (figure 8.9(a)). The permeate 2-butanol content is also predicted higher with the shortcut than with the other two models. In the discrete and the rigorous models, it increases for increasing temperatures but the values of the rigorous model decrease again for temperatures above 50 °C (figure 8.9(b)).

This qualitative evaluation of the models including discretisation shows that the largest discrepancies occur between the shortcut and the other two models. Higher values of the transmembrane flux are calculated over the whole temperature and concentration ranges by the shortcut model. Also the permeate content of the preferred permeating component is over-predicted. In practical use, this overestimation of the membrane performance can lead to severe under-dimensioning of pervaporation modules. In the range of small feed 2-butanol contents, the calculated permeate composition is higher in the shortcut than in the discrete and the rigorous models. Implementation of concentration polarisation additionally reduces the transmembrane flux and thus the permeate composition of the preferred permeating component in the rigorous model.

Thus the use of shortcut models is acceptable for applications in which the concentration and the temperature of the feed/retentate flow do not considerably change during the process. Nevertheless, if the temperature decreases due to large transmembrane fluxes, the use of discrete models is recommended. If additionally, strong concentration polarisation effects are expected, rigorous models should be used to yield trustworthy results.
8. Simulation of the pilot scale pervaporation module

Fig. 8.8.: Overall (a) and detailed view (b) of the retentate temperature simulated with the shortcut ◆, discrete □, and the rigorous △ models (F_{Feed} = 25 kg/h, T_{Feed} = 70 °C, A_{Mem} = 0.637 m² - five envelopes, with discretisation).

8.2. Separation of 2-butanol/water

The pilot scale experiments for the removal of 2-butanol from a mixture with water are conducted at the HZG Research Centre in the scope of a joint research cooperation. The feed molar content of 2-butanol is varied from 0 to 5 mol % and the feed temperature is constant at 50 °C. The feed mass flow is kept at 500 kg/h and 3 - 3,8 bar feed pressure. The permeate pressure is 8 mbar. The membrane module is equipped with five envelopes in five compartments, which yields a membrane area of 0.64 m².

8.2.1. Comparison between laboratory and pilot experiments

To evaluate the experimental results yielded with the new developed pervaporation module, the transmembrane flux and the permeate 2-butanol content from the pilot scale experiments are compared to the experiments performed in laboratory scale (figure 8.10). The laboratory scale experiments are carried out at 40 and 55 °C, whereas the pilot scale experiments are conducted at 50 °C. Therefore, the laboratory experiments are interpolated for a feed temperature of 50 °C. In figure 8.10(a) is shown that the interpolated transmembrane flux through the membrane is higher than the values from the pilot scale experiments for feed 2-butanol contents larger than 2 mol%. As the feed flow during the pilot experiments is very high, polarisation effects can be assumed to be minimal. One possible reason for the apparent lower permeate flux in the pilot scale
8. Simulation of the pilot scale pervaporation module

8.2.2. Simulation of pilot experiments

For the comparison of the models with experimental results from the pilot plant, the geometrical designs of the membrane module and the envelope are implemented in the discrete and the rigorous models. In the rigorous model, adiabatic behaviour for the calculation of the heat transfer, consideration of pressure drops in the retentate and permeate and the film theory for the calculation of concentration polarisation are activated. The simulations are compared to experimental data in figure 8.11. Figure 8.11(a) shows that all three models describe the increasing trend of the transmembrane flux with increasing feed 2-butanol concentration. The three models predict nearly the same values for the transmembrane flux. The molar permeate 2-butanol content is plotted in figure 8.11(b). The shortcut model yields the highest and the rigorous model the lowest results for the permeate concentration. If concentration polarisation is turned off in the rigorous model, the predicted flux and permeate composition are identical to the discrete model.
8. Simulation of the pilot scale pervaporation module

Fig. 8.10.: Comparison of the transmembrane flux (a) and the permeate 2-butanol content (b) in dependency of the molar 2-butanol feed content for the interpolated values of the laboratory test cell and the pilot module at 50 °C.

Although these differences, all three models predict the transmembrane flux and the permeate composition with good accuracy. Besides concentration polarisation, also the neglected heat loss over the module surface in the simulations can affect the transmembrane flux and the permeate 2-butanol content. As the quantitative variance of the pilot scale experiments is not available at this point, a detailed evaluation of the deviations is not possible.

8.3. Separation of isoprene/n-pentane

The separation of isoprene from a mixture with n-pentane by means of established separation technologies like distillation and absorption is a challenging application as both components have very similar boiling points. Pervaporation is a viable possibility to perform this separation task in industrial scale. For this separation task, an organoselctive membrane is manufactured at PolyAn GmbH using the technology of Molecular Surface Engineering (Matuschewski et al. [111]).
8. Simulation of the pilot scale pervaporation module

Fig. 8.11.: Comparison of the experimental and simulated transmembrane flux (a) and permeate 2-butanol content (b) in dependency of the molar 2-butanol feed content (shortcut — — —; discrete — — —; rigorous models — — —) (SCHIFFMANN AND REPKE [116]).

8.3.1. Membrane characterisation

The experimental membrane characterisation is conducted at PolyAn GmbH. The isoprene feed content is about 20 wt.% and the permeate pressure lies in the range of 0-1 mbar. The results are shown in figure 8.12. The experimental transmembrane mass flux and

Fig. 8.12.: Transmembrane flux ◇ and permeate isoprene content □ of an organoselective membrane (a) and molar permeances of isoprene ● and n-pentane ■ (b) (—— trend lines).

the permeate isoprene content (figure 8.12(a)) show a linear trend in dependency of the feed temperature. For the implementation of the membrane characteristics in the simulation tool, the mass fluxes are transformed into molar permeances and plotted over the absolute feed temperature (figure 8.12(b)). Different to the behaviour of the
hydrophilic and organophilic membranes analysed in chapter 6 and 7, the permeances for both components increase for increasing feed temperatures. Although the trend of the isoprene permeance could be described with a polynomial function, a linear approach is used to keep the model simple and due to the small number of experimental values. As the feed composition is kept constant during the experiments, the concentration dependency of the membrane permeance is neglected and the permeances are described with linear functions:

\[ L_i(T) = a_i \cdot T_F + b_i \] (8.1)

The parameters \( a_i \) and \( b_i \) for isoprene and n-pentane are listed in table 8.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( A_i )</th>
<th>( B_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoprene</td>
<td>0.565</td>
<td>-126.57</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.399</td>
<td>-103.03</td>
</tr>
</tbody>
</table>

### 8.3.2. Simulation of pilot scale applications

For the experimental investigation, the pervaporation module is equipped with 17 membranes in 17 compartments, which yields a total membrane area of 2.17 m². The feed mass flow is kept at a value of 250 kg/h. Due to the high volatility of the components, the feed temperature during the experimental investigation was limited to a range of 16 to 50 °C for security reasons. The permeate pressure reached by the liquid ring vacuum pump is dependent on the permeate temperature and permeate mass flow. During the pilot experiments, a minimum pressure of 10 mbar is reached. The average value during the experiments is in the range of 20 mbar.

In the shortcut and the discrete model, the component properties are calculated as described before (section 5.2). The activity coefficients are calculated with the NRTL model and the pure components vapour pressures with the extended Antoine equation. The enthalpy of vaporisation is calculated using the Watson equation and the liquid heat capacity is retrieved from the Aspen Properties™ database.
8. Simulation of the pilot scale pervaporation module

The comparison between the experimental and the simulated results are shown in figure 8.13. The transmembrane flux and the permeate isoprene content is predicted

with good agreement by the three models. Only the experimental value of the permeate composition at 40 °C is higher than the simulated values, but due to the limited data of the pilot scale experiments, the quality of the experimental value cannot be validated.

These results show that the models are capable to be used for the simulation and design of industrial scale pervaporation modules for organophilic applications. Also in this case, concentration polarisation plays a minor role due to the high feed flow compared to the transmembrane fluxes. For a more detailed evaluation of the models and the pervaporation module, experiments at considerably lower feed flow rate are necessary.

Fig. 8.13.: Comparison between experimental and simulated results of the transmembrane flux (a) and permeate isoprene content (b) in dependency of the feed temperature (Experiment: ●; shortcut ◊; discrete □; rigorous △ models).
9. Summary and Outlook

In this work, an integral approach for the design and simulation of membrane modules for organophilic pervaporation is established.

Two different membranes are investigated extensively in laboratory scale in a wide range of feed temperatures and concentrations. Their separation performances are identified and described in temperature and concentration dependent approaches. These approaches are implemented in three computational models, which are set up with increasing modelling depth. The shortcut and the discrete models are implemented in the widely distributed MS Excel™ which allows an easy and comprehensive simulation of pervaporation modules as a stand alone process. By introducing detailed calculation routines of the temperature and concentration dependent components properties, good agreement between simulated values and experimental results in pilot scale are achieved. The rigorous model of this systematic modelling structure is programmed in the equation orientated Aspen Custom Modeler™ including a two-dimensional discretisation of the membrane. In this model, a detailed investigation of the process is possible by implementing additional mass and heat transfer effects such as concentration polarisation.

With this modelling and simulation approach, industrial relevant separation tasks are simulated. Membrane performance data from laboratory scale experiments are implemented in the models. Comparing the results of the models shows that all three yield similar results when the removed permeate is small compared to the feed flow. The discrete and the rigorous models are also comparable for applications where the feed composition, the transmembrane fluxes and the retentate temperature change considerably. With the rigorous model, also concentration polarisation effects can be calculated. Additionally, it can be introduced in Aspen Plus™ and Aspen Dynamics™, which allows the simulation in flowsheeting environment as well as dynamic simulations. The models are embedded
9. Summary and Outlook

in a user friendly software tool which facilitates the handling with the models and the
display and evaluation of the results.

In cooperation with PolyAn GmbH and the HZG Research Centre, organoselective
membranes are manufactures and a novel pervaporation module for organophilic perva-
poration constructed. With this membrane module, the fluid dynamics of the feed and
the pressure drop in the permeate are optimised, which reduces transport resistances
compared to existing module types. 2-butanol/water and isoprene/n-pentane are chosen
as model separation tasks and investigated experimentally in pilot scale. A comparison
of the performed simulations with results of the experimental investigation of the novel
membrane module in pilot scale shows good agreement.

With this work, an important contribution towards more comprehensive process design
and synthesis for industrial applications of pervaporation is made.

In further work, the membrane module needs to be investigated with different process
parameters. Especially smaller feed flows are important to identify the effects of concen-
tration polarisation in the module. Experiments with different component mixtures and
ternary or quaternary systems are necessary for a comprehensive understanding of the
mass transport in the membrane. Furthermore, the implementation of a more detailed
description of the membrane structure and morphology and advanced approaches for the
modelling of the mass transfer on molecular level would help to reduce the experimental
effort when characterising membranes. Additionally, the implementation of this model
in alternative modelling software as ChemCAD™ or Matlab™ would enlarge the user
group. On top of that, programming of a data base including membrane characteristics
and mass transfer models would provide a powerful tool for the development and design
of pervaporation membranes and processes.
A. Appendix

A.1. List of presentations and publications

**Poster presentation:** “Design of pervaporation modules based on computational process modelling”, *Escape 21*, 30.05.2012, Chalkidiki-Greece


**Oral presentation:** “Development and optimisation of the separation process of organic mixtures by pervaporation”, *European Congress of Chemical Engineering*, 25.09.2011, Berlin-Germany

**Oral presentation:** “From lab to pilot scale - Design of membrane modules using a three step modelling approach”, *Berlin Workshop on Gas Permeation*, 5.08.2012, Berlin-Germany

**Oral presentation:** “Production and Purification of Glycerol based Fuel Additives - Combination of synthesis and pervaporation”, *European Congress of Chemical Engineering*, 25.04.2013, The Hague-Netherlands


**Journal article:** Heike Matuschewski et al., “Pilotversuche in der organophilen Pervaporation: Membran, Modul und Simulation - Ein Gesamtkonzept”, In: *Chemie Ingenieur Technik*, Article first published online: 23.05.2013
A. Appendix

**Journal article:** Patrick Schiffmann and Jens-Uwe Repke, “Experimental investigation and simulation of organophilic pervaporation in laboratory and pilot scale”, In: *Chemical Engineering & Technology*, Article submitted: 04.04.2014


## A.2. Property data for isoprene/n-pentane

<table>
<thead>
<tr>
<th>Component</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
<th>$e_i$</th>
<th>$f_i$</th>
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<td>0</td>
<td>-9,4314</td>
<td>9,585</td>
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<td>0</td>
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<td>9,6171</td>
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<td>water</td>
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## A.3. Detailed discussion of experimental error

In the following figures A.1 - A.3, the experimental runs containing erroneous values for the hydrophilic and the hydrophobic membrane are shown and discussed in detail. The data points, which are considered as outlying values are indicated.
A.3.1. Hydrophilic membrane

Figure A.1(a) shows the experimental results of the measured molar feed water content of the hydrophilic membrane for an initial water content of 71 mol%. The measured value at a temperature of 85 °C (●) is more than 30 % higher than the values at temperatures between 25 and 70 °C (□). As the water content in the feed cannot rise in a dehydration application, a contamination of the sample is a probable explanation. For the further evaluation, this data point is omitted. In figure A.1(b), the molar permeate water content of two experimental runs are plotted. In figure A.1(b), at a preset feed water content of 25 mol% (□), the permeate water content shows a strong deviation at 25 °C (●). At a feed water content of 41 mol% (◇) outliers are identified at 25 and 85 °C (●). The experimental values at 40 - 70 °C show the expected trend. Also in this case, contamination of the samples or errors during analysis of the samples are a possible explanation for these deviations.

A.3.2. Hydrophobic membrane

In figure A.2 the transmembrane flux of the hydrophobic membrane for two molar feed 2-butanol contents are plotted which show strong deviations from expected values. For a feed 2-butanol content of 3,8 mol% (figure A.2(a)), the value at a feed temperature of 25 °C is higher than the values at 40 and 65 °C, which is contradictory to the theoretical
trend. In this case, an error during the weighting of the permeate in the cooling trap is the most probable reason. At a feed 2-butanol content of 85.6 mol% (figure A.2(b)), the flux values at the feed temperatures 70 and 85 °C show an exceeding trend (●) compared to a reference measurement at 85.8 mol/mol (○). A detailed inspection of the membrane after this experiment shows that the top layer of the membrane has been partly desintegrated. This is probably due to the long term exposition of the membrane to high temperatures and high 2-butanol feed contents. Although this indicates that the membrane is not suited for these extreme conditions, the reference measurement is taken into account during further evaluation.

Fig. A.2.: Identification of outlying values of the transmembrane flux for the hydrophobic membrane.

In figure A.3, experimental feed and permeate water contents measured for the hydrophobic membrane with noticeable deviations are plotted. In figure A.3(b), the measured feed 2-butanol content of two experimental runs at 3.8 (□) and 3.5 (◇) mol% are plotted over the feed temperature. The values deviating strongly from the preset feed concentration are indicated at temperatures of 25 and 40 °C for 3.8 mol% in the feed and at 70 °C (●) for 3.5 mol%. As the feed 2-butanol content is assumed to be constant during the experimental runs, these alues are considered as outliers and skipped from further investigation. In figure A.3(b), the permeate 2-butanol content for experimental runs at 0.5 (□), 2.8 (△) and 3.8 (◇) mol% feed 2-butanol content are plotted. At 25 °C, all three runs show deviations from the expected trends (●, △, ◇). At 40 °C, also the run at 3.8 mol% feed content, the values are lower than expected. A possible explanation for these outlying values is that the membrane did not reached its final performance although the temperature was constant. A second possibility is that the fluxes at these low temperatures are very small and a contamination of residual water in the permeate
(a) Measured values of the feed 2-butanol content at preset feed water contents of 0.035 (□) and 0.038 (◇) mol/mol.

(b) Measured values of the permeate 2-butanol content at preset feed water contents of 0.005 (□) and 0.028 (∆) and 0.038 (◇) mol/mol.

Fig. A.3.: Identification of outlying 2-butanol mole fractions in the feed (a) and the permeate (b) for the hydrophilic membrane.

The system has a large influence on the final composition. Therefore, these data points are not used in the further evaluation.

A.4. Modelling Approach

Fig. A.4.: Feed water dependency of water permeances for 40 °C (Data used for modelling (◇) and validation (○) — Miscibility gap at 40 °C).
Bibliography


[72] *Aspen Properties V7.2*. 

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