Theoretical and experimental study of the hydrophilic pervaporation of binary and ternary mixtures

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I would like to dedicate this work to the memory of my beloved parents.
Abstract

The production of bio-based alcohols, such as bioethanol and biobutanol, as potential biofuels has gained extensive attention in recent years due to the expected depletion of fossil fuels in the not so distant future on one hand, and human-caused climate change and global warming caused by excessive CO₂ emission on the other. However, the product mixtures of these biotechnological processes are extremely dilute, requiring energy-intensive and expensive separation technologies to gain pure alcohols at the end. Pervaporation has established itself as an energy-efficient and highly selective liquid separation method, which, therefore, has a great potential in biofuel purification. Despite the numerous advantages of this membrane process, its commercialization and industrial application has been hindered due to the high cost of membrane modules and the lack of industrial experience.

In this thesis, the separation performance of commercial hydrophilic composite membranes for the dehydration of binary and ternary aqueous mixtures has been studied on the bases of pervaporation experiments and mathematical modelling. Pervaporation experiments with binary alcohol-water mixtures proved the excellent applicability of these membranes for alcohol dehydration. A semi-empirical solution-diffusion transport model was developed, which is in good agreement with the experimental data, providing a reliable basis for process design and optimization. The suitability of the model was tested on multiple case studies applying hybrid separation methods for alcohol production. Results showed that the coupled distillation-pervaporation systems indeed offer substantial energy savings.

Since the majority of studies in the field of pervaporation are dealing with binary mixtures only, the object of this work was to investigate the water separation performance of composite membranes for ternary mixtures as well. Dehydration experiments revealed a considerable molecule-molecule and molecule-membrane interaction affecting permeation through the polymeric membrane. A further model improvement addressed this interdependence and the flux-coupling effect of the permeating species, resulting in a good accordence with experimental data.

The developed models with their offered simplifications serve as reliable tools for process design involving pervaporative dehydration of the studied binary and ternary mixtures. This work was motivated by the hope of reducing industrial scepticism towards this promising green technology.
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1 Introduction

1.1 Motivation

The numerous products manufactured by chemical, pharmaceutical and bio-based industries are undoubtedly indispensable for our modern life. The already present and continually growing environmental concerns about climate change, as well as the forthcoming depletion of fossil fuel resources drive the need for alternative, bio-based raw materials as well as sustainable production methods with a reduced carbon dioxide footprint.

Bio-based ethanol and butanol production has been in the focus of research attention to secure sustainable fuel production with their numerous benefits, including the reduction of greenhouse gas emissions, the support of rural economies, and offering energy security by the reduction of oil imports. These advantages seem to be justified by a global production of 82.31 megatonnes of oil equivalent of liquid biofuels in 2016 [1].

However, an increasing number of researchers view biofuels as an outworn conception due to the fact that the majority of current biofuel producing technologies use food crops (corn, sugar cane, edible oil seeds) as feedstock, which raises ethical questions. Besides, there are signs that internal combustion vehicles could be phased out in the short to midterm future in favour of electric vehicles [2]. Fermentation processes based on lignocellulosic feedstock could be a remedy for the former argument, which is an intensively researched area at present [3]. Moreover, a transition to an increasingly plant-based diet containing fewer animal products has the potential to significantly reduce the resource demand of food production while creating a room for bio-based fuel production considered as a ‘food and biofuel’ scenario [4].

Furthermore, bioethanol and biobutanol are widely used solvents in the chemical industry, making a well-founded argument for their bio-based production replacing fossil-based chemical manufacture in the long term. Therefore, the consideration of the co-manufacture of biofuels and commodity chemicals in bio-refineries has been gaining momentum, where bioethanol is being produced not just as biofuel, but also as potential platform chemical, realizing the great potentials of bio-based n-butanol and isobutanol as well.
The biocatalytic conversion of carbohydrates in these biorefineries offers numerous routes for the manufacture of other commodity chemicals, such as the widely used solvent, ethyl acetate, produced by acetogenic fermentation.

The fermentation process producing bio-alcohols results in relatively low yield with diverse products and by-products in highly diluted aqueous mixtures, the separation of which generates huge challenges for the bio-industry.

The global primary energy consumption (PEC) is estimated to be 600 EJ per year, or 82 GJ per capita per year [5]. Therefore, even in the short term, conventional fossil-based chemical production methods should be modified or retrofitted in order to be as efficient as possible, reducing their energy demand and recovering valuable side products.

The conventional methods for the downstream processing of these bio-based products, such as distillation, extraction, absorption and adsorption, are often highly energy intensive, or necessitate additional solvents to achieve the required product quality. Membrane processes, including pervaporation, have already showed their great potential as energy-efficient, highly selective separation processes, desperately needed in numerous industries to alleviate their burden on the environment. With the help of pervaporation, the separation of liquid mixtures is possible on a molecular level, offering various options to solve difficult separation problems in an energy-efficient way. Although the process has been applied for ethanol dehydration on an industrial scale for decades, it still struggles to be widely accepted and considered as a viable option. To reduce industrial scepticism towards pervaporation, thorough experimental and process simulation studies are inevitable exploring its applicability for various separation problems.

The aim of my present work was to experimentally investigate the dehydration of binary and ternary model solutions of biotechnological product mixtures with the help of pervaporation, and to create mass transport models for the reliable description of the process. With proper models at hand, it becomes possible to study the possibilities of integrating pervaporation into hybrid processes, and to assess their economic viability, and thus, hopefully, increasing the willingness for its industrial application.
1.2 Thesis overview

Chapter 2 introduces the reader to the theoretical background of membrane separation processes with a special emphasis on pervaporation, its modelling approaches, and the hybrid separation processes applying pervaporation.

The experimental and analytical methods that have been applied to achieve the objectives of this thesis are summarized in Chapter 3.

Chapter 4 demonstrates the experimental results and suggested model development for the pervaporation of binary alcohol-water mixtures, also investigating pervaporation performance and model applicability through several case studies.

Chapter 5 extends the investigation to the dehydration of ternary mixtures. The effect of the variation of components and their concentrations was studied through experiments and described with the help of a further model improvement.

Major new results are summarized in Chapter 6.
2 Theoretical background

2.1 Membrane separation methods

A membrane is an interphase between two phases, through which a selective transport of substances can take place. It is suitable to separate gases, liquids, solids, ions and biological components. Although studies about the membrane phenomena were performed as early as the eighteenth century, the industrial and commercial applications were not introduced until the second half of twentieth century.

At the beginning of the 1960s Loeb and Sourirajan [6] succeeded to produce an asymmetric, defect-free polymer membrane for water desalination. This first “high-flux” membrane proved to be a milestone in the history of membrane processes, catalysing their breakthrough into industrial application. Between 1960 and 1980 high performance membranes in microfiltration, ultrafiltration and reverse osmosis became well-established industrial processes worldwide, thanks to the advances made in the production technique. Multilayer composite polymer membranes packed into modules with large area per volume ratios further revolutionized the industry.

Membrane separation techniques are among the key technologies of the 21st century, since the component separation happens selectively at a molecular level, independent of the vapour-liquid equilibrium. Membrane units can be operated isothermally at low temperatures, decreasing their energy consumption; they do not require additives, and can be integrated into other separation processes. Therefore, certain membrane processes are becoming competitors with traditional separation techniques, such as distillation, extraction, ion exchange, and absorption, for an incredibly wide range of applications from medical, chemical, food, and beverage separation processes to water desalination and wastewater treatment [7].

The driving force of membrane separation processes is the difference in chemical potential between the two sides of the membrane, which can be simplified to pressure, concentration, temperature, or electric potential gradients depending on the specific process. A non-exhaustive list of the most important membrane techniques is presented in Table 1[8].
Table 1 Characterization of the most significant membrane processes

<table>
<thead>
<tr>
<th>Membrane processes</th>
<th>Membrane type</th>
<th>Driving force</th>
<th>Separated components</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Microfiltration (MF)</strong></td>
<td>Microporous</td>
<td>Transmembrane pressure 1-3 bar</td>
<td>Colloids, macromolecules, emulsions, bacteria</td>
</tr>
<tr>
<td><strong>Ultrafiltration (UF)</strong></td>
<td>Microporous</td>
<td>Transmembrane pressure 1-10 bar</td>
<td>Bacteria, viruses, proteins</td>
</tr>
<tr>
<td><strong>Nanofiltration (NF)</strong></td>
<td>Mesoporous, nanoporous</td>
<td>Transmembrane pressure 5-35 bar</td>
<td>Proteins, sugars, salts</td>
</tr>
<tr>
<td><strong>Reverse osmosis (RO)</strong></td>
<td>Porous, dense</td>
<td>Transmembrane pressure 15-80 bar</td>
<td>Soluble salts, sugars</td>
</tr>
<tr>
<td><strong>Gas separation (GS)</strong></td>
<td>Porous, dense</td>
<td>Vapour pressure and concentration gradient</td>
<td>Gases, vapours</td>
</tr>
<tr>
<td><strong>Pervaporation (PV)</strong></td>
<td>Porous, dense</td>
<td>Vapour pressure and temperature gradient</td>
<td>Liquids</td>
</tr>
<tr>
<td><strong>Vapour permeation (VP)</strong></td>
<td>Porous, dense</td>
<td>Vapour pressure and concentration gradient</td>
<td>Vapours</td>
</tr>
<tr>
<td><strong>Electrodialysis (ED)</strong></td>
<td>Ion exchange</td>
<td>Electric potential gradient</td>
<td>Ions</td>
</tr>
</tbody>
</table>

2.1.1 Membrane materials

The material and structural variety of the membranes is incredibly diverse, largely determined by their future application area. They differ in raw-material (natural/synthetic), structural integrity (porous/non-porous), material strength, durability, porosity, etc. A summary of membrane materials and structures is depicted in Figure 1. In the following, synthetic membranes will be discussed in detail due to their dominant position in industrial applications.

Generally, synthetic membranes can be classified into four main groups:

1) porous membranes,
2) homogeneous solid membranes,
3) electrically charged solid membranes,
4) supported liquid membranes with selective carrier components.

The structure of the membranes can be either symmetric (isotropic) or asymmetric (anisotropic). Isotropic porous membranes have voided structures with the pores randomly
distributed in the membrane. They work on the basis of size-exclusion, rejecting solutes with a larger size than the pore diameter. Isotropic dense membranes are made of a dense, uniform film separating via the different solubilities and diffusivities of the solutes. Electrically charged membranes can be either dense or porous with positive (anion-exchange membranes) or negative ions (cation-exchange membranes) attached to the material, where separation occurs according to the charge and concentration of the ions in the solution.

![Classification of membrane materials](image)

**Figure 1** Classification of membrane materials

The production of asymmetric membranes was required to increase the transmembrane flux while preserving their selectivity. The thin selective layer facing the feed mixture is responsible for the separation and determines the permeation rate, while a more robust supporting layer beneath this film provides the membrane with mechanical support. Composite membranes are increasingly used as anisotropic polymer membranes, consisting of two or more different polymer layers. The supporting layer has a porous structure with large pore diameters designed to minimize transport resistance.

Further groups of synthetic membranes are microporous ceramic membranes with great solvent resistant characteristics; metal membranes used for gas separation, and supported liquid membranes providing carrier facilitated transport [7]. The application of inorganic membranes in pervaporation is emerging due to their high selectivity and high
temperature stability. Mixed matrix membranes are composed of organic polymers incorporating inorganic particles such as zeolite, carbon molecular sieves, or nano-size particles. They exhibit a potential to achieve higher selectivity, and permeability compared to polymer membranes.

Pervaporation membranes will be further discussed in detail in Section 2.2.2.

2.1.2 Membrane modules

In order to achieve higher area-to-volume ratios, membranes are arranged into compact structures, called modules. The most common module types are the following:

- Flat membranes: arranged into plate-and-frame or spiral wound modules,
- Tubular membranes: formed into tubular, capillary or hollow fiber modules.

These modules are operated either in dead-end, or cross-flow mode. The typical operation is the latter, where the feed/retentate solution moves parallel to the membrane surface in the form of a turbulent flow with a relatively high speed, thus ensuring uniform conditions in the feed stream, and at the same time “washing” the membrane surface. The removal of any substance deposited on the membrane is crucial, since these can hinder permeation and cause a degradation of the membrane performance, or even the membrane material. Cross-flow mode enables the continuous operation of membrane separation, with as few washing cycles as possible.

In pervaporation (PV) industry, the primarily used membrane module is the plate-and-frame module, since it provides low resistance channels at the feed and permeate side. The latter is inevitable in PV, as it ensures the required very low concentration or partial pressure of the permeating molecules. The essential low permeate-side partial pressure is the reason why hollow fiber modules are inadequate. Very short fibres or large enough diameters would be necessary in that case. Ceramic zeolite PV membranes are usually produced in tubular form [9].

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2.1.3 Industrial application of membranes

The role of membrane separation processes in various industries is becoming more and more important, as they offer solutions for previously unmanageable problems. Involving membrane processes, the development of new separation processes or the retrofitting of existing methods are both achievable. An excerpt of the wide application range of membrane processes is demonstrated in Table 2.

Table 2: Industrial application areas of membranes

<table>
<thead>
<tr>
<th>Industry</th>
<th>Application</th>
<th>Membrane processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edible oil industry</td>
<td>Refining of vegetable oils, oil retention</td>
<td>UF, NF, RO</td>
</tr>
<tr>
<td>Dairy industry</td>
<td>Whey processing, removal of bacteria, casein, and off-flavor from milk/whey, wastewater treatment</td>
<td>UF, NF, RO, ED</td>
</tr>
<tr>
<td>Meat industry</td>
<td>Filtration, concentration, and deashing of pork, bone; meat brine clarification for bacteria removal, brine reuse, gelatin production.</td>
<td>MF, UF, NF</td>
</tr>
<tr>
<td>Textile industry</td>
<td>Recovery of sizing agents from the desizing effluents, recovery of the dyeing effluents</td>
<td>MF, UF, NF, RO</td>
</tr>
<tr>
<td>Pulp and paper industry</td>
<td>Treatment of effluents, water saving, reducing toxic pollutant release</td>
<td>UF, NF, RO</td>
</tr>
<tr>
<td>Pharmaceutical industry</td>
<td>Fractionation of multicomponent mixtures, removal of large biopolymers, recovery of antibiotics, separation of enantiomers, wastewater treatment</td>
<td>MF, UF, NF, RO</td>
</tr>
<tr>
<td>Fruit juice and pulp production</td>
<td>Clarification, concentration, fractionation, deacidification</td>
<td>MF, UF, RO, ED</td>
</tr>
<tr>
<td>Aroma processing</td>
<td>Aroma recovery, flavor processing, concentration of juices</td>
<td>RO, NF, PV</td>
</tr>
<tr>
<td>Beer and wine production</td>
<td>Wine chaptalization, clarification, stabilization, sterile filtration</td>
<td>MF, RO, ED</td>
</tr>
<tr>
<td>Electric industry</td>
<td>Wastewater treatment, water degassing</td>
<td>MF, UF</td>
</tr>
</tbody>
</table>
The application of membranes contributes to drinking water production, rational water use and reuse by water purification; the recycling of valuable raw materials; and the removal of certain contaminants (solids, colloids, volatile organic compounds or ions). The huge consumption of chemicals in certain large-scale operations can be reduced with the recovery and recycling of unreacted raw materials, catalysts, adsorbents, etc. The food industry uses membranes for the demineralization of juices and whey, as well as beer and wine clarification. Membranes contribute to the energy industry as fuel cells, or by producing biofuels (ethanol dehydration, transesterification of fatty acids in membrane reactors), and to environmental applications, such as carbon capture, wastewater treatment, and process water treatment. [10,11].

2.2 Pervaporation

The process of pervaporation was discovered by Kober in 1917, but it was only decades later, in the 1960s, when the first laboratory scale results were published [12–14]. Commercialisation was still hindered, though, due to the lack of market demand and highly selective membranes with high permeabilities. The first commercial application was introduced by the company GFT (Germany) in the 1970s, after which the first industrial pervaporation plant for bioethanol production was put into practice in 1982 [7].

During pervaporation a binary or multicomponent liquid mixture is separated by the selective permeation of one or more components through a nonporous or microporous membrane material. As the name *pervaporation* (permeation and evaporation) suggests, a phase change occurs as the permeating components partially vaporise passing through the membrane to the permeate side. The enthalpy of vaporisation is provided by the sensible heat of the feed mixture.

The feed side is under atmospheric or moderate pressure, while the permeate side is kept at very low absolute pressure (e.g. 1-3 mmHg), below the saturation pressure of the components, usually with the help of a vacuum pump or with a sweep gas. Thus, a high chemical potential gradient (partial pressure gradient) is maintained to ensure an adequate driving force to the process. The permeate vapour is condensed and collected as a liquid phase. The liquid mixture enriched in the retained component(s) is called the retentate (Figure 2) [15].
Although processes involving phase change (e.g. distillation) have a high energy demand, pervaporation has been shown to be energy-efficient based on two features: (1) the concentration of the component(s) to be separated is low in the feed mixture (usually max. ~10 wt%), and (2) pervaporation membranes are highly selective. Thus, only the minor component consumes the latent heat.

The advantage of the process compared to distillation is that vapour and liquid are not in direct contact with each other; therefore it is independent of the thermodynamic vapour/liquid equilibrium. It is governed rather by the selective interaction (sorption and diffusion) of the molecules with the membrane material. This difference in solubility determines the selectivity of the membrane towards one component or the other. Therefore, pervaporation has advantages separating azeotropes, heat sensitive and close-boiling mixtures, due to the mild operating conditions and the lack of necessity for an entrainer.

The mass transfer through the membrane consists of three main steps:

1) sorption of the components on the feed side,
2) diffusion through the membrane material, and
3) desorption of permeated molecules at the permeate side in vapour state [16].

Transport occurs due to the driving force expressed in chemical potential or, in the case of pervaporation, partial pressure difference between the feed and the permeate side of the membrane.
2.2.1 Characterization of pervaporation performance

The evaluation of pervaporation efficiency requires common performance indicators applied in the membrane industry, such as flux, permeance, selectivity, and separation factor. The pervaporation flux is defined as the amount of material permeating through a unit of membrane area in a unit of time. Thus, the permeate flux can be weight, mole or volume based. The partial flux of a component is proportional to its partial vapour pressure difference between the feed and permeate sides of the membrane, i.e. the driving force. The partial molar flux is calculated as:

\[ J_i = \frac{n_i}{A \cdot t} = P_i (x_i y_i p_i^0 - y_i p^P) \]  

(2.1)

where \( J_i \) is the partial flux \([\text{mol}/(\text{m}^2\text{h})]\); \( n_i \) is the amount of the permeating component \([\text{mol}]\); \( A \) is the membrane area \([\text{m}^2]\); \( t \) is pervaporation time \([\text{h}]\); \( P_i \) is the permeance \([\text{mol}/(\text{m}^2\text{h}k\text{Pa})]\); \( x_i \) and \( y_i \) are the mole fractions in the liquid phase and the vapour phase, respectively; \( y_i \) is the activity coefficient; \( p_i^0 \) is the vapour pressure of the pure component \([\text{kPa}]\), and \( p^P \) is permeate pressure \([\text{kPa}]\). Subscript \( i \) denotes component \( i \).

The separation factor is calculated as:

\[ \beta_{ij} = \frac{y_i^P / y_j^P}{x_i^F / x_j^F} \]  

(2.2)

where \( y_i^P \) and \( y_j^P \) are the molar fractions of component \( i \) and \( j \) in the permeate, and \( x_i^F \) and \( x_j^F \) are the molar fractions of component \( i \) and \( j \) in the feed mixture. The separation factor depends on feed concentration, or operating conditions, such as pressure difference to a significant extent, causing it to be less informative for the membrane performance itself.

Pervaporation separation index (PSI) shows the overall performance of the membrane by combining the effects of flux and separation factor, and is defined as:

\[ \text{PSI} = J \cdot \beta_{ij} \]  

(2.3)

Baker et al. [17] found that a comparison between the experimental results of various authors is only possible if membrane performance is reported in permeance and selectivity beside flux and separation factor, since the latter two are highly dependent on operating conditions (e.g. temperature).
The permeance of a component depends solely on the intrinsic properties of the system eliminating the effect of the driving force from the flux:

\[ P_i = \frac{J^P_i}{l} = \frac{D_i K_i}{l} = \frac{J_i}{x_{iP}p_i^P - y_{iP}p_i^P} \]  

(2.4)

where \( J^P \) is permeability \([\text{mol/(m} \cdot \text{h} \cdot \text{Pa})]\); \( D_i \) and \( K_i \) are the diffusion and sorption coefficients, respectively; and \( l \) is membrane thickness.

The selectivity of the membrane towards component \( i \), assuring an efficient separation, can be expressed as the ratio of the permeances of components \( i \) and \( j \):

\[ \alpha_{ij} = \frac{P_i}{P_j} \]  

(2.5)

These parameters are local quantities, meaning that in industrial realization of the process they change along the membrane module. All these parameters bear huge significance in a membrane process economically, and are dependent on the applied membrane material to a great extent.

### 2.2.1.1 The influence of solubility parameters

The selective solubility of different solvent molecules in a membrane material can be evaluated with the help of the solubility parameter theory introduced by Hansen \[18\], stating that components with similar solubility parameters are more likely to be soluble in one another. Hansen solubility parameters comprise of three components: a dispersion force component, a hydrogen-bonding component, and a polar component, in the following way:

\[ \delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]  

(2.6)

where \( \delta_t \) [MPa\(^{1/2}\)] is the total value, \( \delta_d \) is the dispersion component, \( \delta_p \) is the polar component, and \( \delta_h \) is the hydrogen-bonding component, all calculated by group contribution method \[19\]:

\[ \delta_d = \frac{\sum F_{d,i}}{\sum V_i} \]  

(2.7)

\[ \delta_p = \sqrt{\frac{\sum F_{p,i}^2}{\sum V_i}} \]  

(2.8)
\[ \delta_h = \sqrt{\frac{\sum E_{h,i}}{\sum V_i}} \]  

(2.9)

where \( F_{d,i} \) and \( F_{p,i} \) are molar attraction constants of group \( i \) of the dispersion and the polar component, \( E_{h,i} \) is the hydrogen-bonding energy of group \( i \) and \( V_i \) is the molar volume of group \( i \).

The three Hansen solubility parameter components define a three-dimensional space, which can be represented by a sphere, where the solubility parameters of the polymer define the center of the sphere (Figure 3) [18].

![Figure 3](image)

**Figure 3** Representation of Hansen’s modified 3D solubility sphere. P and S denote the membrane polymer and a given solvent, respectively.

A specific radius, i.e. the interaction radius \( (R_0) \), can be assigned to each polymer that defines their solubility region. If the Hansen solubility parameters place a solvent inside this region, the solvent may be soluble in the polymer. Hansen and Skaarup [20] developed the following equation to calculate the solubility parameter distance, \( R_a \), between the center of the sphere defined by the polymer and a given solvent:

\[ R_a^2 = 4\left(\delta_{dp} - \delta_{ds}\right)^2 + \left(\delta_{pp} - \delta_{ps}\right)^2 + \left(\delta_{np} - \delta_{ns}\right)^2 \]  

(2.10)
where subscripts $P$ and $S$ refer to the polymer and the solvent, respectively. If the distance of a solvent or a mixture is smaller than the interaction radius of the polymer, they can be mutually soluble [18].

Solubility parameters of a mixture can be calculated by the mass weighted averages of each parameter:

$$\bar{\delta}_k = \sum_i \varepsilon_i \delta_{ki}$$  \hspace{1cm} (2.11)

where subscript $i$ and $k$ indicate the component and subscripts $d$, $p$, and $h$ indicate the dispersion, polar and hydrogen-bonding Hansen solubility parameters, respectively. $\varepsilon_i$ is the weight fraction of each component in the mixture.

### 2.2.2 Pervaporation membranes and their applications

Depending on the hydrophilic or hydrophobic nature of the membrane, pervaporation is applied for the following purposes [9,21–25]:

- **Solvent dehydration**: the separation of water, as low concentration component, from organic solvents; the separation of azeotropes (e.g. ethanol - water, isopropanol - water); removing water from reaction mixtures, thus shifting the reaction equilibrium (e.g. esterification reactions).
  
  The most common hydrophilic membranes used for dehydration are poly(vinyl alcohol) (PVA), chitosan, alginate, polysulfone, polyimide, polyamide, polyaniline, perfluoropolymers, polybenzimidazole (PBI), ceramic, zeolite and mixed-matrix membranes [26].

- **Selective removal of organics from aqueous mixtures**: process wastewater treatment [27,28]; the removal of organic solvent from process side streams; the separation of organics from fermentation broths [29], aroma compound removal; and dealcoholizing wine or beer.
  
  Hydrophobic or organophilic membranes applied are poly(dimethyl siloxane), polyurethane, poly(ether-block-amide), nitrile-butadiene rubber, styrene-butadiene rubber.

- **The separation of organic/organic mixtures**: separation of organic azeotropes (e.g. methanol - methyl acetate); isomer separation (e.g. xylenes); polar/non-polar separation (methanol - methyl tert-butyl ether), aromatic/aliphatic separation (n-hexane – benzene), and shifting reaction equilibrium by the
removal of solvents (e.g. methanol - butyl acetate, ethanol - methyl acetate at transesterification reactions).

Organophilic membranes suitable for these objectives are polyimide, blended polymer membranes (e.g. cellulose acetate – polyphosphonate), membranes with blended nanoparticles (e.g. perfluorosulfonate - Ag⁺) and zeolite membranes (e.g. silicalite-1, Mordenite, Ferrierite). For the removal of methanol, often hydrophilic membranes are adopted.

In nonporous membranes, permeating molecules are moving continuously through spaces in between the polymer segments. The difference in the diffusion speed of the components defines the selectivity of the membrane. In inorganic membranes the transport takes place in the fixed pores across the membrane.

In general, the separation of organic solvents from water suffers from low selectivity; therefore, PV can hardly compete with adsorption. On the other hand, pervaporation exceeds adsorption when the concentration of the organic solvent is relatively high, because PV is a continuous technology and cannot be saturated, in contrast with adsorption. From the 1980s onwards, the most widely accepted application of pervaporation is alcohol dehydration [30–32], later extended by the dewatering of, for instance, benzene, tetrahydrofuran and caprolactam [26,33–35].

Although new membrane materials and modifications of existing structures have been rapidly emerging in the literature, the most prevalent membrane material for the dehydration of solvents with pervaporation is still poly(vinyl alcohol) (PVA) (Figure 4).

![The structure of poly(vinyl alcohol)](image)

Figure 4 The structure of poly(vinyl alcohol)

Water shows a distinctive behaviour in polymers due to its small size and its tendency to form hydrogen bonds with water molecules as well as with polar groups in the polymer material. Sorption and diffusion are both affected by this behaviour not only in hydrophilic membranes, but in less polar ones as well, caused by the association of water
molecules (i.e. cluster formation). A great number of polar groups present in the polymer results in an increased sorption affinity of water. Beside the number of polar groups, the degree of crystallinity is an equally important factor, since crystallites are inaccessible to water, even though their surface polar groups can react with them. If a polymer contains numerous polar groups, water diffusivity increases with water content [36]. With more water around a limited number of polar structural units, the polymer will swell, expanding the space between the chains and segments of the polymer and water molecules become more mobile. Solubility dominates in the swollen side, while in the non-swollen layer diffusivity defines the transport [37].

PVA is a linear crystalline polymer, which is highly hydrophilic due to the hydroxyl groups attached to its chains. These OH- groups can easily form hydrogen bonds with permeating components, especially water [26]. PVA is a derivative of poly(vinyl acetate) (PVAc), and its structure is highly dependent on the branches in PVAc as well as the degree of its hydrolyzation, the preparation technique and the subsequent crosslinking [38]. Because of the swelling or plasticizing effect, it is of crucial importance for the selective skin layer and the supporting layer of a composite membrane to swell in a coordinated manner. Otherwise the membrane structure can disintegrate. To decrease the swelling degree, the selective top polymer material is usually crosslinked. Crosslinking decreases the mobility of polymer chains by creating bonds between them, resulting in decreased swelling degree and free volume, hence more stability. Various crosslinking agents are used for increasing the rigidity of the PVA chains, such as citric acid, maleic acid and glutaraldehyde, the latter being the most common [39–41]. The number of OH-groups in PVA decreases by increased crosslinking, affecting its hydrophilicity, therefore influencing the membranes selectivity towards water or alcohol [42].

The two main manufacturers of commercially available membranes are DeltaMEM AG (producer of PERVAP membranes, formerly distributed by the Sulzer Chemtech Ltd.) and Pervatech BV. The former produces polymer composite and inorganic PV membranes for solvent dehydration, methanol separation, aroma recovery and esterification processes. Pervatech offers organophilic polymer membranes and ceramic membranes also for dehydration purposes [43,44].

The importance of cross-linking agents was demonstrated by Qiao et al., who studied the structure of two PVA/PAN (poly(vinyl alcohol)/polyacrylonitrile) membranes, PERVAP 2510 and PERVAP 2201 (provided by the Sulzer Chemtech company, which
manufactured the composite membranes applied in the present study as well). They found that the two membranes, although both have a PVA selective layer on a PAN sheet, exhibit significant differences in permeation characteristics both for isopropanol/water and butanol/water binary mixtures. The dissimilarities were most probably caused by the different cross-linking agents (PERVAP 2510 – maleic or citric acid, PERVAP 2201 – glutaraldehyde) [45].

Dehydration of solvents is the most developed application of PV due to the small size of the water molecule, causing it to be the preferentially dissolved and transported component. Pervaporation data of alcohol dehydration collected from the literature are presented in Table 3 and Table 4 for ethanol, n-butanol and isobutanol dehydration, showing the results achieved by laboratory experiments with various membrane materials beside PVA. These specific alcohols are highlighted as they are in the focus of the experimental section of the present work. Although some results shown in the tables are very promising, the large-scale production of the majority of these membranes has not been implemented yet, either because of complicated manufacturing methods or extremely high costs.
Table 3 Experimental data for ethanol dehydration achieved by different membranes

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>T [°C]</th>
<th>w_{FW} [wt%]</th>
<th>J_{total} [kg/m²h]</th>
<th>β [-]</th>
<th>α [-]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol / water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA-CA blend</td>
<td>45</td>
<td>15</td>
<td>0.21</td>
<td>40</td>
<td>250</td>
<td>Zhou et al. [46]</td>
</tr>
<tr>
<td>PVDF hollow fiber</td>
<td>50</td>
<td>15</td>
<td>1.29</td>
<td>40</td>
<td></td>
<td>Zhang et al. [47]</td>
</tr>
<tr>
<td>PA/PAN</td>
<td>70</td>
<td>10</td>
<td>13.9</td>
<td>4491</td>
<td></td>
<td>Hung et al. [48]</td>
</tr>
<tr>
<td>CS/GG/PAN</td>
<td>80</td>
<td>10</td>
<td>0.8</td>
<td>2329</td>
<td></td>
<td>Wu et al. [49]</td>
</tr>
<tr>
<td>NaY zeolite</td>
<td>75</td>
<td>10</td>
<td>2.1</td>
<td>105</td>
<td></td>
<td>Zhang et al. [50]</td>
</tr>
<tr>
<td>Zeolite X</td>
<td>65</td>
<td>10</td>
<td>3.37</td>
<td>296</td>
<td></td>
<td>Zhou et al. [51]</td>
</tr>
<tr>
<td>PVA-CS/ZrO₂-Al₂O₃ ceramic</td>
<td>50</td>
<td>8</td>
<td>2.22</td>
<td>500</td>
<td></td>
<td>Zhu et al. [52]</td>
</tr>
<tr>
<td>PVA-CNTs/PES-polyester</td>
<td>30</td>
<td>10</td>
<td>0.47</td>
<td>78</td>
<td></td>
<td>Panahian et al. [53]</td>
</tr>
<tr>
<td>Matrimid® (PI) -MOF</td>
<td>42</td>
<td>10</td>
<td>0.43</td>
<td>&gt;200</td>
<td></td>
<td>Sorribas et al. [54]</td>
</tr>
<tr>
<td>PDMS-zeolite/CA</td>
<td>40</td>
<td>10</td>
<td>0.35</td>
<td>14.1</td>
<td></td>
<td>Ji et al. [55]</td>
</tr>
<tr>
<td>Silica-CS hybrid</td>
<td>30</td>
<td>10</td>
<td>0.59</td>
<td>5282</td>
<td></td>
<td>Pandey and Shahi [56]</td>
</tr>
</tbody>
</table>

T: temperature; w_{FW}: feed water content; J_{total}: total flux; β: separation factor; α: selectivity; PVA: poly(vinyl alcohol); CA: cellulose acetate; PVDF: polyvinylidene fluoride; PA: polyamide; PAN: polyacrylonitrile; CS: chitosan; GG: guar gum; CNTs: carbon nanotubes; PES: polyethersulfone; PI: polyimide; MOF: metal-organic framework; PDMS: polydimethylsiloxane
### Experimental data for n-butanol and isobutanol dehydration achieved by different membranes

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>T [°C]</th>
<th>w&lt;sub&gt;FW&lt;/sub&gt; [wt%]</th>
<th>J&lt;sub&gt;total&lt;/sub&gt; [kg/m&lt;sup&gt;2&lt;/sup&gt;h]</th>
<th>β</th>
<th>α</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PERVAP® 2510 (PVA/PAN)</td>
<td>60</td>
<td>10</td>
<td>0.89</td>
<td>116</td>
<td>5</td>
<td>Guo et al. [57]</td>
</tr>
<tr>
<td>PVA (crosslinked with citric acid)</td>
<td>30</td>
<td>10</td>
<td>0.082</td>
<td>171</td>
<td></td>
<td>Burshe et al. [58]</td>
</tr>
<tr>
<td>PBI-ZIF-8</td>
<td>60</td>
<td>15</td>
<td>0.082</td>
<td>3417</td>
<td></td>
<td>Shi et al. [59]</td>
</tr>
<tr>
<td>PERVAP 2510 (PVA/PAN)</td>
<td>80</td>
<td>5</td>
<td>0.8599</td>
<td>7.62</td>
<td></td>
<td>Qiao et al. [45]</td>
</tr>
<tr>
<td>QP4VP/CMC-Na/PS</td>
<td>60</td>
<td>10</td>
<td>2.24</td>
<td>1120</td>
<td></td>
<td>Liu et al. [60]</td>
</tr>
<tr>
<td>Matrimid® (PI)</td>
<td>80</td>
<td>15</td>
<td>1.8</td>
<td>53</td>
<td></td>
<td>Jiang et al. [61]</td>
</tr>
<tr>
<td>PVA-NaAlg</td>
<td>45</td>
<td>10</td>
<td>0.585</td>
<td>606</td>
<td></td>
<td>Dong et al. [62]</td>
</tr>
<tr>
<td>BTESE</td>
<td>95</td>
<td>5</td>
<td>3.4 (water)</td>
<td>837</td>
<td></td>
<td>Castricum et al. [63]</td>
</tr>
<tr>
<td>MPD-TMC with nano NaX, zeolite/PAN</td>
<td>25</td>
<td>10</td>
<td>2.9</td>
<td>~200</td>
<td></td>
<td>Fathizadeh et al. [64]</td>
</tr>
<tr>
<td>PAA/PEI-modified GO</td>
<td>50</td>
<td>5</td>
<td>~0.3</td>
<td>~614</td>
<td></td>
<td>Wang et al. [65]</td>
</tr>
<tr>
<td>Zeolite LTA, porous Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>80</td>
<td>5</td>
<td>2.39</td>
<td>2800</td>
<td></td>
<td>Huang et al. [66]</td>
</tr>
<tr>
<td>PERVAP® 2510 (PVA/PAN)</td>
<td>60</td>
<td>10</td>
<td>0.21</td>
<td>326</td>
<td>23</td>
<td>Guo et al. [57]</td>
</tr>
</tbody>
</table>

T: temperature; w<sub>FW</sub>: feed water content; J<sub>total</sub>: total flux; β: separation factor; α: selectivity; PVA: poly(vinyl alcohol); PAN: polyacrylonitrile; PBI: polybenzimidazole; ZIF-8: zeolitic imidazolate frameworks; QP4VP: quaternized poly(4-vinylpyridine); CMC-Na: sodium carboxymethyl cellulose; PS: polysulfone; PI: polyimide; NaAlg: sodium alginate; BTESE: 1,2-(bistriethoxysilyl)ethane; MPD: m-phenylenediamine; TMC: trimesoyl chloride; PAA: polyacrylic acid; PEI: poly(ethyleneimine); GO: graphene oxide; Zeolite LTA: zeolite Linde Type A
2.2.3 Modelling of mass transfer in pervaporation membranes

The various possible component-component and component-membrane interactions make the mathematical description of the transport phenomena in polymeric and porous membranes rather complicated and difficult. The modelling of mass transfer in pervaporation has drawn the attention of numerous authors with various approaches according to the diverse aims of basic research, membrane development, or process design/synthesis. The modelling depth varies in accordance with these aims and so does the number of parameters taken into consideration during model development. All approaches need to establish a certain relationship between the flux of at least one permeating component and the changing process parameters (pressure, temperature, concentration, etc.). A possible classification ranks the different modelling approaches into three groups [67,68]:

- pure empirical models,
- semi-empirical or phenomenological models and
- theoretical models.

The analytical depth determines the applicability of the models (membrane development or process design). As opposed to membrane development, where a deep analytical understanding of the mass transfer is required, process design necessitates the reasonable representation of the main parameters affecting the overall mass transfer.

Pure empirical models are used when dealing with a practical problem involving the membrane-mixture combination regarded as a black box. They are useful for initial membrane screening and process design. The parameters of these models, on the other hand, have no physical background and are relevant only for the specific operation range investigated, therefore they cannot be extrapolated.

The second group incorporates the so-called semi-empirical models. This approach combines the empirical method with the physical understanding of the system to be modelled. The parameters describing the elemental physical/chemical processes are grouped together and are identified experimentally. The advantage of this approach, in contrast to empirical models, is that the number of experiments for a wide operation range can be reduced. Extrapolation outside this given range is more acceptable, thus the predictability of the model is also better. These models are detailed enough for process design and optimization without compromising computation capacity.
Theoretical models are based on the understanding of the molecular parameters and their physical/chemical relations using physical chemistry and thermodynamics. The parameters are determined by independent experiments. Theoretical models facilitate a fundamental understanding of the mass transfer on a molecular level, but also require a large number of parameters, inevitably leading to high mathematical complexity. These are the models to be used in membrane development, but effective process design is often hindered by them [68].

The huge variance of polymer behaviour has led to a multitude of theoretical, semi-empirical and empirical models developed during the last decades. There are different approaches and model modifications according to the type of the polymer (glassy, semi-crystalline, rubbery, etc.), which describe the relationship between the equilibrium concentration of a component in the membrane and its activity, partial pressure or fugacity in the adjacent liquid and vapour phases.

There are models solely for describing the sorption or the diffusion of components and models for the overall mass transfer through the membrane material (both the selective and the supporting layer). Shao and Huang [9] studied the transport mechanisms of water and organic solvents through various membranes extensively, and found that the transport behaviour of the molecules is always case- and membrane-specific. Considering the vast variety of membrane materials (various polymer or inorganic membranes), molecule properties (shape, size and polarity) and their interactions, mass transport in membranes is extremely complex. Thus, it can be stated, that a general predictive model based on merely physical properties of the permeating components and the membrane does not exist to date. The pervaporation mass transport models are, therefore, predominantly system-specific.

2.2.3.1 Sorption models

Sorption and diffusion are the most important rate- and selectivity-determining steps of the mass transfer of components through the membrane. In this section the most significant models for the explanation of the sorption behaviour are summarised. A detailed overview an explanation of these models can be found for instance in the work of Lipnizki and Trägårdh [68]
Langmuir and Henry’s Law Isotherms

With the help of gravimetric or quartz crystal microbalance methods the sorption process, sorption equilibrium and thus the sorption isotherm can be predicted [69–71]. In pervaporation the vapour sorption data are required for pure components as well as for the mixture. However, these are not sufficient for modelling the mass transfer inasmuch as in the case of PV the membrane comes into contact with a liquid feed under saturated conditions. Single component isotherms can be used to predict the behaviour of multicomponent systems with the help of the UNIQUAC method or the Maxwell-Stefan Theory.

Solubility Parameter Theory

This semi-quantitative model describes the interactions between the components and the membrane material. Hansen [18] created the three-dimensional model, composed of three parameters representing the energy needed to separate the components in the liquid by overcoming the intermolecular forces: dispersion forces, polar interactions and hydrogen bonds. The molecule which has a similar solubility parameter to that of the polymer will have high solubility in it. The parameter calculation methods can be found in section 2.2.1.1.

According to Nagai [37], the affinity of a solvent-water mixture with the membrane polymer depends on the congruence between their solubility parameters. Since the theory takes only the energetic effects into account, leaving the entropic effects out, it is more suitable for a qualitative prediction of the permeation preferences of the membrane.

Flory-Huggins Theory

The theory predicts the sorption behaviour of membranes toward liquid mixtures using the Gibbs free energy, $\Delta G_{mix}$, of the mixture.

$$\frac{\Delta G_{mix}}{RT} = x_i \ln \Phi_i + x_j \ln \Phi_j + x_p \ln \Phi_p + \chi_{i,j}x_i\Phi_j + \chi_{i,p}x_i\Phi_p + \chi_{j,p}x_j\Phi_p$$ (2.12)

where $x_i$ is the concentration of component $i$, $\chi$ is the binary interaction parameter between components $i, j$, or between the components and the polymer $P$, $\Phi$ is the volume fraction of component $i, j$ or the polymer.

Dimensionless binary Flory-Huggins interaction parameters describe the interactions between the components of a binary liquid mixture, which can be calculated either using the excess free energy of mixing $\Delta G^E$, or by using molar volumes of the components and
the polymer, as well as volume fractions and the activity coefficients calculated by NRTL, UNIQUAC or UNIFAC models [72]:

$$\chi_{i,j} = \ln \frac{\gamma_i - \ln \phi_i + \left( V_i / V_j - 1 \right) \phi_j}{\phi_j}$$  \hspace{1cm} (2.13)

Component-polymer interaction parameters are determined by swelling experiments using semi-empirical models regressed to experimental data. It has been studied by various researchers with moderate success: in the case of interactions between polar liquids, homogeneous polymers and copolymers the predictions were inadequate [73,74]. The model has later been modified to fit specific polymers, such as crosslinked, semicrystalline and glassy polymers. It is suitable for membrane development purposes, while its combination with other models (e.g. free-volume theory) also makes process design possible.

**UNIQUAC models**

The Universal Quasi Chemical (UNIQUAC) model of Abrams and Prausnitz [75] is an activity coefficient model predicting liquid phase equilibria in multicomponent mixtures. According to this model, the activity coefficient of component i of a binary mixture is a combination of a combinatorial and a residual part [76]:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$  \hspace{1cm} (2.14)

where $\gamma_i$ is the activity coefficient of component i, and superscripts C and R indicate its combinatorial and residual parts, respectively. Thus, a deviation from ideal solubility is taken into account by the different molecular shapes and the mixing-caused change of the interacting forces between the components of the binary mixture. All of the model parameters are derived from pure component data, except for the so-called interaction parameters, which must be determined experimentally. The activity coefficients in a multicomponent mixture can also be calculated with the model requiring solely the binary interaction parameters.

For systems which form hydrogen bonds, the residual part of the model is modified ($\gamma_i^{R-HB}$). Heintz and Stephan [77] showed the applicability of the model for multicomponent systems of water, ethanol, methanol, i-propanol, tetrahydrofuran and acetone with PVA membrane.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^{R-HB}$$  \hspace{1cm} (2.15)

A free-volume term was added to the model by Jonquières et al. [78] to account for the free-volume ($FV$) effect and anomalies caused by polymer-solvent interactions:
\[
\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R + \ln \gamma_i^{FV}
\] (2.16)

The latter two modifications can be combined to account for hydrogen bonds (HB) and the free volume (FV) effect alike [78].

\[
\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^{R-HB} + \ln \gamma_i^{FV}
\] (2.17)

With the UNIQUAC model the sorption of mixtures can be predicted, therefore it is suitable for membrane development. However, an additional model (e.g. Maxwell-Stefan) is also necessary to predict trans-membrane fluxes for process design purposes.

**UNIFAC models**

The UNIFAC models are group contribution methods based on the structural groups of the molecules [79]. In the absence of experimental data, phase equilibria can be predicted by this model consisting of a combinatorial and a residual part, as in the case of the UNIQUAC model. For solvent-polymer systems, however, certain modifications have been suggested to take the free-volume, swelling and the different polymer structures into account [80–82].

**2.2.3.2 Membrane diffusion models**

Diffusion through the polymer matrix of a membrane is a particularly complex process due to the multiple interactions between the components of the mixture, and between the diffusing molecules and the membrane material. These can result in coupling effects between the components and in the swelling of the membrane. Making predictions based on pure component data is extremely difficult, since the given multicomponent systems have specific interactions and a detailed knowledge of the membrane material and structure should be at hand with respect to the polymer type, the crosslinking and possible filling particles (e.g. nanoparticles).

Numerous empirical approaches have appeared in the literature based on Fick’s law of diffusion to describe and predict trans-membrane diffusion. The diffusion coefficients were variously modified depending on the given mixture to be separated (binary or multicomponent, ideal or non-ideal) and the membrane material. For instance, Meuleman et al. [83] suggested the following model for non-ideal mixtures with mutual interactions taken into account:

\[
D_i = D_{i,0} + f(\Phi_i + g\Phi_j)^h
\] (2.18)
where $D_i$ is the diffusion coefficient; $D_{i0}$ is the Fickian diffusion coefficient at infinite dilution of the permeant; $\Phi_i$ is the volume fraction of component $i$; while $f$, $h$, and $g$ are empirical constants.

The various empirical models are suitable for a good representation of experimental data; however, their empirical nature narrows their application down to process design instead of membrane development.

**Free volume theory**

Fujita [84] developed the free volume theory describing component diffusion as the movement of the diffusing molecule through appropriate temporary spaces, voids or free volumes in the membrane. The model was first applied to glassy polymers, later extended to semi-crystalline, rubbery and crosslinked membranes and ternary systems as well. The temperature dependency of the diffusion coefficient above the glass transition temperature is described as:

$$D_i(T(\Phi_i, \Phi_{C,P}, T)) = RT \cdot A_{di} \cdot \exp \left( \frac{B_{di}}{f_{iP}^{FV}(\Phi_i, \Phi_{C,P}, T)} \right), \quad i = 1, ..., n$$

(2.19)

where $\Phi_i$ is the volume fraction of component $i$; $\Phi_{C,P}$ is the volume fraction of crystalline parts in the polymer, $A$ represents the size and shape of the component, and $B_i$ refers to the size of sorption places in the membrane polymer. $f_{iP}^{FV}$ is the free volume depending on the volume fraction of the solvent. This model is particularly suitable for membrane development.

In theory, the unknown parameters can be estimated based on pure component data or group contribution methods, although some researchers insist on the crucial importance of transport data from experiments to accurately define model parameters [85].

**Dual sorption model**

Vieth et al. [86,87] developed the dual sorption model for glassy polymers, which considers uniformly distributed free microvoids in the membrane created by the movement of the polymer chains. Molecules with appropriate size can occupy these voids, and diffusion occurs when the free space, which was left behind by the moving molecule, is taken by another molecule. Two parallel mechanisms are distinguished: diffusing molecules and immobilized molecules in the microvoids.
2.2.3.3 Trans-membrane mass transfer models

The overall trans-membrane mass transfer models combine the description of sorption, diffusion and desorption in one flux model. Flux models are especially useful to determine the investment demand of the designed process, as the permeate flux determines the necessary size of the membrane system. Among the most widely applied models are the Maxwell-Stephan theory, the pore-flow model (for porous zeolite membranes) and the solution-diffusion model (commonly used for polymeric membranes). The solution-diffusion model is the most widespread mass-transfer model for pervaporation dehydration, since its applicability has been demonstrated for numerous mixtures. As the modelling part of the present work is also based on this approach, this model will be explained in detail in this section, whereas for the thorough description of the other models, the reader is referred to the review paper of Lipnizki and Tragardh [68].

The Maxwell-Stephan theory

The theory is based on the thermodynamics of irreversible processes. Every component is affected by the chemical potential gradient as a driving force and a friction force, caused by the interactions between the components of the system [88]. The sum of the friction forces acting on the component is proportional to the average relative velocity of the components, and it is balanced by the driving force. This highly complex model includes so-called effective diffusion coefficients and interactions parameters, and involves equilibrium models to calculate component concentration in the membrane [77,89].

Pore flow model

The concept of the pore flow model was introduced to pervaporation by Okada and Matsuura [90,91]. The model assumes that cylindrical pores are distributed evenly across the selective layer of the membrane. While, according to the solution-diffusion model, the evaporation takes place at the permeate side of a dense membrane, the pore flow model assumes that the pores are filled with the feed liquid solution to a certain depth and the remaining length of the pores is filled with the permeate vapour. Phase change occurs at the interface, where the pressure is equal to the saturated vapour pressure. The driving force is derived from the difference between the saturated pressure and the vapour pressure at the permeate side.

\[ J_l = \frac{A_{pore}}{l_l} \cdot (p^l - p^0) \]  

(2.20)
\[ J_v = \frac{B_{\text{pore}}}{l_v} \cdot (p^0 - p^v) \]  
(2.21)

\[ J = J_l = J_v \]  
(2.22)

where \( l \) and \( v \) denote the liquid and vapour phase, respectively; and A and B are empirical constants. This model also neglects the coupling effects of the component fluxes. Based on its semi-empirical nature, the pore flow model is suitable for process design rather than membrane development.

**The solution-diffusion model**

The popularity of the solution-diffusion model for the description of mass transport in membranes is due to its simplicity and good description of experimental results. It was developed for gas separation, later adopted to dialysis and reverse osmosis [67,92] and to pervaporation by Binning et al. [93].

According to this approach, the consecutive steps of permeation are:

1. sorption of the feed components into the membrane polymer,
2. diffusion of the permeating species through the membrane material, and
3. desorption of the permeate on the permeate side.

The model uses the following assumptions:

- the transport occurs only by diffusion, and not by convection,
- the pressure is constant in the membrane and equals the feed side pressure,
- chemical equilibrium exists at the membrane interfaces at the feed and permeate sides,
- coupling between permeating molecules is neglected.

**Figure 5** illustrates the chemical potential, pressure and activity gradients across the membrane.
Separation occurs due to the difference in the solubilities and diffusion rates of the permeating components. A detailed explanation of the model can be found in the works of Wijmans and Baker [67], and Lipnizki and Trägårdh [68], the practical equations most widely used are demonstrated here.

Fick’s first law sufficiently describes the diffusion in ideal systems with concentration gradient as the driving force:

$$J_i = -D_i \frac{dc_i}{dz}$$  \hspace{1cm} (2.23)

Based on the Fickian equation a general equation for the permeate flux can be written as:

$$J_i = \frac{D_i c_i}{a_i} \cdot \frac{1}{l} \cdot (a_{F,i} - a_{P,i})$$  \hspace{1cm} (2.24)

where $D_i$ is the Fickian diffusion coefficient [m$^2$/s], $c_i$ is the concentration of component $i$ in the membrane [kmol/m$^3$], $a_i$ is the activity in the membrane, $l$ is the membrane thickness, $a_{F,i}$ and $a_{P,i}$ are the activity in the feed and permeate, respectively. Subscript $i$ denotes component $i$.

The experimental determination of $D_i$, $c_i$ and $a_i$ is difficult and involves uncertainties, so the three parameters are lumped together into one parameter called permeability $J_i^P$:

$$J_i^P = \frac{D_i c_i}{a_i}$$  \hspace{1cm} (2.25)
The utilization of permeability is advantageous, as it is easier to determine with pervaporation experiments, and its application leads to the following practical expression of permeate flux:

\[ J_i = \frac{P_i}{l} \cdot (a_{F,i} - a_{P,i}) \]  

(2.26)

Permeability is often described to have Arrhenius-type temperature dependence:

\[ J_i^P = J_{i0}^P \cdot \exp \left[-\frac{E_i}{R} \left(\frac{1}{T_0} - \frac{1}{T_F}\right)\right] \]  

(2.27)

where \( J_{i0}^P \) is the pre-exponential factor of permeance, \( R \) is the universal gas constant (J/mol K), \( T \) is the temperature (K), and \( E_i \) is the activation energy of component \( i \) (J/mol).

This original solution-diffusion theory does not consider possible interactions between the permeating species; thus, this model is only applicable when flux coupling is negligible.

Rautenbach et al. [94] proposed a semi-empirical model based on the solution-diffusion theory which serves as the basis of the model development in the present thesis. An equation analogous to Fick’s law describes the non-ideal systems better with the chemical potential as driving force. In the case of real gases/vapours, fugacity is used instead of pressure in chemical potential:

\[ J_i = -c_i D_{i0}^{\text{RT}} \nabla \mu_i = c_i D_{i0}^{\text{RT}} \nabla \ln f_i / f_{i0} \]  

(2.28)

where \( D_{i0} \) is the thermodynamic diffusion coefficient, which was described by Rautenbach as much less concentration-dependent than the diffusion coefficient.

The model uses the average activity coefficient \( \bar{\gamma}_i \) within the membrane material, which is the geometric mean of the activity coefficients at the feed side and permeate side of the membrane:

\[ \bar{\gamma}_i = \sqrt{\gamma_{iF} \cdot \gamma_{iP}} \]  

(2.29)

The activity coefficients can be determined according to the thermodynamic models of Wilson, UNIQUAC, NRTL, etc. Changes of concentration on the feed side or the permeate side necessarily generate a change in the mean activity coefficient accordingly.

Assuming a thermodynamic equilibrium at the feed and permeate interfaces of the selective layer, the integration of Eq. (2.28) is possible, making a separate sorption model and thus sorption experiments unnecessary. The integration of Equation (2.28) results in:
\[ J_i = \frac{cD_{i0}}{l\gamma_i} \cdot \Delta f_i = \frac{cD_{i0}}{l\gamma_i} \cdot \left( \frac{f_{iF} - f_{iI}}{f_{i0}} \right) = \frac{D_{i0}}{\gamma_i} \cdot \left( \frac{f_{iF} - f_{iI}}{f_{i0}} \right) \]  \hspace{1cm} (2.30)

where \( f_{iF} \) is the fugacity at the feed side, \( f_{iI} \) is the fugacity at the interface of the selective and supporting layer of the membrane, and \( \overline{D_{i0}} \) is the transport coefficient grouping together the concentration, the thermodynamic diffusion coefficient and the membrane thickness \( l \):

\[ \overline{D_{i0}} = \frac{cD_{i0}}{l} \]  \hspace{1cm} (2.31)

Pervaporation is strongly temperature-dependent, expressed by an Arrhenius-type temperature dependency of the transport coefficient:

\[ \overline{D_{i0}} = D_{i0}^* \exp \left[ \frac{E_i}{RT} \cdot \left( \frac{1}{T} - \frac{1}{T^*} \right) \right] \]  \hspace{1cm} (2.32)

where \( D_{i0}^* \) is a pre-exponential factor, \( E_i \) represents the activation energy for component \( i \) associated with the transport coefficient, and \( T^* \) is the reference temperature, equal to 293 K.

Due to the moderate pressures, fugacities can be replaced with partial pressures in the equation:

\[ J_i = \frac{D_{i0}}{\gamma_i} \cdot \left( \frac{p_{iF} - p_{iI}}{p_{i0}} \right) \]  \hspace{1cm} (2.33)

The partial flux through the supporting porous layer is described by Rautenbach as:

\[ J_i = Q_0 \cdot \Delta p_s = Q_0 \cdot (p_{iI} - p_{iP}) \]  \hspace{1cm} (2.34)

where \( Q_0 \) is the permeability coefficient, \( \Delta p_s \) is the pressure drop on the porous support, \( p_{iI} \) is the partial pressure of component \( i \) at the interface between the active and the supporting layer of the composite, and \( p_{iP} \) is the permeate pressure of component \( i \).

After expressing the driving force from Equations (2.33) and (2.34) and adding these equations together, we get the Rautenbach model for component transport through a composite membrane:

\[ J_i = \frac{1}{1 + \left( \frac{D_{i0}}{\gamma_i} \right) \cdot \left( \frac{p_{iF} - p_{iP}}{p_{i0}} \right)} \cdot \left( \frac{p_{iF} - p_{iI}}{p_{i0}} \right) \]  \hspace{1cm} (2.35)

Vapour pressures can be calculated according to the Antoine equation:

\[ \log p_{i0} = A - \frac{B}{C + T} \]  \hspace{1cm} (2.36)

where \( p_{i0} \) is the vapour pressure of the pure \( i \) component (bar), \( T \) is the temperature, \( A \) and \( B \) are component-specific constants.
It can be seen that modelling the mass-transfer through a membrane in pervaporation is mainly approximated with semi-empirical models, where parameters related to sorption and diffusion are grouped together in empirical parameters. Usually, with the increase of component number in the mixture, the models are becoming more complicated due to the higher number of parameters. Therefore, these models have been typically applied for the modelling of binary mixtures. A crucial requirement of modelling, besides simplicity, is the applicability of these models in a flowsheeting environment, whereby complicated separation processes can be designed and optimized, facilitating the broader utilization of energy-efficient processes in a wide range of industries.

Pervaporation is rarely applied alone due to insufficient product purity or the high cost of membranes. To utilize its advantages and alleviate its drawbacks, PV is usually coupled with other conventional separation techniques, such as distillation, adsorption, extraction, etc. In the following chapter distillation will be described in detail, as pervaporation-distillation hybrid systems are applied throughout the present work. The nature of these hybrid coupled structures will be dealt with in section 2.4.

2.3 Distillation

Distillation has been preserving its paramount importance in process industries for centuries. Petroleum industry, for instance, uses distillation for the great majority of separations. The process has a long history that started 5000 years ago, with a large-scale development of the industrial procedure from the 19th century onwards. Thanks to its versatility and a well-founded, mature knowledgebase surrounding the technique, distillation is frequently the first option that comes to mind facing any fluid separation problem. Only when the separation task hits a bottleneck or a thermodynamic constraint emerges, are other alternative methods considered. Distillation exploits the differences in the volatility of the components; therefore, a successful design of the process necessitates the knowledge of the vapour-liquid equilibrium and residue curves of the mixture. A comprehensive summary of the principles, design and analysis of distillation can be found in the work of Górak and Sorensen [95].

In the case of multicomponent mixtures or thermodynamically challenging separations, such as the case of azeotropes, the process requires a complex separation structure where multiple columns are necessary to reach the desired product quality.
and heuristic rules to achieve the most adequate and energy-efficient sequence of splits and the recycle structure [96]. To overcome the thermodynamic or economic constraints, often so-called hybrid separation methods are formed with the coupling of different operational units. The processes demonstrated in the following are restricted to the distillation and hybrid techniques specifically applied in the present research.

2.3.1 Heteroazeotropic distillation

The separation of a mixture exhibiting a miscibility gap can be achieved by heteroazeotropic distillation: the combination of distillation and decantation. In the case of a minimum boiling heteroazeotrope, the azeotropic mixture leaves the column at the top, subsequently fed to a decanter, where a liquid-liquid split occurs. One phase is directed back to the top of the column as the reflux, whereas the other phase is either considered as the product, or directed to another distillation column for final polishing. Even if the mixture does not form a heteroazeotrope, phase splitting might be induced by an entrainer, which is recovered in an additional column. Residual curves, heuristics and literature serve as the base for the process design.

2.3.2 Extractive distillation

In the case of miscible, minimal boiling azeotrope-forming mixtures, a common choice for separation is extractive distillation, where an additional, non-volatile, high boiling solvent is added at the top of the distillation column. This solvent forms a stronger interaction with the less volatile component of the initial azeotropic mixture, extracting it at the bottom of the column, while the pure volatile product leaves at the top. To reduce waste production while decreasing fresh solvent demand, the bottom product is to be separated in a subsequent column and recycled to the first column. The entrainer is often applied in large quantities, excessively increasing the energy demand of the primary distillation. It is a widely used process for the separation of ethanol-water with various entrainers, such as benzene, cyclohexane, toluene, etc.

Apparently, the combination of several distillation columns can be expensive in terms of operational cost, due to the extreme energy frequently demanded by the reboiler. In addition, the utilisation of entrainers leads to further cost increase by the necessity of an additional regenerating column. Environmental concerns should drive process engineers towards process synthesis with decreased energy consumption, and the avoidance of
unnecessary solvents. In certain cases, membrane (pervaporation) assisted distillation might offer a reasonable and more sustainable alternative.

### 2.3.3 Pervaporation assisted distillation

Pervaporation is a promising and well-established separation technology for a number of specific tasks. However, most of the time pervaporation cannot be applied as a standalone process, either because its products might not be pure enough for subsequent processing or waste disposal [97]; or because of the high investment and replacement costs of the membranes [10]. To comply with the demands of more economical and environmentally sound production processes, hybrid separation techniques have been promoted, generating an intensively researched new area of process intensification. The combination of conventional separation methods with promising novel processes (such as membrane separation), a synergy of their individual advantages can be achieved with huge economic and social benefits. The technical and/or thermodynamical limitations of the individual constituting processes can be overcome with their combination, while the recovery, reuse or recycling of water and other applied chemicals is also made feasible [10]. Integrating a membrane process with a conventional technique allows the rationalization of the direct and indirect energy consumption of the system, while improving product quality.

The aim of process intensification is to achieve high product quality with the lowest possible cost. Installing hybrid separation methods or retrofitting a conventional process unit with a novel energy-efficient method, like pervaporation, is a great example for process intensification at the process level [98]. In order to utilize the full potential of such a hybrid system, PV should be used in the operation window, where it outperforms conventional methods.

According to Lipnizki et al. [97], two different types of hybrid processes can be distinguished in relation to pervaporation:

- Hybrid processes where the constituent parts are performing the same task, such as separation, which could not be achieved by either component alone.
- Hybrid processes consisting of two (or more) different processes, such as the combination of a PV unit and a reactor.
Table 5 lists a few examples of the two industrially realized hybrid systems involving pervaporation: reactor-PV and PV-distillation systems.

Table 5 Application examples of hybrid PV-distillation and PV-reactor separation systems

<table>
<thead>
<tr>
<th>Hybrid process</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pervaporation – (reactive)</td>
<td>Separation of benzene-cyclohexane azeotrope</td>
<td>[16,99]</td>
</tr>
<tr>
<td>distillation</td>
<td>Separation of carboxylic-acid – ester – methanol azeotrope</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>Separation of dimethyl carbonate – methanol azeotrope</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>Separation of fusel oil – water azeotropes</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td>Separation of water – isopropanol azeotrope</td>
<td>[103,104]</td>
</tr>
<tr>
<td></td>
<td>Separation of water – methylisobutylketone azeotrope</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>Separation of dimethyl methanol – methyl tert-butyl ether/C4</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>Separation of water – ethanol</td>
<td>[107,108]</td>
</tr>
<tr>
<td></td>
<td>Butyl acetate production via transesterification</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>Production of aroma concentrate</td>
<td>[110]</td>
</tr>
<tr>
<td>Pervaporation – reactor</td>
<td>Removal of water from reactor – butyl acetate production</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>Removal of water from reactor - isopropyl propionate</td>
<td>[112,113]</td>
</tr>
<tr>
<td></td>
<td>Removal of water from reactor - propyl propionate production</td>
<td>[112,113]</td>
</tr>
<tr>
<td></td>
<td>Removal of water from reactor - n-butyl oleate production</td>
<td>[114]</td>
</tr>
</tbody>
</table>
2.4 Pervaporation-distillation hybrid process

The first pervaporation based hybrid process was designed for the separation of ethanol-isopropanol mixtures by Binning and James in 1958 [115]. As already mentioned, pervaporation can easily overcome the difficulty of azeotrope separation, as it is not restricted by the vapour-liquid equilibrium. With the application of pervaporation, the addition of a solvent and its subsequent removal is avoidable. Furthermore, pressure variations and high distillation tray numbers necessary for a multi-column system are also evitable. Therefore, investment and operational costs can be significantly reduced for a given separation task in case of such a combined method with high product purity. PV can be coupled with distillation in several ways [96,116,117]:

- processing a side stream of the distillation column,
- prior to the distillation column (e.g. to split azeotropes), or
- as a final polishing step, either at the top or the bottom of the column (with optional azeotrope splitting).

Figure 6 illustrates the possible configurations of membrane-assisted distillation. Alternative A can be used to separate a three-component mixture, where the minor component of the ternary mixture leaves the system as the permeate stream. Configuration B is suitable for the pre-fractionation of a mixture prior to the distillation column, allowing smaller distillation columns and lower reflux ratios. Variation C can be applied if PV has to overcome a separation boundary (e.g. azeotrope) where the permeate stream is recycled to the first distillation column, while the second column performs the final separation. If the azeotropic point is near the desired product concentration, then PV can be the final polishing step, as depicted in alternative D. A configuration similar to A is also applicable for the separation of ternary mixtures, where a side stream of the column is processed by the PV unit, which provides one pure product in the permeate (e.g. water), and the column separates the remaining two products [98,118].
2.4.1 Process design of a hybrid system

There are two options for process design involving membranes [119]:

1) Process design and optimization is performed with the membrane performance parameters as free variables.
2) Process design with an experiment-based, empirical or semi-empirical pervaporation model.

The former provides important data for membrane developers and manufacturers about the desired parameters of a membrane to reach a given separation performance, whereas for the latter it is crucial to determine the separation characteristics of existing membranes. The drawback of an experiment-based model is the lack of extrapolation capacity; thus, it is applicable only in the investigated operational window.
The conceptual design of a new chemical process consists of the following major steps:

- identification of the flow-sheet structure and unit operations suitable for the task;
- creating combination variations of the unit operations to pursue the desired product; and
- sizing and costing of alternatives, based on which the selection of the optimal process is possible.

Based on the thorough investigation of process intensification design by Lutze et al. [120], Figure 7 illustrates the design steps of a pervaporation based hybrid process. The first step is to identify if pervaporation is a suitable process for the given problem or overcoming a process bottleneck. This can be difficult to evaluate, however, literature data and a priori experience with the process are useful tools. If the mixture to be separated forms an azeotrope, or the distillation column has an excessive energy demand, PV should be considered as an option. Usually, an initial screening of possible options, costs and operational parameters is possible through shortcut models.

Possible membrane shortcut models were investigated by several researchers [121–123]. The drawback of all approaches is the oversimplification of a membrane separation process (often described only by a constant driving force) and that the majority is restricted to binary mixtures only. In reality, process conditions like temperature and pressure, or impurities in a mixture have a huge effect on the separation performance of a membrane. In addition, solvent-solvent and solvent-membrane interactions strongly influence the separation. Therefore, if the real potential of a configuration is to be determined, an experiment-based investigation of the pervaporation performance is inevitable.
For this, the selection of a suitable membrane is the next challenging step. In the case of commercially available membranes, the manufacturer provides information about their application areas, temperature resistance and the maximal concentration of aggressive chemicals allowed. Based on these data and information from the literature, one or more membranes are selected, after which experiments should be carried out with different concentrations of the key component under various operating conditions. With the experimental results at hand, a suitable mass-transfer model should be used or developed, with the help of which the process flowsheet variables can be evaluated according to optimized product requirements, investment and operational costs [96,98].

Suk and Matsuura [124] reviewed membrane-assisted distillation hybrid systems extensively, while Lipnizki et al. [97] narrowed their study to PV-distillation hybrids. They found that such hybrid systems offer a significant reduction of operational costs, but investment costs can be substantial due to high price of membranes.

The present work is aimed at the investigation of the applicability of the presented hybrid processes for bio-alcohol production by the separation of their binary and ternary aqueous mixtures. In the following sections, the materials and methods applied for the pervaporation experiments will be demonstrated in detail, followed by the presentation of the experimental results based on which a transport model development became possible. The developed model provides the tool for the simulation of the hybrid process models involving PV and distillation.
3 Materials and methods

3.1 Selection of the materials and mixtures

In the following sections the characteristics and importance of the studied binary and ternary aqueous mixtures are described. The given mixtures were selected based on their current and future importance in the bio-industry as bio-based fuels or commodity chemicals. They were studied by means of a thorough experimental investigation of their pervaporative dehydration, as well as by the theoretical modelling of the experimentally acquired data.

3.1.1 Binary alcohol - water mixtures

The studied alcohols of ethanol, n-butanol and isobutanol all count as either current or potential future biofuels, and as equally significant platform molecules (ethanol) or important solvents used in diverse industries. These binary alcohol-water systems of ethanol-water, n-butanol-water and isobutanol-water exhibit azeotrope compositions in which water is the minor component. The potential application of pervaporation for dehydration was considered based on the industrial importance of these aqueous solutions, and the thermodynamic constraints of the separation occurring in the case of distillation. Experiments with isobutanol-water are presented in detail, whereas experimental results of ethanol–water and n-butanol–water separation were previously measured data by Koczka and Fodor [125,126].

3.1.2 Ternary mixture of ethanol - n-butanol - water

The application of membranes for the dehydration of organic solvents (e.g. ethanol, isopropanol, n-butanol, ethyl acetate) have been extensively investigated in the literature [26,127–129], although studies about the dehydration of ternary or multicomponent mixtures is quite limited [130–133]. To explore the possible changes in the permeation characteristics by the addition of a third component, two ternary mixtures were chosen for experimental investigations.

Ethanol-n-butanol-water mixture (E/B/W) was studied due to its relevance in processing renewable biofuels, bioethanol and biobutanol. This ternary mixture appears, for instance, in the processing of the fermentation product of the so-called Acetone-Butanol-Ethanol (ABE) fermentation process, where a highly diluted aqueous mixture is
produced with the help of microorganisms [134]. The subsequent separation of this multicomponent solution presents challenges, as it contains the homogeneous azeotrope of ethanol-water and the heterogeneous azeotrope of butanol-water, rendering the mixture highly non-ideal and the separation problem rather complex [29]. Eliminating water with pervaporation after a pre-concentrating distillation step might bring economic and processing benefits.

3.1.3 Ternary mixture of ethanol - ethyl acetate - water

The ethanol-ethyl acetate-water (E/A/W) mixture was chosen partly to compare experimental results with that of the ethanol-butanol-water mixture, thus evaluating the possible effects of a different third component (butanol versus ethyl acetate) on the pervaporation characteristics. On the other hand, ethyl acetate has an unarguably huge role in the chemical industry as a solvent for coatings, pharmaceuticals, herbicides, adhesives, etc., due to its low toxicity, non-hygroscopy and good solubility in organic solvents [132]. Its bio-based production can be carried out both in first and second generation biorefineries by acetogenic fermentation. Here, glucose is converted to acetic acid, which is subsequently converted to ethyl acetate by a reaction with ethanol. Ethyl acetate can even be further converted to ethanol by catalytic hydrogenation.

Currently, it is most widely produced by the Fischer esterification of acetic acid with excess ethanol [135]. In the reaction, ethyl acetate forms a ternary azeotrope with the remaining ethanol and water, making the production of pure ethyl acetate rather challenging. Conventional separation of this azeotrope requires multiple distillation columns and the addition of an entrainer, rendering the downstream process even more complicated. Pervaporation could potentially simplify the purification by breaking the azeotrope, as suggested by numerous authors [132,136–138]. Another possible solution is the incorporation of the pervaporation membrane into the reactor to remove water from the product mixture, thus shifting the equilibrium towards product formation, resulting in higher yield, faster reaction, and higher product purity [139].

The structure of the studied solvents is depicted in Figure 8, where the different molecular length, linearity and functional groups can be seen, which can all contribute to dissimilar transport characteristics through a polymer membrane.
The boiling points and azeotrope compositions of the solvents and their aqueous mixtures are demonstrated in Table 6, whereas Table 7 summerizes molecular weights, solubility parameters, solubility parameter distances and molar volumes of the studied solvents and the PVA membrane.

According to Hansen, water as a single molecule may have a small molar volume, but its tendency to associate makes it a rather “unpredictable” species. Therefore, two sets of solubility parameters for water are listed in Table 7: the first is calculated from the energy of vaporization relating to a single molecule, whereas the second is based on correlation calculations including both good and bad solvents of water (for a detailed explanation, see the work of Hansen [18]). The second, correlated values have been found to explain the behaviour of aqueous mixtures better [18], therefore these parameters were used for calculations in the present work. The difference can be seen in the significantly lower solubility parameter distance ($R_a$) values for the correlated parameters. Based on these values, the solubility order for PVA is water > ethanol > n-butanol > isobutanol > ethyl acetate. Pure ethyl acetate has an $R_a$ value of 12.0, which exceeds the 10.9 interaction radius ($R_o$) of PVA [18], indicating that EtAc is a bad solvent of the polymer.
Table 6 Boiling points and azeotrope compositions of the investigated solvents predicted by ChemCAD [140] software, according to the UNIQUAC model under the pressure of 1.013 bar

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point [°C]</th>
<th>Azeotrope composition [mole fraction]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>78.3</td>
<td>EtOH 0.902 n-BuOH 0.255 iBuOH 0.336 EtAc 0.683 Water 0.745</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>117.7</td>
<td></td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>77.1</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Ethanol - Water</td>
<td>78.2</td>
<td>0.902</td>
</tr>
<tr>
<td>n-Butanol - Water</td>
<td>92.2</td>
<td>0.255</td>
</tr>
<tr>
<td>Isobutanol - Water</td>
<td>89.9</td>
<td>0.336</td>
</tr>
<tr>
<td>Ethyl Acetate - Water</td>
<td>71.2</td>
<td>0.683</td>
</tr>
<tr>
<td>Ethanol - Ethyl Acetate</td>
<td>71.8</td>
<td>0.454</td>
</tr>
<tr>
<td>Ethanol - Ethyl Acetate - Water</td>
<td>70.2</td>
<td>0.127</td>
</tr>
</tbody>
</table>

Table 7 Molecular weights, solubility parameters and molar volumes of the studied solvents and the PVA polymer

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Water</th>
<th>EtOH</th>
<th>n-BuOH</th>
<th>iBuOH</th>
<th>EtAc</th>
<th>PVA [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight [g/mol]</td>
<td>18.02</td>
<td>46.07</td>
<td>74.12</td>
<td>74.12</td>
<td>88.11</td>
<td></td>
</tr>
<tr>
<td>δ_d</td>
<td>15.5^a</td>
<td>18.1^b</td>
<td>15.8</td>
<td>16</td>
<td>15.1</td>
<td>15.8</td>
</tr>
<tr>
<td>δ_p</td>
<td>16^a</td>
<td>17.1^b</td>
<td>8.8</td>
<td>5.7</td>
<td>5.7</td>
<td>5.3</td>
</tr>
<tr>
<td>δ_h</td>
<td>42.3^a</td>
<td>16.9^b</td>
<td>19.4</td>
<td>15.8</td>
<td>16.0</td>
<td>7.2</td>
</tr>
<tr>
<td>δ_t</td>
<td>47.8^a</td>
<td>30.1^b</td>
<td>26.5</td>
<td>23.2</td>
<td>22.7</td>
<td>18.2</td>
</tr>
<tr>
<td>Solubility parameter distance (R_a)</td>
<td>27.2</td>
<td>4.2</td>
<td>6.8</td>
<td>8.3</td>
<td>9.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Molar volume [cm³/mol][18]</td>
<td>18.0</td>
<td>58.5</td>
<td>91.5</td>
<td>92.8</td>
<td>98.5</td>
<td></td>
</tr>
</tbody>
</table>

^a see section 2.2.1.1, Equation (2.10)

^b data derived from the energy of vaporization of water at 25°C

^c data based on a correlation of the solubility of various solvents in water using the SPHERE program [18]
3.2 Applied chemicals

Analytical grade ethanol (EtOH), n-butanol (BuOH), isobutanol (iBuOH), and ethyl acetate (EtAc) were provided by VWR International with purities greater than 99.5%. For the composition of the binary and ternary mixtures, distilled water was used.

3.3 Applied membranes

The composite membranes applied for the dehydration experiments of binary and ternary mixtures in the present study all have a poly(vinyl alcohol) (PVA) selective layer with a polyacrylonitril (PAN) supporting layer, cast on a non-woven porous polyester sheet (Table 8). The membrane sheets were provided by Sulzer Chemtech Ltd. (now DeltaMem AG). Since these membranes are commercial ones, the exact manufacturing process, the applied crosslinking agents and the degree of cross-linking are unknown by the customers.

Table 8 Hydrophilic membranes applied in the pervaporation experiments

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutanol - Water</td>
<td>PERVAP 1510</td>
</tr>
<tr>
<td>Ethanol - Water</td>
<td>PERVAP 2210</td>
</tr>
<tr>
<td>n-Butanol – Water</td>
<td>PERVAP 1210</td>
</tr>
<tr>
<td>Ethanol – n-Butanol - Water</td>
<td>PERVAP 1210</td>
</tr>
<tr>
<td>Ethanol - Ethyl Acetate- Water</td>
<td>PERVAP 1210</td>
</tr>
</tbody>
</table>

Sulzer Chemtech Ltd. provided a data sheet with the purchased membrane samples (an extract can be seen in Table 9). The data sheet serves as guidance for membrane selection, based on extensive testing. Performance data are not provided, as they largely depend on operational parameters and the given mixture. The application of organic and mineral acids is either limited or excluded as they can damage the membrane material. The selection of the suitable membranes for the experiments in this study was based on this data sheet and previous experiences with the membrane types.
<table>
<thead>
<tr>
<th>Membrane type</th>
<th>PERVAP 1510</th>
<th>PERVAP 1210 (later named as 2210)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main applications</td>
<td>for neutral alcohols and their mixtures, e.g. C3 and higher</td>
<td>for volatile organics and their mixtures</td>
</tr>
<tr>
<td>Max. temperature, Continuous [°C]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Max. temperature, Short term [°C]</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Max. feed water content [wt%]</td>
<td>&lt;30</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Material compatibility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldehydes &amp; derivatives</td>
<td>excluded</td>
<td>≤10 ppm</td>
</tr>
<tr>
<td>Organic acids (e.g. acetic acid)</td>
<td>&lt;0.1%</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>Formic acid</td>
<td>excluded</td>
<td>excluded</td>
</tr>
<tr>
<td>Aromatic amines</td>
<td>excluded</td>
<td>excluded</td>
</tr>
<tr>
<td>Aromatic HCs, Ketones, Esters, Ethers</td>
<td>excluded</td>
<td>no limitations</td>
</tr>
<tr>
<td>Special solvent as DMF, DMSO, NMP, etc.</td>
<td>excluded</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>5-7</td>
</tr>
</tbody>
</table>

### 3.4 Pervaporation experiments

The experiments were carried out with a multi-purpose P-28 membrane unit provided by CM-Celfa Membrantechnik AG, shown in Figure 9, suitable for experimenting with micro-, ultra-, nanofiltration, reverse osmosis and pervaporation in cross-flow mode. The inserted membrane with 28 cm² effective area was placed and secured on a sintered plate. The capacity of the double-jacketed feed tank is 500 cm³. Constant concentration of the feed mixture was assumed, caused by the sufficiently high volume of the feed mixture compared to the small amount of the collected permeate sample. The applied high flow rate of ~1.6 l/min of the feed/retentate mixture was provided by a gear pump, minimizing the effects of concentration and temperature polarization. The 2.7 mbar permeate pressure achieved by a Vacuubrand PC 2003 VARIO vacuum pump kept the permeate side at a constant, low partial pressure. The desired feed temperature was adjusted and maintained by a thermostat filled with distilled water and monitored with built-in thermometers.
The high flow rate and the thorough insulation of the system assured the isothermal operation. Permeate vapour was collected in two cold traps connected in parallel, and cooled with liquid nitrogen in a Dewar vessel.

Prior to inserting, membrane samples were pre-conditioned and swollen in the feed solution for 24 hours, in order to acquire constant performance faster during the experiments. The experimental procedure began each time with circulating the feed mixture with a given concentration in the membrane cell for 5 minutes to ensure uniform concentrations and to clean out minor remainders of previous experiments from the equipment. After this cleaning, a feed sample was taken, and then the mixture was weighed and refilled into the tank. The solution was circulated until the temperature reached the pre-set value. Meanwhile, the permeate pressure was adjusted to 2.7 mbar with closed permeate valves. The feed pressure was set to ~1-2 bars in the case of ethanol-water, n-butanol and isobutanol-water mixtures, and 4 bars in the case of the ternary mixtures. The solution was circulated for an hour to ensure proper membrane swelling and constant conditions. Following this one-hour conditioning time, the permeate valve was opened towards the first cold trap for 10 minutes, as it was observed that in the first few minutes greater amount of permeate left the membrane, often in the form of liquid drops. After 10 minutes the permeate was directed towards the second trap to collect steady state permeate samples until there was enough permeate for analysis (~1 g). The sampling time varied based on the temperature and feed water content: ~5 h at 60°C, 1-3wt% water and ~30-45 min at 90°C, 15wt% water. Permeate flux was calculated from the weight difference of the traps before and after the experiments.

Figure 9 Schematic figure of CM-Celfa P-28 membrane unit
The experiments were carried out at different temperatures and feed water concentrations to investigate the temperature- and concentration-dependence of the process. The actual examined composition ranges and temperature values are listed in Table 10.

**Table 10** Applied temperature values and concentration ranges for the laboratory experiments with the binary alcohol-water mixtures

<table>
<thead>
<tr>
<th>Alcohol-water mixture</th>
<th>Temperature</th>
<th>Range of feed water concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(mole fraction)</td>
</tr>
<tr>
<td>Isobutanol - Water</td>
<td>70, 80, 90</td>
<td>0.05-0.4</td>
</tr>
<tr>
<td>Ethanol - Water</td>
<td>60, 80</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>n-Butanol – Water</td>
<td>60, 75, 90</td>
<td>0.05-0.4</td>
</tr>
<tr>
<td>Ethanol – n-Butanol- Water</td>
<td>60, 75, 90</td>
<td>0.08-0.41</td>
</tr>
<tr>
<td>Ethanol - Ethyl Acetate- Water</td>
<td>60, 75, 90</td>
<td>0.05-0.39</td>
</tr>
</tbody>
</table>

The feed water concentration ranges were chosen according to the industrial practice, where up to 0.5 mole fraction of water is usually considered for hydrophilic pervaporation applications. Koczka [125] investigated industrial coupling variations for hybrid separation systems including distillation and pervaporation, and proved the heuristic rule that mixtures with higher feed water concentrations should be first distilled. Generally speaking, mixtures with the smallest feed water content should be introduced to a dehydration pervaporation unit. The studied temperature intervals did not exceed the long-term temperature durability of 95°C of the membrane.

In the case of the ternary mixtures, one of the main goals was to investigate if the concentration of the organic components affects the PV dehydration. In order to investigate this possible interdependence, 2:1; 1:1 and 1:2 concentration ratios of ethanol to n-butanol in the E/B/W mixture, and ethanol to ethyl acetate in the E/A/W mixture were studied. This way, the extent of the mutual interactions can be observed as well as their effect on the dehydration performance of the PV membrane.
3.5 Sample analysis

3.5.1 Isobutanol-water mixtures

The alcohol content of the feed was measured with GC-14B gas chromatograph provided by Shimadzu, with a CP-SIL-5CB WCOT FUSED SILICA (0.32 mm × 0.45 mm × 1.2 μm, length: 50 m) column connected to a flame ionization detector. The column temperature was kept at a constant 120°C while the detector and injector were thermostated to 350°C. The pressure of hydrogen, air and the carrier gas, nitrogen, were kept at 50, 50 and 120 kPa, respectively.

3.5.2 Ternary mixtures

A Shimadzu GCMS-QP2010 SE gas chromatograph equipped with an SGE BP5 column (0.22 mm × 0.33 mm × 0.25 μm, length: 25 m) coupled with a mass spectrometer (MS) was used to analyse the organic solvent content of the feed mixture, the retentate and the permeate samples. The column temperature was kept at a constant 60°C with an injector temperature of 250°C. The pressure of the helium carrier gas was kept at 90 kPa. MS ion source temperature was set to 250°C.

The water concentration of the feed and retentate of all investigated mixtures was analysed by Karl-Fisher titration. In both analytical methods, the results were the average of three analyses.
4 Experimental investigation and modelling of the pervaporative dehydration of binary mixtures

Experimental results of ethanol-water and n-butanol-water dehydration were used solely for modelling purposes; the results themselves can be found elsewhere [125,126]. The results of isobutanol-water dewatering are presented in the following section.

4.1 Results of isobutanol-water separation

Pervaporation measurements were carried out at 70, 80, and 90°C at various feed water concentrations. The total fluxes and separation factors were calculated according to Equations (2.1) and (2.2), and the results are depicted in Figure 10. The increase of total fluxes with the feed water content and the temperature is in good accordance with the literature [57]. Accordingly, the highest permeate flux was measured at 90°C and about 14 wt% feed water content. The separation factor achieved by the PERVAP 1510 membrane for water shows that the membrane is more permeable to water than to isobutanol, as expected in the case of a hydrophilic membrane. The separation factor decreases with increasing water concentration caused by the possible swelling of the hydrophilic membrane also demonstrated by the lower solubility parameter distance ($R_a$), thus stronger interaction, between water and PVA shown in Table 7. Due to the swelling, the interstices extend between the polymer chains in the membrane that reduce the separation efficiency. Temperature does not have a significant effect on the separation factor.

![Graph showing changes of total flux and separation factor at 70, 80, and 90°C depending on the feed water content](image)

**Figure 10** Changes of total flux and separation factor at 70, 80, and 90°C depending on the feed water content
Expressing pervaporation data with permeance values (Equation (2.4)) removes the effects of the vapour liquid equilibrium from the true permeation properties of the membrane, emphasized by Baker et al. [17]. Eliminating the driving force of partial pressure difference from the flux shows the performance characteristics of the membrane better, also making it easier to compare results of experiments performed under different operating conditions. Figure 11 shows how permeances increase with increasing water concentration in the feed. It can be seen that the influence of temperature is largely reduced. The anomalies appearing at elevated water concentrations in the case of isobutanol are probably caused by a measurement error.

![Figure 11](image)

**Figure 11** Changes of permeance values of water and isobutanol at 70, 80, and 90°C depending on feed water content

The pervaporation separation index shows the combined effects of the flux and the separation factor (see Equation (2.3)). Figure 12 shows that the PSI values also increase with increasing temperature and with increasing water concentration, which means that the separation efficiency of the membrane is better at elevated water concentrations despite the reduced separation factor.
4.2 Proposed mass transport model

The basic solution-diffusion model described in Section 2.2.3.3 in its original form is valid for the description of mass transfer of ideal mixtures through non-swollen membranes. However, flux coupling may occur when the interactions are strong between the permeating solvents. One permeant affects the Gibbs free energy of the other component, changing the permeation characteristics of the membrane [141,142]. In addition, membranes applied for the dehydration of strongly non-ideal systems tend to swell, causing the sorption and diffusion coefficients to become highly concentration-dependent. This calls for a modification of the basic solution-diffusion model.

In a swollen membrane the free volumes between polymer segments are enlarged by the diffusion of the swelling component(s), causing an increased diffusion coefficient for the permeating component. When more species contribute to the plasticization, all of them promote an increased diffusion coefficient.

Mulder [72] found, that in the case of liquid diffusion through a dense polymer layer, the permeability is much higher than in the case of gas diffusion due to stronger interactions and increased chain mobility. He concluded that this plasticizing effect causes the permeability to be concentration- or activity-dependent.

Heintz and Stephan [143] also stated in their work that the solubility coefficient and diffusivity depend on the composition of the liquid feed mixture. They proposed a model for the pervaporation of binary mixtures using UNIQUAC activity data, amended by interaction parameters fitted to vapour sorption isotherms of the pure components in the

![Figure 12 Changes of PSI values at 70, 80, and 90°C depending on feed water content](image-url)
membrane polymer. In their experiments they showed a huge deviation between ideal and experiment-based real solubility coefficients, caused by the synergistic solubility effect of water and the studied organic components in the membrane.

In previous works the validity of the Rautenbach model was confirmed [144] for total fluxes in the case of water-ethanol mixtures, although, for water-isopropanol binary mixtures, significant deviation was observed at the higher feed water concentration (over 0.3 mol fraction) range [8,145].

The applicability of the original model of Rautenbach was tested for the isobutanol-water mixture of the present study as well. It was found that also in the case of this binary mixture, the model underestimates the partial water fluxes already at around 0.15 mol fraction of water in the feed, and completely fails to describe the permeation of isobutanol. Huge discrepancies were discovered fitting the model to previous experimental results of ethanol – water and n-butanol – water binary mixtures [125,126].

Since industrial pervaporation applications might be expected to work at different concentration ranges, a more accurate model is inevitable for the design and operation of such PV processes, properly approximating the real behaviour of the system. The aim of my work is the improvement of Equation (2.35), i.e. the Rautenbach model (Model I), to widen its application range to higher water concentration regions. The reason of the underestimation of the measured data by Model I may be that the transport coefficient is not constant in a wide range of concentration. Although Rautenbach suggested negligible concentration dependence for the transport coefficient [21,94], our experiments suggest a strongly divergent, more complicated relationship. The tendency of measured fluxes suggests that partial fluxes depend on the feed concentration of the permeating compound in an exponential way; therefore, this exponential tendency is enhanced in the improvement of Model I by complementing it with an exponential term. The exponential factor includes the feed concentration of the given component, thus providing more accurate results in an extended concentration range than the basic model recommended by Rautenbach et al. [94]. Partial fluxes can be calculated by the extended model (Model II) in the following way:

\[
J_i = \frac{1}{1+\left(\frac{D_{i0}\exp(B_i\chi_{IP})}{\bar{y}_i\bar{v}_{IP}/\bar{v}_{0}}\right)} \cdot \frac{\bar{D}_{i0}\exp(B_i\chi_{IP})}{\bar{y}_i} \cdot \frac{(p_{IP}-p_{IP})}{p_{IP}} \tag{4.1}
\]
$D_{i0}$, $E_{i0}$, $Q_0$, and $B_i$ are fitted to the experimental results performed with the given membrane and liquid mixture. It must be stressed that although the model parameters have a limited physical meaning, they are not true material properties.

The heat demand of the pervaporation process is covered by the latent heat of the feed solution. While the model of Rautenbach et al. describes an isothermal case, Mizsey et al. [146] have developed the model by implementing the heat balance for the membrane:

$$\frac{c_p F \Delta T}{A} = \sum_{i=1}^{k} \lambda_i J_i \quad i = (1, \ldots, k)$$

(4.2)

where $c_p$ is the specific heat at constant pressure (J/mol), $F$ is the feed stream [mol/h], $A$ is the membrane area [m$^2$], $\lambda_i$ is the heat of evaporation of component $i$ [J/mol], and $J_i$ is the partial flux [mol/(m$^2$h)].

Since the model is semi-empirical, therefore reliable experimental data are necessary based on the flow and transport properties of the actual pervaporation system, the given mixture and membrane material.

### 4.2.1 Parameter estimation

According to the methodology of Lovasz et al. [144], after the laboratory measurements the next step of model development is the parameter fitting procedure, in the course of which Model I and Model II can be compared. The estimated parameters based on the measured data are the pre-exponential factor of the transport coefficient, the permeability coefficient, the activation energy for both components ($D_{i0}^{*}$, $Q_0$ and $E_i$) and the extra $B_i$ constants of Model II. The estimation is performed according to Equation (4.1) and Equation (2.32) in the STATISTICA program environment.

Input parameters required for the regression of the non-linear equation are the following:

- The vapour pressure of component $i$ ($p_{i0}$) calculated according to the extended Antoine equation:

$$p_{i0} = \exp \left( A + \frac{B}{T} + C \ln T + DT^E \right)$$

(4.3)

where $A$, $B$, $C$, $D$, $E$ are material constants obtainable e.g. from the ChemCAD flowsheeting software database. Constants for isobutanol and water can be found in Table 11.


**Table 11** Constants for the calculation of the saturated vapour pressure of isobutanol and water obtained from the ChemCAD [140] database

<table>
<thead>
<tr>
<th>Constants</th>
<th>Isobutanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>187.79</td>
<td>72.55</td>
</tr>
<tr>
<td>B</td>
<td>-12 955</td>
<td>-7207</td>
</tr>
<tr>
<td>C</td>
<td>-24.29</td>
<td>-7.14</td>
</tr>
<tr>
<td>D</td>
<td>0.14·10^{-4}</td>
<td>0.41·10^{-5}</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

- The partial pressure of component $i$ in the feed mixture:
  \[ p_{iF} = \gamma_{iF} \cdot x_{iF} \cdot p_{i0} \] (4.4)

- Permeate pressure of component $i$:
  \[ p_{iP} = \gamma_{iP} \cdot p_P \] (4.5)
  where $\gamma_{iP}$ is the permeate concentration of component $i$ in molar fractions and $p_P$ is the permeate pressure (bar)

- The activity coefficients of component $i$ in the feed ($\gamma_{iF}$) and the permeate ($\gamma_{iP}$), from which the average activity coefficients can be calculated:
  \[ \bar{\gamma_i} = \sqrt{\gamma_{iF} \cdot \gamma_{iP}} \] (4.6)

Activity coefficients can be obtained by the appropriate thermodynamic model e.g. Wilson, UNIQUAC, NRTL, etc. For the isobutanol-water mixture Wilson model was used.

With the calculated input parameters, a nonlinear estimation process is applied by defining a user specified regression custom loss function. The objective function (OF) to be minimized is the deviation of the modelled and the measured values:

\[ OF = \sum_{i} \left( \frac{J_{i,\text{measured}} - J_{i,\text{modelled}}}{J_{i,\text{measured}}} \right)^2 \] (4.7)

The variation of the initial value of the permeability coefficient ($Q_0$) influenced the value of the objective function to a great extent. Depending on the assumed pressure in the porous layer of the membrane, the value of the permeability coefficient alters. The lowest values for the objective function are obtained if $Q_0$ tends to infinity. This corresponds to
the situation that the porous layer has practically no resistance. This has been shown by Lovasz et al. [147] stating that the support layer of the composite membranes has practically no resistance to the permeation. In this case the value of the first factor of Equation (4.1) is regarded as equal to 1, i.e. the pressure drop of the porous layer can be neglected. Thus, the modified Rautenbach model can be simplified:

\[ J_l = \frac{D_{i0} \exp(B_iX_{IP})}{\bar{y}_i} \left( \frac{p_{IF} - p_{IP}}{p_{I0}} \right) \]  

(4.8)

Table 12 shows the minimized objective functions and the estimated values for \( D_{i0}^*, E_0, \) and \( B_i \) parameters of the two models.

The comparison of the measured and calculated fluxes is depicted in Figure 13. It can be seen that the improved model (Model II) results in a significantly better fit (lower objective function values) than the model of Rautenbach (Model I). The partial fluxes of water calculated according to Model I are in acceptable agreement with the measured ones at the lowest range of feed water content. At higher water concentration of the feed, however, a great deviation appears in the case of both water and isobutanol partial fluxes.

The two models were also tested for the experimental data of the dehydration of ethanol–water and n-butanol-water binary mixtures with PERVAP 2210 and 1210 membranes. Table 12 summarizes the objective function values and the estimated parameters for these mixtures too. Figure 14 and Figure 15 show the comparison of measured and calculated fluxes for ethanol-water and n-butanol-water mixtures, respectively. The estimated flux values of Model II show better agreement with the measured ones in these cases as well.
Table 12 Modelling results for the binary alcohol-water mixtures based on Model I and Model II (Equations (2.35) and (4.8)). $D_{i0}^*$ and $E_i$ are regressed parameters of the pre-exponential factor of the transport coefficient and the activation energy (Equation (2.32)), whereas $B_i$ is the exponential factor for Model II. OF represents the objective functions of the regression.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Component</th>
<th>Model</th>
<th>$D_{i0}^*$</th>
<th>$E_{i0}$</th>
<th>$B_i$</th>
<th>OF</th>
<th>R</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol–water mixture</td>
<td>Water</td>
<td>Model I</td>
<td>3.34E-04</td>
<td>80042</td>
<td>0.9330</td>
<td>0.8987</td>
<td>0.8077</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Model II</td>
<td>2.02E-04</td>
<td>77877</td>
<td>2.63</td>
<td>0.1444</td>
<td>0.9932</td>
<td>0.9864</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Model I</td>
<td>1.89E-07</td>
<td>95414</td>
<td>5.0261</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Model II</td>
<td>1.93E-05</td>
<td>128573</td>
<td>-8.68</td>
<td>2.2473</td>
<td>0.9626</td>
<td>0.9265</td>
<td></td>
</tr>
<tr>
<td>n-Butanol–water mixture</td>
<td>Water</td>
<td>Model I</td>
<td>1.77E-07</td>
<td>157381</td>
<td>7.4660</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>n-Butanol</td>
<td>Model II</td>
<td>3.44E-04</td>
<td>25711</td>
<td>10.32</td>
<td>1.3584</td>
<td>0.9000</td>
<td>0.8099</td>
<td></td>
</tr>
<tr>
<td>n-Butanol</td>
<td>Model I</td>
<td>6.24E-06</td>
<td>39929</td>
<td>8.9527</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butanol</td>
<td>Model II</td>
<td>5.82E+00</td>
<td>29711</td>
<td>-14.37</td>
<td>1.0618</td>
<td>0.9694</td>
<td>0.9397</td>
<td></td>
</tr>
<tr>
<td>Isobutanol–water mixture</td>
<td>Water</td>
<td>Model I</td>
<td>3.06E-04</td>
<td>78175</td>
<td>4.8579</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Isobutanol</td>
<td>Model II</td>
<td>1.17E-03</td>
<td>49815</td>
<td>5.05</td>
<td>0.3927</td>
<td>0.9764</td>
<td>0.9533</td>
<td></td>
</tr>
<tr>
<td>Isobutanol</td>
<td>Model I</td>
<td>3.89E-06</td>
<td>72818</td>
<td>9.3267</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobutanol</td>
<td>Model II</td>
<td>7.41E-02</td>
<td>45121</td>
<td>-8.47</td>
<td>1.6077</td>
<td>0.8712</td>
<td>0.7591</td>
<td></td>
</tr>
</tbody>
</table>
Figure 13 Measured partial fluxes (■) of water (a–c) and isobutanol (d–f) compared to fluxes calculated with Model I (—), Model II (- - -) at 70, 80 and 90°C in a function of the feed water content in molar fraction.
Figure 14 Parameter fitting results for the dehydration of ethanol–water mixture using PERVAP 2210 membrane. Measured partial fluxes (●) of water (a, c) and ethanol (b, d) compared to fluxes calculated with Model I (—), Model II (- - -) at 60 and 80°C related to the molar fraction of the feed water content.
Figure 15 Parameter fitting results for the dehydration of n-butanol–water mixture with PERVAP 1210 membrane. Measured partial fluxes (■) of water (a–c) and butanol (d–f) compared to fluxes calculated with Model I (—), Model II (– - -) at 60, 75 and 90°C in a function of the feed water content in molar fraction
The results of parameter estimation for all three binary mixtures show that Model I underestimates the measured fluxes, especially at higher water content, as opposed to the improved model of Model II, which results in a better fit to the experimental data. The reason for this is that the transport coefficient depends on the component concentration to a greater extent than Rautenbach et al. [94] suggested (based on Bird et al. [148]). This concentration-dependency is an exponential one expressed in Equation (4.8). It is widely accepted that the diffusion coefficient has a strong dependence on the feed concentration. Many authors have suggested an exponential relationship between the diffusion coefficient and feed concentration [68,149]. The transport coefficient, however, is accepted to be less affected by feed concentration changes than Fick’s diffusion coefficient. Moreover, it was assumed as practically constant by Rautenbach et al. [94] that is definitely applicable for really small permeating compound compositions in the feed. For some non-ideal mixtures (e.g. chloroform–diethyl ether), its dependence on component concentration was found to be linear [148]. In contrast, the dehydration experiments with mixtures of isobutanol–water, n-butanol–water and ethanol–water point to the assumption that $D_{i0}$ depends on the component concentration to a great extent. If the concentration of the permeating compound is far from zero, like in the case of pervaporation of azeotropic mixtures with high water content, e.g. n-butanol–water, isobutanol–water (water concentration of 42.5 and 33 wt%, respectively), and many others, the newly developed model of Model II, based on the modified transport coefficient, proves to be applicable. The dependency of the feed composition of the modified transport coefficient was found to be an exponential one.

To comply with the requirements of more reliable modelling of the pervaporation process, the improved model (Model II) is the right choice instead of the original model of Rautenbach (Model I). Process modelling, design and optimization of pervaporation and PV based hybrid separation methods in flowsheeting software packages is more accurate with Model II than the application of the basic model.
4.3 Case study 1: Model comparison through simulations of alcohol dewatering hybrid separation systems

4.3.1 Aim

Commercial process simulators do not contain a built-in membrane model because of the lack of a predictive pervaporation model, which could be extrapolated and be suitable for the selection of the most appropriate membrane [96]. Thus, user-added models are frequently programmed into MATLAB, gPROMS and process simulators, like Aspen Plus, Aspen HYSIS, and ChemCAD [119]. Many authors have published numerous ways of simulating the component transport so far [150–152].

The improved semi-empirical model of Model II (explained above) reduces the modelling and computational effort compared to a detailed, rigorous model, while still obtaining accurate results regarding the investigated systems for a wider concentration range, i.e. an extended operational window. During operational anomalies or the start-up and shutdown of an industrial system, this wider operational range can be very important to simulate. A user-added pervaporation model was written and applied in the ChemCAD process simulation software, with the help of which calculations could be made with both the original model of Rautenbach (Model I) and our improved solution-diffusion model (Model II). In this section, the comparison of Model I and Model II is demonstrated on a hybrid separation system comprised of a distillation column and several pervaporation units for the separation of isobutanol (iBuOH)-water and ethanol (EtOH)-water binary mixtures.

4.3.2 Model verification

With a user added membrane module in the ChemCAD 6.4.3 software environment the verification of the developed exponential model becomes possible. A model verification step was carried out with the input of model parameters of $D_o$, $E_i$ and $B_i$ of Equation (4.8), previously fitted to experimental data (Table 12), and given operating conditions ($A=0.0028$ m$^2$; $P_f=4$ bar; $P_p=0.0027$ bar). In accordance with our expectations, verification proved that the basic model of Rautenbach shows a significantly greater deviation from the experimental data than the improved Model II in the case of both binary mixtures, especially at higher water concentration ranges. It can be seen in Figure 16 that with Model II, the measured and simulated values are in good agreement.
The ChemCAD model can also distinguish adiabatic and isothermal separation conditions. The ideal isothermal case of PV results in the smallest membrane area, whereas the adiabatic option resembles the real conditions, and usually gives a greater membrane surface area.

4.3.3 Simulation of the hybrid separation systems

With the successful simulation of the PV process in ChemCAD at hand, the design of hybrid separation processes becomes available applying the user-added module. Each simulated hybrid system consists of a distillation column and several subsequent pervaporation units. The aim of the processes is to produce isobutanol and ethanol with a purity of min. 99.7 wt%. A pervaporation unit can be inserted into a hybrid system in three ways (see Section 2.4):

- prior to the distillation column (PV+D),
- in between distillation columns (D+PV+D), or
- processing either the bottom or the top product of the column to reach the desired product purity (D+PV).

Koczka [125] has shown that the optimal arrangement for alcohol dehydration purposes is the D+PV structure, a distillation column followed by a membrane unit.

**Figure 16** Validation of Model I and Model II with total fluxes of isobutanol-water (a) and ethanol-water (b) mixtures
Accordingly, in the case of iBuOH-water and EtOH-water separation the PV units are connected to the top of the distillation column to separate the azeotropic mixtures. Pervaporation units are connected in series to reach the desired product purity.

Since the heat requirement of evaporation is assured by the sensible heat of the feed mixture, it cools down during the pervaporation process. To ensure high flux and effective separation, operation temperatures should be as high as possible (restricted by the long-term temperature durability of the membrane). Thus, only a limited temperature drop is allowed in a single membrane unit, and the retentate stream has to be reheated after each pervaporation unit by heat exchangers [153]. The applied membrane area per unit should be limited to a size that ensures an acceptable temperature drop. If the temperature decreases too much, the pervaporation process stops. The hybrid system for isobutanol dehydration is depicted in Figure 17.

![Simulated hybrid separation system for isobutanol-water mixture](image)

**Figure 17** Simulated hybrid separation system for isobutanol-water mixture

The first step of the simulation procedure was to optimize the distillation column and its operating parameters (number of theoretical plates, reflux ratio, etc.) to produce the azeotropic mixture at the top and a maximum of 0.05 wt% alcohol content of the bottom product. Optimized operating parameters of the distillation columns for both mixtures are shown in Table 13.
Table 13 Operating parameters of the distillation columns

<table>
<thead>
<tr>
<th></th>
<th>Isobutanol-water dehydration</th>
<th>Ethanol-water dehydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow rate (kg/h)</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Alcohol conc. in the feed (wt%)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Number of theoretical stages</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>Number of the feed tray</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Alcohol conc. in the distillate (wt%)</td>
<td>67.6</td>
<td>92.7</td>
</tr>
<tr>
<td>Distillate temperature</td>
<td>89.6</td>
<td>77.9</td>
</tr>
</tbody>
</table>

In the case of isobutanol, a phase separator is connected to the top of the column, as isobutanol forms a heteroazeotropic mixture with water. The distillate stream, or in the case of isobutanol dewatering: the organic, rich top phase, is reheated in a heat exchanger to 90°C prior to the first membrane unit. The retentate stream of each membrane unit is also the feed stream of the following one, except for the last module, where the retentate is the final product, the concentrated alcohol. Permeate streams leaving the pervaporation units are collected, mixed, condensed and recycled to the column. The feed pressure of the membranes is adjusted to 4 bar, while permeate pressure is kept at 0.0027 bar. These hybrid processes clearly integrate green technology and circular economy aspects, since the bottom product is almost pure water, where only heat contamination should be eliminated. Every other stream is recycled in the system. The energy demand could be further reduced with heat integration between heat exchangers (not investigated in the presented cases). Thus, with such a coupled system, operational costs can be lower and environmental fines, which would be issued based on waste emission, can be avoided [154].

4.3.4 Simulation Results

Results of the simulations with both models (Models I and II) are listed in Table 14. There are notable differences between the basic Rautenbach and the developed exponential model in case of both alcohol-water mixtures.
<table>
<thead>
<tr>
<th></th>
<th>F (kg/h)</th>
<th>n_{PV}</th>
<th>A_{PV} (m²)</th>
<th>F_{PV} (kg/h)</th>
<th>R (kg/h)</th>
<th>P (kg/h)</th>
<th>Q_{reb} (MJ/h)</th>
<th>Q_{PV} (MJ/h)</th>
<th>W_{ibu} (wt%)</th>
<th>W_{w} (wt%)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>iBuOH/water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model I</td>
<td>817.6</td>
<td>8</td>
<td>40</td>
<td>137.5</td>
<td>119.9</td>
<td>17.60</td>
<td>490.3</td>
<td>37.70</td>
<td>99.8</td>
<td>96.7</td>
<td></td>
</tr>
<tr>
<td>Model II</td>
<td>818.9</td>
<td>9</td>
<td>45</td>
<td>139.0</td>
<td>120.1</td>
<td>18.93</td>
<td>493.2</td>
<td>38.60</td>
<td>99.7</td>
<td>89.9</td>
<td></td>
</tr>
<tr>
<td>Deviation (%)</td>
<td>+0.16</td>
<td>+12.50</td>
<td>+12.50</td>
<td>+1.09</td>
<td>+0.17</td>
<td>+7.56</td>
<td>+0.59</td>
<td>+2.39</td>
<td>-0.15</td>
<td>-6.96</td>
<td></td>
</tr>
<tr>
<td><strong>EtOH/water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model I</td>
<td>810.1</td>
<td>4</td>
<td>116</td>
<td>129.8</td>
<td>119.7</td>
<td>10.8</td>
<td>618.1</td>
<td>20.81</td>
<td>99.9</td>
<td>89.1</td>
<td></td>
</tr>
<tr>
<td>Model II</td>
<td>809.7</td>
<td>7</td>
<td>140</td>
<td>129.4</td>
<td>119.7</td>
<td>9.7</td>
<td>633.6</td>
<td>21.26</td>
<td>99.7</td>
<td>96.7</td>
<td></td>
</tr>
<tr>
<td>Deviation (%)</td>
<td>-0.05</td>
<td>+75.00</td>
<td>+20.69</td>
<td>-0.31</td>
<td>-</td>
<td>-10.19</td>
<td>+2.51</td>
<td>+2.16</td>
<td>-0.25</td>
<td>+8.53</td>
<td></td>
</tr>
</tbody>
</table>

F  Feed flow rate of the distillation column  
F_{PV}  Feed flow rate to the first membrane module  
R  Retentate flow rate leaving the last module  
P  Recycled permeate flow rate  
Q_{reb}  Heat requirement of the reboiler of the column  
Q_{PV}  The sum of the heat demand of the pervaporation units  
W_{ibu}  Isobutanol content of the product  
W_{w}  Water content of the recycled permeate flow
An increased membrane area is required for generating the same product quality with the improved model. In the case of ethanol dehydration, the requirements are met with a total membrane area of 116 m² (Model I) and 140 m² (Model II). The calculated stream flow rates and compositions also deviate in the two models.

It has been shown that for isobutanol dehydration the basic Rautenbach model underestimates the isobutanol flux. This underestimation results in a decreased organic loss of the retentate in ChemCAD, therefore higher organic concentration is calculated in the product of the hybrid process. The decreased permeate stream requires less heat for evaporation in case of Model II. As more water permeates through the membrane in the case of the exponential model, recycled permeate flow is also increased, resulting in a slightly greater heat demand of the reboiler of the distillation column than in the case of Model I.

The ethanol-water mixture behaves a little differently from the isobutanol-water mixture, where the Rautenbach model underestimates the experimental flux in the whole investigated feed concentration range. For the ethanol-water system, Model I overestimates real partial fluxes until around 0.28 mole fraction of water in the feed (Figure 14), above which it underestimates the partial flux. The improved model fits experimental data better in the whole range. Since the concentration of ethanol in the feed stream of the first membrane unit is 0.16 mole fraction, the basic model produces a higher organic flux. In case of the subsequent membrane units, this feed concentration decreases further. Therefore, Model I requires a smaller overall membrane area than the exponential model to produce the same product quality.

4.3.5 Cost estimation

The conceptual phase of designing an industrial process takes a small portion of project costs, but offers a huge cost reduction opportunity for the whole project [155]. Hybrid systems for the dehydration of both alcohol-water mixtures and both models were compared also from an economic point of view. Capital costs of the distillation columns depend on many parameters (e.g.: number of theoretical plates, the volume of the managed streams, and purity of the distillate). These costs were calculated after the optimization procedure of the system, where column and heat exchanger costs were calculated according to the cost correlations of Douglas [156]. Investment costs of membrane modules were calculated according to Koczka [125] (see cost equations in
Appendix A). Capital investment costs of the membrane system depend on the area of the membranes and the heat exchangers between the modules, the permeate cooling and the vacuum pump. Calculating the capital costs for permeate cooling, a COP=2 value is applied.

Operational costs were calculated based on industrial utility price data for 8000 operation hours per year. Literature data suggest the necessity of replacing a PV membrane approximately every 2-5 years; therefore, 2.5 years were taken as membrane depreciation time in this work. These depreciation costs, as well as a 10 year depreciation time for the rest of the operational units, were also included in the economic evaluation. Results of the cost comparison are depicted in Figure 18 and Figure 19.

![Figure 18](image)

**Figure 18** Comparison of the capital costs of the hybrid isobutanol-water and ethanol-water dehydration systems

Capital costs for Model II are higher in both cases. It can be seen that capital costs for isobutanol-water systems are quite similar, due to the same column structure and the slight difference in membrane areas. The increase of capital cost in the case of Model II is in a range of 0.32-7.7% regarding the different operational units. The greatest deviation is caused by the membrane area increase. In the ethanol case a greater difference (0.53-88.9% cost increase) appears between Model I and II. The 88.9% increase is caused by a greater discrepancy in membrane areas and accordingly, the reheating heat exchangers.
Operational costs of ethanol dehydration are higher than that of isobutanol dewatering; with only a moderate increase in the case of Model II: 0.67-2.01% for isobutanol and 0.64-4.38% for ethanol dewatering.

**Figure 19** Comparison of the operational costs of the hybrid isobutanol-water and ethanol-water dehydration systems

### 4.3.6 Conclusion

In this section the Rautenbach model and the improved exponential model were verified and compared with the simulation of hybrid separation processes for the dehydration of ethanol-water and isobutanol-water mixtures in the ChemCAD software environment. The improved model is in better agreement with the experimental results for the investigated separation problems, which resulted in higher estimated costs. Simulation results of the hybrid separation process show that Model II gives greater pervaporation membrane area in both cases. This means that using an inadequate pervaporation model can lead to false results for the design and optimization of complex separation processes that can cause an unpleasant surprise during the realization, resulting in poorer product quality during operation. These results stress the necessity and the importance of adequate process models to obtain reliable design data.
4.4 Case study 2: Separation alternatives for the dehydration of isobutanol

4.4.1 Aim

Since a reliable process model is present for the pervaporation of isobutanol, the hybrid system investigated above can be compared with a conventional separation approach. As the isobutanol-water mixture forms a heteroazeotrope, the obvious choice is heteroazeotropic distillation. PV is frequently referred to as a more economic choice compared to distillation, based on the lower energy need of the process. In this section, the hybrid separation structure of distillation and pervaporation is compared with heteroazeotropic distillation, based on an economic analysis of capital-, operational- and total annual costs.

The product requirement for the investigated processes was to produce isobutanol with a purity of 99.7 wt% and water of 99.95 wt% without the addition of an extra entrainer solvent. To compare the systems, a feed mixture of 800 kg/h was to be separated with an isobutanol concentration of 15 wt% and the decanter was set to 40°C in both cases. The separation alternatives were optimized to minimize total annual costs (TAC), while meeting the product requirements. Cost calculations were based on a 10 year depreciation time.

\[
TAC = \frac{\sum \text{Capital costs}}{10} + \sum \text{Operational costs}
\]  

(4.9)

The investigated and optimized process alternatives are discussed in the following:

- Heteroazeotropic distillation (HD)

The heteroazeotropic system comprises of two distillation columns with a decanter in between them. The first column enriches isobutanol to the azeotropic point in the distillate, which then enters a decanter, from where the organic phase is fed to the second column while the aqueous phase is recycled to the first column. Isobutanol product leaves at the bottom of the second column, while the top product is recycled to the phase separator.
The simulated hybrid system consists of a distillation column, a decanter and subsequent hydrophilic pervaporation units, similar to the system studied in Case Study 1. The distillation column enriches the mixture to the azeotropic concentration at the top, which enters a decanter, where the organic phase is then introduced to the membrane modules connected in series. Pervaporation temperature is set to 90°C to maximize the
permeate flux without compromising the separation efficiency of the membrane (Figure 10). Membrane area in a single unit is also limited here to 5 m$^2$ per unit. The retentate stream of the last membrane unit is the isobutanol product. Permeate streams of each module are collected, condensed and recycled into the feed stream of the distillation column. Feed and permeate pressures of the membrane units were adjusted to 4 bar and 0.0027 bar, respectively. Purified water leaves the system at the bottom of the column.

### 4.4.2 Simulation results

The optimization of the number of stages for the first (and only, in case of the hybrid system) distillation column resulted in 11 stages, and 10 for the second column of the heteroazeotropic system. In both cases, 120 kg/h isobutanol and 680 kg/h water were produced. Simulated and optimized parameters of the four systems are shown in detail in Table 15. It can be seen from the data, that the reboiler duty of the first column in the hybrid case could be reduced by nearly 35%, since C1 in the HD setup has to deal with the recycle stream form the second column as well.

**Table 15** Simulated parameters of the investigated systems

<table>
<thead>
<tr>
<th></th>
<th>HD</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>C2</td>
</tr>
<tr>
<td>Feed (kg/h)</td>
<td>800</td>
<td>216</td>
</tr>
<tr>
<td>Butanol conc. in feed (wt%)</td>
<td>15</td>
<td>85.4</td>
</tr>
<tr>
<td>Number of stages</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>Feed stage number</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Number of membrane modules</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Membrane area (m$^2$)</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Feed temperature (°C)</td>
<td>20</td>
<td>49</td>
</tr>
<tr>
<td>Recycle stream (kg/h)</td>
<td>82.7</td>
<td>95.3</td>
</tr>
<tr>
<td>Permeate stream (kg/h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reboiler duty (MJ/h)</td>
<td>741</td>
<td>256</td>
</tr>
<tr>
<td>Condenser duty (MJ/h)</td>
<td>474</td>
<td>217</td>
</tr>
<tr>
<td>Heat duty of heat exchangers</td>
<td>49</td>
<td>68</td>
</tr>
<tr>
<td>Permeate cooling (MJ/h)</td>
<td></td>
<td>48</td>
</tr>
</tbody>
</table>
4.4.3 Cost estimation

Investment costs of the columns and their internals (valve tray), heat exchangers and permeate cooler were calculated according to the cost correlations of Douglas [128] (see Appendix A), applying 1604.6 as the Marshall & Swift Cost Index of April 2017. The depreciation of the membranes was taken into account with their replacement every 2.5 years. For the rest of the operational units, a 10 year depreciation time was included in the cost calculations.

Operating costs were estimated based on the utility costs (obtained from MOL Hungary company through personal communications in 2017) shown in Table 16, calculated for 8000 operation hours per year. Calculated total annual costs are shown in Table 17. Results of the cost calculations are depicted in Figure 22 and Figure 23.

Table 16 Utility costs applied for calculations of operational costs

<table>
<thead>
<tr>
<th></th>
<th>Electricity [$/kWh]</th>
<th>Steam [$/t]</th>
<th>Cooling water [$/t]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>0.0928</td>
<td>22.96</td>
<td>0.0781</td>
</tr>
</tbody>
</table>

Table 17 Total annual costs of the process alternatives for isobutanol dehydration

<table>
<thead>
<tr>
<th></th>
<th>HD</th>
<th>Hybrid</th>
<th>Hybrid 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAC (1000 USD/year)</td>
<td>106.2</td>
<td>125.9</td>
<td>84.8</td>
</tr>
</tbody>
</table>

Figure 22 Comparison of the capital costs of the of the process alternatives of the isobutanol dehydration systems
Figure 23 Comparison of the operational costs of the process alternatives of the isobutanol dehydration systems

The capital cost of the hybrid system is significantly (more than 3.3 times) higher compared with the heteroazeotropic system, which is caused by the high cost of the membrane modules. This extreme cost-elevating factor of the pervaporation aided system cannot be compensated even by the approximately 30% lower operating costs of the hybrid systems. This results in a 19% increase of the total annual cost of the hybrid system compared with the HD alternative.

The main component in the extreme capital cost of the hybrid system is the cost of the membrane modules. The calculations were made according to the cost equation of Koczka [125], which was based on personal communications with Sulzer Chemtech Ltd. In the case of Hybrid 2 systems indicated in Table 17, Figure 22 and Figure 23, the cost of the PV modules was chosen to decrease the TAC of the hybrid system below the TAC of the conventional HD system. This optimized cost resulted in 1000 $/m² (Hybrid 2) in comparison with the original price of ~9000 $/m² of the Hybrid system.

4.4.4 Conclusions

The simulated results show that the application of pervaporation indeed results in a notable decrease in energy and operating cost, as well as a reduced total environmental impact. However, the high price of the membranes (~9000 $/m²) hinders the profitability of this more economical and green technology. In the case of the studied system, a reduction of the membrane prices to 1000 $/m² would result in a competitive option, causing a 20% decrease in the total annual cost compared with the heteroazeotropic distillation.
4.5 Case study 3: Investigation of process alternatives for the separation of ethanol/n-butanol/water ternary mixture

Biofuel production from renewable sources has been in the focus of research for decades, due to the growing environmental concerns and energy crisis [157]. Bioethanol and biobutanol are renewable and clean fuel alternatives/additives in transportation with a potential of reducing global warming emissions. Additionally, biobutanol has the advantages of a non-hygroscopic nature and lower volatility than ethanol, with an unrestricted blending ratio with petrol, as opposed to ethanol.

Both alcohols can be produced through a biotechnological route from renewable resources such as lignocellulosic biomass, which is a low-cost non-food feedstock [158,159]. Although, fermentation results in a highly diluted broth containing only very low concentrations of the bioalcohols [160]. Among the traditional methods for separating this diluted mixture to obtain pure products are azeotropic distillation, extractive distillation, vacuum distillation, adsorption, gas-stripping, or extraction [29]. In addition, the ternary ethanol-n-butanol-water (E/B/W) mixture is a complex, highly non-ideal system forming azeotropes (see Table 6), thus making the downstream separation costly and energy-intensive.

In the course of the current section, separation alternatives of a diluted ethanol – n-butanol – water ternary mixture are proposed and simulated in the ChemCAD [161] flowsheeting software. The alternatives were evaluated based on economic aspects – the total annual cost (TAC) of each alternative – revealing the potentials and drawbacks of PV in a complex separation task.

4.5.1 Process alternatives and simulation results

A feed stream of 800 kg/h was suggested in this case study, too, consisting of ethanol (2 wt%), n-butanol (2 wt%), and water (96 wt%), modelling the dilute product mixture of ABE fermentation. Figure 24 depicts the initial separation steps of the mixture. The ternary mixture was preheated to 93°C, near to its boiling point, and fed into the first column (C1), where the ternary mixture was separated to a binary ethanol-water (E/W) mixture at the top of the column, and the dilute binary mixture of n-butanol-water (B/W) at the bottom. This C1 column is the common first step of all alternatives. Two different options are investigated for the separation of the binary E/W mixture leaving the top of the C1 column, and two additional options for the binary B/W mixture leaving the bottom of
the C1 distillation column. The E/W mixture near its azeotropic composition can be separated either through extractive distillation using ethylene glycol [162] as entrainer (C2 and C3) or by hydrophilic pervaporation (PV1) shown in Figure 24 and Figure 25, respectively.

The production of pure n-butanol from the bottom product of C1 was realized by heteroazeotropic distillation (C4 and C5) or by a distillation-pervaporation hybrid separation method (C4 and PV2) depicted in Figure 26 and Figure 27. The aim was to produce ethanol and n-butanol with a purity of 99.7 wt%, while water should leave the system with a maximal organic contamination of 10 ppm. All columns are operated at 1 atm. Mass stream values, number of theoretical stages, feed stages, reflux ratios, membrane area and component concentrations resulted from the optimization are indicated in the figures of each process alternative.

The objective function of finding the optimal alternative was the minimization of the total annual cost (TAC - Equation (4.9)), the sum of the annual capital costs (calculated with a depreciation of 10 years) and the annual operating costs. The operating costs include the entrainer cost, and the annual steam, cooling water, and electrical energy expenses. Capital costs incorporate the costs of the columns with bubble cap trays, the reboilers and condensers, the heat exchangers for cooling or reheating purposes, the permeate cooling unit and the costs of the membrane modules.

Figure 24 Extractive distillation structure for ethanol production
Figure 24 depicts the extractive distillation option. The top product of C1 is the binary E/W mixture with 16 kg/h flow rate and an ethanol concentration of 94.7 wt%. This near azeotropic mixture enters at the 10\textsuperscript{th} stage of C2, while the extractive agent of ethylene glycol is fed to the 3\textsuperscript{rd} stage of the column. The 99.7 wt% ethanol product leaves the top of C2. Ethylene glycol is regenerated in C3, from the bottom of which it is recycled to the system. Only a negligible amount of the entrainer must be added due to a small, inevitable ethylene glycol loss.

![Extractive Distillation Diagram](image)

Figure 25 Production of ethanol with hydrophilic pervaporation

The pervaporation alternative is shown in Figure 25. The top product of C1, with the same composition as discussed above, is separated with multiple hydrophilic pervaporation modules connected in series (only one module is depicted in the figure). Retentate reheating to 90°C is also applied between the modules in this system. Feed and permeate pressures of the membrane units were adjusted according to the experimental conditions to 4 bar and 0.0027 bar, respectively. Permeate streams are collected and condensed with a cooler. The stream contains 2.6 wt% EtOH, therefore it is recycled to the C1 column. A membrane area of 16 m\textsuperscript{2} was sufficient to concentrate the retentate ethanol product to 99.7 wt%.
The separation of the bottom product of C1 is more energy- and cost-intensive, due to its high, ~784 kg/h, mass flow rate and the negligible 2 wt% BuOH content. The first alternative to produce pure n-butanol from this stream is heteroazeotropic distillation shown in Figure 26. The dilute butanol mixture is introduced to the C4 column with 15 theoretical stages. The top product with 30 wt% BuOH content enters a decanter, where the stream splits into a butanol-rich top phase, and an aqueous bottom phase. The organic phase enters the C5 column, where the bottom product is the 16.04 kg/h n-butanol stream with a purity of 99.7 wt%. The top product of C5 with an azeotropic composition is recycled to a mixer prior to the phase separator. C5 has 6 theoretical stages and its feed stream enters at the 3rd stage.

Figure 26 n-Butanol production with heteroazeotropic distillation

Figure 27 illustrates the hybrid option, coupling the C4 column with a hydrophilic PV unit. Here, the organic phase leaving the phase separator is introduced to the PV unit, following a preheating to 90°C. The total membrane area is 75 m², where the area of a single unit is limited by the temperature drop. The area of one unit was optimized, so that the temperature of the retentate stream leaving a unit exceeds 50°C (where the PV process becomes extremely slow). The retentate of the last membrane module is the n-butanol product. Permeate streams are collected, condensed and recycled the same way as
described above. Feed and permeate pressures were also adjusted to 4 bar and 0.0027 bar, respectively. Purified water leaves at the bottom of C4.

![Diagram of n-Butanol production with hybrid distillation-PV system](image)

**Figure 27** n-Butanol production with hybrid distillation-PV system

### 4.5.2 Cost estimation

Number of theoretical plates, reflux ratios and mass flow values of the streams, based on which cost calculations were performed, are indicated in the corresponding figures. Investment costs of the columns and their internals (valve tray), heat exchangers and pumps were calculated according to the cost correlations of Douglas [156] (see Appendix A), applying 1604.6 as the Marshall & Swift Cost Index of April 2017. Investment costs per unit of membrane area for the PV modules was 1000 €/m², based on personal communication with the manufacturer DeltaMem Ltd in 2018. The depreciation of the membranes was taken into account with their replacement every 2.5 years. For the rest of the operational units a 10 year depreciation time was included in the cost calculations.

Operating costs were estimated based on the utility costs shown in Table 16, calculated for 8000 operation hours per year. Energy requirements of the columns and the heat exchangers are shown in Table 18. TAC results of the cost calculations are depicted in Figure 28.
Table 18 Energy requirements of the operational units

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>PV1</th>
<th>PV2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler duty (MJ/h)</td>
<td>538.2</td>
<td>14.3</td>
<td>12.5</td>
<td>125.1</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Condenser duty (MJ/h)</td>
<td>534.7</td>
<td>25.7</td>
<td>10.5</td>
<td>102.1</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat duty of membrane heat exchangers (MJ/h)</td>
<td>2.2</td>
<td>6.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat duty of permeate cooler (MJ/h)</td>
<td>2.3</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 28 Total annual costs of the process alternatives

It can be seen in Figure 28 that the TAC of the C1 column is the highest of the whole process with 113,691 $/y. In the case of ethanol production the hybrid system has lower operational and investment costs than the extractive distillation alternative, due to the fact that the latter includes two distillation columns, while the PV system requires only a relatively small membrane area. The TAC of the hybrid system is 41.5 % lower than that of the extractive option, with 72.8 % lower operational cost. However, for the n-butanol production options the TAC of the hybrid structure is almost twice as much as the TAC of the heteroazeotropic distillation, caused by the combined costs of the membrane modules and the heat exchangers between the modules. The operational costs of the two alternatives are comparable, but the annual investment cost of the C4+C5 system is 30 % of that of the hybrid system, due to the large membrane area required for n-butanol
production with 99.7 wt% purity. The reason for the large membrane area in the case of n-butanol separation can be found in the membrane characteristics. In contrast to ethanol dewatering, where a sufficiently high driving force is maintained in the whole examined concentration region, the membrane applied to butanol dehydration exhibits a rather low water flux at low feed water concentration. Thus, the driving force (partial pressure difference) of its permeation is extremely small (Figure 15). This means that reaching a product purity of 99.7 wt% n-butanol demands an increased membrane area.

4.5.3 Conclusions

In this section, process alternatives for the separation of a diluted ethanol–n-butanol–water mixture were proposed and simulated in the ChemCAD flowsheeting software. The different structures were optimized and evaluated based on their total annual cost. Configurations of extractive, heteroazeotropic distillation and hybrid distillation-pervaporation systems for ethanol and n-butanol production were optimized according to the economical evaluation based on the total annual costs. It can be concluded that the hybrid system should be applied for ethanol production, while n-butanol can be produced more economically with heteroazeotropic distillation in the case of such a highly diluted feed stream of bioalcohols. Further simulations and optimizations could reveal the effects of heat integration with a potential for cost reduction.
5 Experimental investigation and modelling of the pervaporative dehydration of ternary mixtures

Contrary to the extensively investigated modelling options of binary mixtures, mass transport models for multicomponent mixtures are far less investigated in the literature. The increased number of possible interactions between mixture components, and between components and membrane results in a significantly more complex permeation behaviour. Doong et al. [81] proposed a model for multicomponent permeation based on the solution-diffusion mechanism incorporating predictive solubility and diffusivity models, such as the free volume theory. The model showed reasonable agreement with the measured data; however, it was tested solely for polyethylene membrane and organic solvents. Composite and mixed matrix membranes were not investigated.

As it has been previously established, hydrophilic polymer membranes are usually plasticized by water to a great extent, therefore in certain models the concentration dependence of permeation is often assigned to solely the water concentration in the feed mixture [163]. Huang and Shao [164] developed a model for the dehydration of ethylene glycol by a sulfonated poly(ether ether ketone) homogeneous membrane, in which they considered only the overwhelming affinity of water to the membrane, ignoring the less permeable species. Their proposed model included only the water concentration, as the main plasticizer, and water-related plasticization coefficients. A solution-diffusion model – based also on the simplification that water is the main plasticizing agent – was used by Koch and Górak for the ternary mixture of acetone-isopropanol-water [130]. They found that this approach described this studied system reasonably well.

The complicating factor in multicomponent mixtures is that both the solubilities and diffusivities are affected by the interactions between the components. Therefore, the component transport is characterized by flow coupling and preferential sorption caused by thermodynamic interaction. During flow coupling, one component is “dragged” through the membrane by the other, the extent of which is difficult to predict, or even measure. Mulder [165] identified two types of interaction, thermodynamic and kinetic coupling. Thermodynamic coupling is caused by the interactions between the permeating components based on their mutual effect on their Gibbs free energy, which, in turn, changes the sorption behaviour of the molecules. Kinetic coupling is responsible for the changes of the diffusion coefficients of the species in a plasticized membrane. The latter,
therefore, is membrane- and system specific, as the molecule-membrane interactions strongly depend upon the membrane material. The degree of the coupling effect depends on membrane properties, such as the degree of cross-linking, temperature dependent structure changes and water affinity [45]. The combined consequence is that the diffusion characteristics of the different components of a mixture are interdependent.

In order to explore the reality and extent of this interdependence, the pervaporative dehydration of two ternary mixtures (ethanol-n-butanol-water and ethanol-ethyl acetate-water) was experimentally investigated in various concentration ratios of the organic components. The effects of the different third components (n-butanol or ethyl acetate) were also studied. Based on the experimental results a mass transport model modification was suggested for ternary mixtures based on the binary model of Equation (4.8).

5.1 Experimental results

The experimental results presented below serve as an extensive database for the investigation of the permeation characteristics of ternary mixtures. Experiments were conducted according to the method described in section 3.4. Fluxes, permeances, selectivities and separation factors are demonstrated in the following for the examined mixtures as a function of temperature and water concentration (or water activity) in the feed. To be able to compare the ternary results with binary ethanol-water experimental results, pervaporation experiments were performed with this binary mixture under the same conditions (feed water concentration range, feed pressure of 4 bars, permeate pressure of 0.0027 bar, and temperature values of 60, 75, 90°C) and the same PERVAP 1210 polymeric membrane. These experimental results can be found in Appendix B.

5.1.1 Ethanol/n-butanol/water (E/B/W) ternary mixture

The effect of temperature and the molar fraction of water on total fluxes of the ternary mixture can be seen in Figure 29 (a). The values show an Arrhenius-type increase with temperature [166]. Figure 29 also presents the partial fluxes of water (b), ethanol (c) and n-butanol (d) only at 75°C for better visibility of the results. The same exponential increase with increasing water content can be observed here as in the case of the binary mixture presented previously, indicating a significant swelling effect of water on the membrane.
Figure 29 Effect of water concentration and temperature on total fluxes (a) at 2:1, 1:1 and 1:2 EtOH to BuOH ratios, and partial fluxes of water (b), ethanol (c) and n-butanol (d) at 75°C for E/B/W ternary mixture.

Water flux does not show significant changes with the different organic ratios. The ethanol flux values at 2:1 and 1:2 EtOH to BuOH ratios are similar with minimal values at 1:1 ratio. Butanol fluxes, on the other hand, show a clear maximum at 1:2 ratio, i.e. greater butanol content of the feed mixture, also with minimum values at 1:1. These trends were similar at all investigated temperatures (not shown here).

The permeation rate decreased with increasing molecular length of alcohols, also found by Huang and Lin [167]. Organic fluxes are proportional to, and are also governed by, water permeation [133,168]. Van Baelen et al. [133] studied the dehydration of the water-methanol-ethanol mixture with a PERVAP 2201 membrane. They found, that a sufficient amount of water molecules is required for the organic components to permeate through the membrane, as water and alcohol components form a superstructure, which is polar enough to permeate. This was also observed in the case of the E/B/W ternary mixture.
mixture of the present study, although organic concentration changes have a notable effect on organic permeation. The reason for the decreased fluxes at the 1:1 ratio might be that the interactions between the organic components are stronger than those between the organics and the membrane or the organics and water. Ethanol and butanol molecules in the feed mixture might form aggregates at this ratio, hindering their permeation.

**Figure 30** Effect of water concentration and temperature on the permeances of water (a), ethanol (b), n-butanol (c), and the water content of the permeate (d) for the E/B/W mixture

Permeances, as described earlier, reflect the actual permeability of a membrane towards a solute eliminating the effects of operating conditions, therefore temperature has little or no effect on permeances. Water permeances of the E/B/W mixture (**Figure 30** (a)) are in accordance with the results published by Koch and Górak [130] for the water-acetone-isopropanol ternary mixture (with PERVAP 1210 membrane), although they investigated membrane performance in a much higher water concentration range (5-30 wt%). Water permeances show a rather linear characteristic in that range, as opposed to
the exponential trend presented for the ethanol-n-butanol-water mixture of this work. The effect of different organic solvent ratios is more pronounced here. Permeances of ethanol and butanol (Figure 30 (b) and (c)) show a minimum at 1:1 ratio similar to the fluxes, but the clear maximal values are at 1:2 ethanol to n-butanol ratio, with the most significant differences at the high feed water content range. The figure suggests that butanol molecules might permeate more easily than ethanol molecules. The permeate water content is the highest at the 1:1 ratio, while the values for the 2:1 and 1:2 ratios are comparable.

![Figure 30](image)

**Figure 30** The activity of water as a function of water content and temperature (a), and the effect of water activity and temperature on the permeances of water (b), ethanol (c) and n-butanol (d) for the E/B/W ternary mixture

To examine if the elevated permeances of the 1:2 mixtures are dependent of the activity of water, the differences of water activity between the three organic ratios were calculated and illustrated in **Figure 31**.

![Figure 31](image)

**Figure 31** The activity of water as a function of water content and temperature (a), and the effect of water activity and temperature on the permeances of water (b), ethanol (c) and n-butanol (d) for the E/B/W ternary mixture
Figure 31 (a) depicts the activity of water as a function of water concentration, showing that the water activity in the 1:2 EtOH:BuOH ratio is slightly higher than that of the 1:1 and 2:1 ratios. Therefore, component permeances were plotted in the function of water activity as well in Figure 31 (b), (c) and (d). This representation brought the curves closer and caused the 2:1 ratios to exceed that of the 1:2 ratios for all three components at lower water activities. This suggests that the elevated permeances of ethanol and butanol at 1:2 ratio in Figure 30 was possibly caused by the elevated water activity at that concentration ratio. However, mixtures with the 1:1 EtOH:BuOH ratios still generally exhibit the lowest permeances for ethanol and butanol. Exponential increase is still very much pronounced for all components. It can be seen in Table 7 that the solubility parameter distance of water (value indicated by superscript ^b in the table) is the smallest, meaning that it is the best solvent for PVA. This supports the well-known swelling effect of water on PVA membranes, and explains the exponential increase of permeances with increasing water concentration. The $R_a$ distance of ethanol is smaller than that of butanol, suggesting its better swelling ability, which can explain the elevated values for the 2:1 ratio in Figure 31.

Increasing the water content in the feed results in decreased selectivity (Figure 32), i.e. lower permeate concentration of water (Figure 30 (d)) with the highest values at the 1:1 EtOH:BuOH ratio, which can also prove the theory of larger aggregates at 1:1.

![Figure 32 Influence of feed water concentration and EtOH:BuOH ratio on the selectivity of PERVAP 1210 membrane.](image-url)
5.1.2 Ethanol/ethyl acetate/water (E/A/W) ternary mixture

The influence of feed water content and temperature on total and partial fluxes of water, ethanol and ethyl acetate is depicted in Figure 33. All fluxes follow an exponential increase with the feed water content, also increasing with elevated temperatures. Partial fluxes of water follow the same trend as the total fluxes with no clear influence of organic ratios. Ethanol fluxes are the highest at 2:1 EtOH to EtAc ratios while partial fluxes of ethyl acetate are the highest at 1:2 ratios, likely caused by their higher driving forces. An overall minimum of 1:1 ethanol to ethyl acetate ratio can be noticed in the case of the E/A/W mixture, similar to what has been observed with the E/B/W ternary mixture.

Figure 33 Effect of water concentration and feed EtOH:EtAc ratios on total fluxes (a) at 60, 75 and 90°C, and on partial fluxes of water (b), ethanol (c) and ethyl acetate (d) at 75°C for E/A/W ternary mixture
Figure 34 shows that the 1:2 EtOH to EtAc ratio resulted in higher permeances for both organics at higher water content of the feed mixture. A minimum at 1:1 ratio was also found here, whereas no clear difference can be seen at water permeances. The effect of temperature on permeances is far less pronounced than on fluxes. The permeate has the highest water content at 1:1 EtOH to EtAc ratio, similar to that of the E/B/W mixture with a maximum at around 0.15 molar fraction of water in the feed. Permeate water concentrations exceed 94 mol% at every experimental point for both ternary mixtures.

![Figure 34](image)

Figure 34 Effect of water concentration on the permeance of water (a), ethanol (b), ethyl acetate (c) and the water content of the permeate (d) for the E/A/W ternary mixture at 60, 75 and 90°C and ethanol ethyl acetate ratios of 2:1, 1:1 and 1:2.

The effects of water activity were studied for this mixture too, therefore changes of the activity of water at different solvent ratios were depicted in Figure 35 (a).
Figure 35 Activity of water as a function of water content (a) and the effect of water activity on the permeance of water (b), ethanol (c), ethyl acetate (d) for the E/A/W ternary mixture at 60, 75 and 90°C and ethanol ethyl acetate ratios of 2:1, 1:1 and 1:2.

The activities of the 1:2 ratio exceed those of the other two solvent ratios, even further than in the case of the E/B/W mixture. Water permeances (Figure 35 (b)) reflect slightly the solubility order established by Table 7, but the permeances are generally quite comparable for all ratios. The permeances of the 2:1 EtOH:EtAc ratios are the highest at lower water content for both EtOH and EtAc with no clear difference between the 1:1 and 1:2 mass ratios (Figure 35 (c) and (d)). Higher values for the ratio with greater ethanol content reflect, again, the solubility order based on the solubility difference values of the solvents, where ethanol is the closest to the PVA in the solubility sphere of the polymer.

Yuan et al. [129] experimented with a ternary mixture of EtAc/EtOH/water with feed concentrations of 90/2/8 wt% through a self-prepared PVA/PAN composite membrane. They found that ethyl acetate concentration in the permeate was higher than that of ethanol, even though the affinity of ethanol towards PVA should be higher. The authors
explained this behavior by the very high (90 wt%) concentration of EtAc in the feed increasing its driving force so that it exceeds the effect of the higher solubility of ethanol. Experiments of the present study resulted in higher concentration of ethanol in the permeate at all investigated organic ratios, with maximal values at 0.055 mol/mol EtOH and 0.005 mol/mol EtAc (not shown here). The highest selectivity was achieved at 1:1 ratios at all temperatures (Figure 36), which clearly indicates the dependence of membrane performance from the concentration ratios of the two organics.

Figure 36 Influence of feed composition on the selectivity of PERVAP 1210 membrane at 60, 75 and 90°C for the different ratios of EtOH:EtAc in the E/A/W ternary mixture.

A maximum can be seen at ~0.15 molar fraction of water, above which selectivity decreased. This can be caused by a competition between water and organic molecules for the sorption places in the membrane [133]. Until this threshold, organic components can occupy the sorption sites, hindering water components from sorption and permeation. At water concentration of 0.15-0.2 there are enough water molecules to sorbe and permeate, however, exceeding this concentration, the swelling of the membrane increases organic permeation. The significance of this phenomenon is less expressed with increasing temperature, as the effect of the thermal movement of polymer chains dominates permeation.
5.1.3 Comparison of membrane performance for the studied mixtures

To compare experimental results of the two ternary mixtures, partial fluxes of water and ethanol for all investigated mixtures at 90°C are depicted in Figure 37 (a) and (b), with the addition of experimental results of binary ethanol/water (E/W) dehydration (see Appendix B).

![Figure 37 Comparison of partial fluxes of water (a), ethanol (b), n-butanol and ethyl acetate (c) and membrane selectivity (d) for E/W, E/B/W and E/A/W mixtures measured with PERVAP 1210 membrane at 90°C](image)

Water fluxes are higher for the binary mixture than for both ternary mixtures, suggesting that the addition of BuOH and EtAc hinders permeation as they are worse solvents of the PVA with decreased swelling ability. The different third component (ethyl acetate or n-butanol) does not have significant influence on water fluxes, i.e. the performance of the membrane in the case of the ternary mixtures. Organic ratios had more influence on ethanol fluxes. Binary fluxes exceed that of the ethanol-dominated 2:1 ratios. In E/B/W mixtures, a minimum can be seen at 1:1 ratio, caused probably by the
aforementioned aggregate formation between ethanol and BuOH. For E/A/W mixtures 1:2 ratio has the lowest ethanol permeance.

Butanol partial fluxes are generally higher than ethyl acetate fluxes (Figure 37 (c)) at all ratios, with particularly high BuOH fluxes of the 1:2 ratio, resulting from the greater driving force of BuOH. Selectivity of the binary E/W mixture is higher than that of the 2:1 ratios (Figure 37 (d)). This means that adding a relatively low amount of a third component decreases membrane selectivity, however, values of the 1:1 ratios exceeded binary results.

Permeance of water is the highest in all experiments due to the hydrophilic nature of PVA. Permeances for ethanol and butanol of the E/B/W ternary mixture were in the same range, while ethanol has an order of magnitude higher permeance than ethyl-acetate in all investigated temperatures in the case of the E/A/W mixture (see Figure 30 and Figure 34). This behaviour can be predicted based on the solubility parameter theory (section 2.2.1.1 and Table 7).

Hansen solubility parameters of the studied components and PVA are shown in Table 7. Water has a total solubility parameter closest to that of the PVA polymer, while the $\delta_t$ value of ethyl acetate differs most from that of the membrane. Permeances of ethyl acetate are more than an order of magnitude smaller than that of ethanol, which may be the result of the solubility parameter differences of PVA and the solvents, beside their size difference. However, conclusions can be better drawn on the basis of the solubility parameters of the actual mixtures, which were calculated by Equation (2.11), followed by the calculation of the solubility parameter distances ($R_a$) of these compositions from PVA, as the center of its interaction sphere. The exact $R_a$ results can be found in Appendix C. Figure 38 (a) depicts that with the increasing water content of the feed $R_a$ values are decreasing, indicating that with the addition of water as a good solvent, the mixtures are becoming more soluble in PVA. According to the figure, 2:1 ethanol to solvent ratios of both mixtures have the lowest $R_a$ values, thus, the highest solubility in PVA. They are followed by the 1:1 and 1:2 ratios, as the concentration of the poorer solvents (n-butanol and ethyl acetate) increases. This trend is partially reflected in the results of the ternary mixtures of the present study, where the permeances of the ethanol dominated mixtures with 2:1 ratios were the highest. However, 1:2 mixtures had similar or even higher permeances than 1:1 ratios. This might be caused by the elevated activities of water, as the best solvent, at 1:2 ratios shown in Figure 31 (a) and Figure 35 (a).
On the other hand, Hansen emphasizes in his work that molar volumes should also be considered in the solubility investigations [18]. This is demonstrated in Figure 38 (b), showing the decreased permeances of the components with greater molar volume. In the case of these ternary mixtures of E/A/W and E/B/W the excess molar volume caused by the complex intermolecular forces between the components can also play a role in the permeation characteristics of the different compositions.

**Figure 38** Influence of water concentration on the Hansen solubility parameter distances of the mixtures (a) and molar volume (b) of the studied mixtures on their measured permeance values at 90°C with 15 wt% feed water content.

It can be seen that the combined effects of solubility parameters and molar volumes is rather complicated, therefore the explanation of the permeation behaviour of these highly non-ideal aqueous mixtures by solubility parameters alone is insufficient. Both size and solubility parameters (polarity, hydrogen-bonding capacity) have an influence on permeation, and the aspect ratio (i.e. linearity) of the molecules also plays an important role according to Qiao et al. and Jiang et al. [45,61]. They investigated the dehydration of isopropanol and butanol isomers and found that the higher the linearity, the easier it is for the alcohol to penetrate the membrane network, which results in higher fluxes and permeances.

### 5.2 Proposed transport model

The applicability of the modified, exponential semi-empirical model suggested above in section 4.2 was tested for the ternary mixtures. To determine \( D_{i0}^* \), \( E_i \) and the exponential constant, the same parameter fitting procedure was carried out in the Statistica
program as described in section 4.2.1. The results were evaluated based on the objective function defined in Equation (4.7).

Modelling results can be seen in Table 21 and Table 22 for the EtOH/BuOH/water and the EtOH/EtAc/water ternary systems, respectively. In the Model column of the tables, the different tested exponential terms of the transport coefficient are listed. It was found that Equation (4.8) (only taking into account the concentration of the key component) resulted in huge deviations between measured and predicted partial fluxes in the case of the ternary mixtures. These modelling results can be seen in the first rows of each solvent in Table 21 and Table 22.

Koch and Górak [130] also revealed a strong coupling between molar permeances of water and organic components in their investigated acetone-isopropanol-water ternary system. However, as they observed, there was no coupling between the organic components of acetone and isopropanol. Thus, their mass transport model for molar permeances included a dependence only on water mass fraction. Several authors only included water concentration in their models, considering exclusively the coupling between organic and water fluxes. This option was also tested, including only the water molar fraction in the feed mixture in one case, and water molar fraction times its mean activity coefficient in the other. These models were in significantly better accordance with measured fluxes of the E/A/W system (R>0.9), but still showed poor results for the E/B/W ternary system (R≈0.5-0.6). In the case of the water-acetone-isopropanol mixture [130], acetone and isopropanol have very similar activity coefficients both at the feed mixture and on the permeate side of the membrane. The ternary mixtures in this current work, however, exhibit strong non-ideality with great differences between the activity coefficients of ethanol-ethyl acetate and ethanol-n-butanol under permeate conditions, reflected also by the several binary and ternary homogeneous and heterogeneous azeotropes (Table 6).

The experimental results showed that in the case of EtOH/EtAc/water and EtOH/BuOH/water ternary mixtures, the ratio of the two organic compounds was an important factor beside water concentration. Therefore, a further development of the model became necessary, including the feed concentrations of all three components and their mean activity coefficients through the composite membrane, resulting in the following complete model:
\[ J_i = \frac{D_0 i \exp(A_{ii} x_i \bar{Y}_i + B_{ij} x_j \bar{Y}_j + C_{ik} x_k \bar{Y}_k)}{\bar{Y}_i} \left( \frac{p_{iF} - p_{iP}}{p_{i0}} \right), \]

(5.1)

where the number of parameters to be fitted is reduced to 5: \( D_0 i, E_i, A_{ii}, B_{ij}, \) and \( C_{ik}. \)

Activity coefficients in the mixtures at the feed side and the permeate side were determined by the UNIQUAC model of Abrams and Prausnitz [75], broadly used for the description of vapour-liquid and liquid-liquid equilibria.

The reason why the amendment was necessary is that the sorption of permeants is likely to be non-ideal in these ternary systems; therefore, the activity coefficients across the membrane are not constant. Preferential sorption might occur on the feed side, causing a strong variation of activity coefficients [169]. This proposed model does not contain the expression and calculation of activity coefficients inside the membrane material (used for example in Flory–Huggins thermodynamics [170]), although they are taken into consideration by the average activity coefficients. These averages include both the feed side and the permeate side activity coefficients, without having to conduct additional sorption experiments.

Table 19 and Table 20 show the activity coefficients of the binary and ternary mixtures of the solvents applied in the present study, as well as the solvents (acetone, isopropanol, water) used by Koch and Górak [130], at fixed water or ethanol concentrations in the mixtures at the feed and the permeate side, respectively.

| Table 19 Activity coefficients at 30 mol% water, 60°C (30 mol% EtOH in EtOH-BuOH, EtOH-EtAc) calculated with the UNIQUAC model in Aspen Properties |
|---|---|---|---|---|---|---|---|
| Ternary | Binary | Binary | Ternary | Binary | Binary | Binary | Ternary |
| EtOH- | EtOH- | EtAc- | EtOH- | BuOH- | EtOH- | EtOH- | Ace- |
| EtAc- | Water | Water | BuOH- | Water | BuOH | EtAc | Ipa- |
| Water | Water | Water | Water | Water | Water | Water | Water |
| Water | 2.5154 | 1.8573 | 3.8902 | 2.2775 | 2.7593 | 2.1774 |
| Ethanol | 1.1447 | 1.0701 | 1.0065 | 1.0488 | 1.5850 |
| Ethyl acetate | 1.6779 | 1.1373 | 1.0940 |
| n-Butanol | 1.2131 | 1.0859 | 1.0104 |
| Acetone | 1.2908 |
| Isopropanol | 1.2880 |
Table 20 Activity coefficients at 98 mol% water, 60°C (98 mol% EtOH in EtOH-BuOH, EtOH-EtAc) calculated with the UNIQUAC model in Aspen Properties

<table>
<thead>
<tr>
<th></th>
<th>Ternary EtOH-</th>
<th>Binary EtOH-Water</th>
<th>Ternary EtOH-EtAc-Water</th>
<th>Ternary EtOH-BuOH-Water</th>
<th>Binary EtOH-BuOH-Water</th>
<th>Ternary EtOH-EtAc-Water</th>
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<td>1.0039</td>
<td>1.0020</td>
<td>1.0032</td>
<td>1.0018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.6014</td>
<td>4.8092</td>
<td>4.6091</td>
<td>1.0000</td>
<td>1.0003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>64.879</td>
<td>58.508</td>
<td></td>
<td>2.4391</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butanol</td>
<td></td>
<td></td>
<td>25.478</td>
<td>23.835</td>
<td>1.0861</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.7367</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.256</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen that the activity coefficients in the ternary mixtures differ from that of the binary ones, showing a difference in the extent of non-idealities. In the ternary mixture of acetone-isopropanol-water the activity coefficients of the organic solvents are quite similar both at the feed and the permeate side compared to the ternary mixtures of E/B/W and E/A/W. This can explain why the model of Koch and Górak included solely the water concentration and gave good results, as the permeating organics do not affect each other significantly. Regression of the amended, “complete” mass transport model (Equation (5.1)) resulted in the best fit to measured data shown in the last rows for each component in Table 21 and Table 22. The comparison of the measured and predicted total fluxes is depicted in Figure 39 (a) and (b) for the E/A/W and E/B/W mixtures, respectively.

Figure 39 Measured and modelled total fluxes (Equation. (5.1)) for the E/A/W ternary mixture (a) and E/B/W mixture (b) for 2:1, 1:1, and 2:1 organic ratios at 60, 75 and 90°C on PERVAP 1210 membrane
Table 21: Modelling results for the ethanol-n-butanol-water ternary mixture based on Equation (5.1), changing the exponential term of the transport coefficient. $D_{i0}^*$, $E_i$, $A_{ii}$, $B_{ij}$, $C_{ik}$ are regressed parameters of the pre-exponential factor of the transport coefficient, the activation energy (Eq. (2.32)) and the constants for each component of the mixture, respectively. OF represents the objective functions of the regression.

<table>
<thead>
<tr>
<th>Component</th>
<th>Model</th>
<th>$D_{i0}^*$</th>
<th>$E_{i0}$</th>
<th>$A_i$ ($A_{ii}$)</th>
<th>$B_{ij}$</th>
<th>$C_{ik}$</th>
<th>OF</th>
<th>$R^2$</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$\exp(A_w \cdot x_{w1})$</td>
<td>4.07E-04</td>
<td>57603</td>
<td>5.53</td>
<td></td>
<td></td>
<td>5.1958</td>
<td>0.9089</td>
<td>0.8262</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_w \cdot x_{w1} \overline{y}_w)$</td>
<td>2.64E-04</td>
<td>61359</td>
<td>4.18</td>
<td></td>
<td></td>
<td>5.6686</td>
<td>0.9149</td>
<td>0.8370</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_{ww} \cdot x_{w1} \overline{y}<em>w + B</em>{we} \cdot x_{e1} \overline{y}<em>e + C</em>{wb} \cdot x_{b1} \overline{y}_b)$</td>
<td>3.35E-02</td>
<td>40097</td>
<td>1.37</td>
<td>-1.01</td>
<td>-0.45</td>
<td>2.6049</td>
<td>0.9262</td>
<td>0.8579</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$\exp(A_e \cdot x_{e1})$</td>
<td>3.01E-05</td>
<td>58682</td>
<td>-4.33</td>
<td></td>
<td></td>
<td>22.6921</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_e \cdot x_{w1})$</td>
<td>8.50E-08</td>
<td>89002</td>
<td>13.25</td>
<td></td>
<td></td>
<td>14.7477</td>
<td>0.6202</td>
<td>0.3846</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_e \cdot x_{w1} \overline{y}_w)$</td>
<td>2.81E-08</td>
<td>97503</td>
<td>10.37</td>
<td></td>
<td></td>
<td>15.1674</td>
<td>0.6446</td>
<td>0.4155</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_{ee} \cdot x_{e1} \overline{y}<em>e + B</em>{eb} \cdot x_{b1} \overline{y}_b)$</td>
<td>2.25E+00</td>
<td>21488</td>
<td>-4.93</td>
<td>-1.30</td>
<td></td>
<td>4.3227</td>
<td>0.9091</td>
<td>0.8265</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_{ee} \cdot x_{e1} \overline{y}<em>e + B</em>{eb} \cdot x_{b1} \overline{y}<em>b + C</em>{ew} \cdot x_{w1} \overline{y}_w)$</td>
<td>4.11E-01</td>
<td>26548</td>
<td>-4.37</td>
<td>-1.18</td>
<td>1.42</td>
<td>3.7888</td>
<td>0.9135</td>
<td>0.8345</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>$\exp(A_b \cdot x_{b1})$</td>
<td>4.66E-05</td>
<td>46755</td>
<td>-5.92</td>
<td></td>
<td></td>
<td>18.0525</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_b \cdot x_{w1})$</td>
<td>1.17E-07</td>
<td>83679</td>
<td>11.08</td>
<td></td>
<td></td>
<td>15.5124</td>
<td>0.5507</td>
<td>0.3032</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_b \cdot x_{w1} \overline{y}_w)$</td>
<td>4.14E-08</td>
<td>93319</td>
<td>8.41</td>
<td></td>
<td></td>
<td>16.3616</td>
<td>0.5637</td>
<td>0.3178</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_{bb} \cdot x_{b1} \overline{y}<em>b + B</em>{be} \cdot x_{e1} \overline{y}_e)$</td>
<td>4.09E-01</td>
<td>29329</td>
<td>-1.33</td>
<td>-4.25</td>
<td></td>
<td>6.4219</td>
<td>0.9062</td>
<td>0.8212</td>
</tr>
<tr>
<td></td>
<td>$\exp(A_b \cdot x_{b1} \overline{y}<em>b + B</em>{be} \cdot x_{e1} \overline{y}<em>e + C</em>{wb} \cdot x_{w1} \overline{y}_w)$</td>
<td>2.54E-02</td>
<td>32555</td>
<td>-1.07</td>
<td>-3.24</td>
<td>2.56</td>
<td>4.0555</td>
<td>0.9359</td>
<td>0.8760</td>
</tr>
</tbody>
</table>
Table 22 Modelling results for the ethanol/ethyl acetate/water ternary mixture based on Equation (5.1), changing the exponential term of the transport coefficient. \( D_{i0} \), \( E_i \), \( A_{ii} \), \( B_{ij} \), \( C_{ik} \) are regressed parameters of the pre-exponential factor of the transport coefficient, the activation energy (Equation (2.32)) and the constants for each component of the mixture, respectively. OF represents the objective functions of the regression.

<table>
<thead>
<tr>
<th>Component</th>
<th>Model</th>
<th>( D_{i0} )</th>
<th>( E_i )</th>
<th>( A_{i} (A_{ii}) )</th>
<th>( B_{ij} )</th>
<th>( C_{ik} )</th>
<th>OF</th>
<th>( R^2 )</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>( \exp(A_w \cdot x_{w1}) )</td>
<td>6.50E-04</td>
<td>51730</td>
<td>5.25</td>
<td></td>
<td></td>
<td>1.3248</td>
<td>0.9754</td>
<td>0.9513</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_w \cdot x_{w1} \cdot \bar{y}_w) )</td>
<td>4.42E-04</td>
<td>54180</td>
<td>4.18</td>
<td></td>
<td></td>
<td>1.3226</td>
<td>0.9795</td>
<td>0.9593</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_w \cdot x_{w1} \cdot \bar{y}<em>w + B</em>{we} \cdot x_{e1} \cdot \bar{y}<em>e + C</em>{wa} \cdot x_{a1} \cdot \bar{y}_a) )</td>
<td>2.42E-03</td>
<td>49312</td>
<td>3.14</td>
<td>-0.52</td>
<td>-0.19</td>
<td>1.1015</td>
<td>0.9724</td>
<td>0.9456</td>
</tr>
<tr>
<td>Ethanol</td>
<td>( \exp(A_e \cdot x_{e1}) )</td>
<td>1.56E-04</td>
<td>51943</td>
<td>-4.74</td>
<td></td>
<td></td>
<td>19.3801</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_e \cdot x_{w1}) )</td>
<td>4.69E-07</td>
<td>63466</td>
<td>15.20</td>
<td></td>
<td></td>
<td>11.2334</td>
<td>0.9047</td>
<td>0.8184</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_e \cdot x_{w1} \cdot \bar{y}_w) )</td>
<td>1.28E-07</td>
<td>68533</td>
<td>13.01</td>
<td></td>
<td></td>
<td>10.4007</td>
<td>0.9466</td>
<td>0.8961</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_e \cdot x_{e1} \cdot \bar{y}<em>e + B</em>{ea} \cdot x_{a1} \cdot \bar{y}_a) )</td>
<td>7.32E+00</td>
<td>21909</td>
<td>-5.69</td>
<td>-1.46</td>
<td></td>
<td>2.0957</td>
<td>0.9717</td>
<td>0.9442</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_e \cdot x_{e1} \cdot \bar{y}<em>e + B</em>{ea} \cdot x_{a1} \cdot \bar{y}<em>a + C</em>{ew} \cdot x_{w1} \cdot \bar{y}_w) )</td>
<td>1.31E+00</td>
<td>25855</td>
<td>-5.08</td>
<td>-1.32</td>
<td>1.34</td>
<td>1.8158</td>
<td>0.9708</td>
<td>0.9424</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>( \exp(A_a \cdot x_{a1}) )</td>
<td>9.14E-07</td>
<td>61183</td>
<td>3.56</td>
<td></td>
<td></td>
<td>19.5027</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_a \cdot x_{w1}) )</td>
<td>2.61E-07</td>
<td>64797</td>
<td>12.36</td>
<td></td>
<td></td>
<td>10.5431</td>
<td>0.9299</td>
<td>0.8646</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_a \cdot x_{w1} \cdot \bar{y}_w) )</td>
<td>8.33E-08</td>
<td>69872</td>
<td>10.59</td>
<td></td>
<td></td>
<td>10.2964</td>
<td>0.9752</td>
<td>0.9510</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_a \cdot x_{a1} \cdot \bar{y}<em>a + B</em>{ae} \cdot x_{e1} \cdot \bar{y}_e) )</td>
<td>2.14E-01</td>
<td>27347</td>
<td>-1.13</td>
<td>-4.64</td>
<td></td>
<td>3.3068</td>
<td>0.9797</td>
<td>0.9597</td>
</tr>
<tr>
<td></td>
<td>( \exp(A_a \cdot x_{a1} \cdot \bar{y}<em>a + B</em>{ae} \cdot x_{e1} \cdot \bar{y}<em>e + C</em>{aw} \cdot x_{w1} \cdot \bar{y}_w) )</td>
<td>1.17E-01</td>
<td>29240</td>
<td>-1.09</td>
<td>-4.44</td>
<td>0.46</td>
<td>3.2781</td>
<td>0.9792</td>
<td>0.9589</td>
</tr>
</tbody>
</table>
5.2.1 Testing the complete model for binary cases

This further model development was also tested for the binary mixtures of section 4. The concentrations of both components were included along with their average activity differences. Results of the calculations can be seen in Table 23. Although the extended, complete model improved the fitness of the model, this improvement is not as significant as in the ternary cases. Therefore, the application of Model II., that is, Equation (4.8), is suggested for modelling the pervaporative dehydration of binary mixtures.
Table 23: Modelling results for binary mixtures based on Equation (5.1), changing the exponential term of the transport coefficient. $D_{i0}$, $E_i$, $A_{ii}$, $B_{ij}$, are regressed parameters of the pre-exponential factor of the transport coefficient, the activation energy (Eq. (2.32)) and the constants for each component of the mixture, respectively. OF represents the objective functions of the regression.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Component</th>
<th>Model</th>
<th>$D_{i0}$</th>
<th>$E_{i0}$</th>
<th>$A_i$ ($A_{ii}$)</th>
<th>$B_{ij}$</th>
<th>OF</th>
<th>$R^2$</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol–water</td>
<td>Water</td>
<td>$\exp(A_w \cdot x_{w1})$</td>
<td>2.02E-04</td>
<td>77877</td>
<td>2.63</td>
<td>0.1444</td>
<td>0.9932</td>
<td>0.9864</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_w \cdot x_{w1} \cdot \bar{y}_{w})$</td>
<td>1.72E-04</td>
<td>78697</td>
<td>2.22</td>
<td>0.1717</td>
<td>0.9909</td>
<td>0.9819</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_{ww} \cdot x_{w1} \cdot \bar{y}<em>{w} + B</em>{we} \cdot x_{e1} \cdot \bar{y}_{e})$</td>
<td>1.21E-03</td>
<td>75605</td>
<td>1.06</td>
<td>-0.73</td>
<td>0.1628</td>
<td>0.9932</td>
<td>0.9865</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>$\exp(A_e \cdot x_{e1})$</td>
<td>1.93E-05</td>
<td>128573</td>
<td>-8.68</td>
<td>2.2473</td>
<td>0.9626</td>
<td>0.9265</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_{ee} \cdot x_{e1} \cdot \bar{y}<em>{e} + B</em>{we} \cdot x_{w1} \cdot \bar{y}_{w})$</td>
<td>3.26E-02</td>
<td>100973</td>
<td>-5.96</td>
<td>-2.99</td>
<td>0.4488</td>
<td>0.9874</td>
<td>0.9750</td>
</tr>
<tr>
<td></td>
<td>n-Butanol</td>
<td>Water</td>
<td>3.44E-04</td>
<td>25711</td>
<td>10.32</td>
<td>1.3584</td>
<td>0.9000</td>
<td>0.8099</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_w \cdot x_{w1})$</td>
<td>1.09E-04</td>
<td>31854</td>
<td>8.39</td>
<td>0.5633</td>
<td>0.9694</td>
<td>0.9397</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_{ww} \cdot x_{w1} \cdot \bar{y}<em>{w} + B</em>{wb} \cdot x_{b1} \cdot \bar{y}_{b})$</td>
<td>4.85E-05</td>
<td>35640</td>
<td>8.57</td>
<td>0.09</td>
<td>0.4601</td>
<td>0.9887</td>
<td>0.9775</td>
</tr>
<tr>
<td></td>
<td>n-Butanol</td>
<td>$\exp(A_{b} \cdot x_{b1})$</td>
<td>5.82E+00</td>
<td>29711</td>
<td>-14.37</td>
<td>1.0618</td>
<td>0.9694</td>
<td>0.9397</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_{bb} \cdot x_{b1} \cdot \bar{y}<em>{b} + B</em>{wb} \cdot x_{w1} \cdot \bar{y}_{w})$</td>
<td>2.55E-06</td>
<td>31200</td>
<td>-0.13</td>
<td>11.26</td>
<td>0.6112</td>
<td>0.9979</td>
<td>0.9957</td>
</tr>
<tr>
<td></td>
<td>Isobutanol</td>
<td>Water</td>
<td>1.17E-03</td>
<td>49815</td>
<td>5.05</td>
<td>0.3927</td>
<td>0.9764</td>
<td>0.9533</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_w \cdot x_{w1})$</td>
<td>9.33E-04</td>
<td>50199</td>
<td>3.77</td>
<td>0.2467</td>
<td>0.9878</td>
<td>0.9757</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_{ww} \cdot x_{w1} \cdot \bar{y}<em>{w} + B</em>{wibu} \cdot x_{ibu1} \cdot \bar{y}_{ibu})$</td>
<td>3.73E-05</td>
<td>53897</td>
<td>4.44</td>
<td>0.73</td>
<td>0.1439</td>
<td>0.9883</td>
<td>0.9767</td>
</tr>
<tr>
<td></td>
<td>Isobutanol</td>
<td>$\exp(A_{ibu} \cdot x_{ibu1})$</td>
<td>7.41E-02</td>
<td>45121</td>
<td>-8.47</td>
<td>1.6077</td>
<td>0.8712</td>
<td>0.7591</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\exp(A_{ibu} \cdot x_{ibu1} \cdot \bar{y}<em>{ibu} + B</em>{bw} \cdot x_{w1} \cdot \bar{y}_{w})$</td>
<td>3.81E-06</td>
<td>46250</td>
<td>0.26</td>
<td>6.52</td>
<td>0.9623</td>
<td>0.9314</td>
<td>0.8675</td>
</tr>
</tbody>
</table>
5.2.2 Model simplification options

To avoid redundancy, this extended model can be simplified with a minimal decrease of the coefficient of determination. In the case of water, which is the preferably permeating component, it is sufficient if the exponential factor of the transport coefficient contains only the feed water concentration and its mean activity coefficient. As the permeating amount of the organic components is small, the exclusion of their concentrations from the water flux model is acceptable causing only a small relative standard error. Similarly to our previous model for binary mixtures, the concentration of water can be omitted from the description of the organic partial fluxes. Molar fractions and mean activity coefficients of both organic components have to be included, though, in order to achieve the desired accuracy of the model, since their permeation is interdependent. The same absolute error caused by neglecting the organic components effect would result in a greater relative error here. Applying these simplifications, the model accuracy is sufficient for both mixtures. Objective functions are close to the ones of the complex model (Equation. (5.1)) and R superscript 2 values exceed 0.97 and 0.90 for E/A/W and E/B/W mixtures, respectively. Regression of the various model modifications was also performed for the experimental data of Koch and Górak, the results of which can be found in Appendix D.

Taking these aspects into consideration, Table 24 summarizes the suggested models for both binary and ternary mixtures for hydrophilic pervaporation.

<table>
<thead>
<tr>
<th></th>
<th>Binary mixture</th>
<th>Ternary mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$J_i = \frac{D_{i0} \exp(A_i x_{iF})}{\bar{y}<em>i} \left(\frac{p</em>{IF} - p_{iP}}{p_{i0}}\right)$</td>
<td>$J_i = \frac{D_{i0} \exp(A_i x_{iF} y_i)}{\bar{y}<em>i} \left(\frac{p</em>{IF} - p_{iP}}{p_{i0}}\right)$</td>
</tr>
<tr>
<td>Organic component 1</td>
<td>$J_j = \frac{D_{j0} \exp(A_j x_{jF})}{\bar{y}<em>j} \left(\frac{p</em>{jF} - p_{jP}}{p_{j0}}\right)$</td>
<td>$J_j = \frac{D_{j0} \exp(A_j x_{jF} y_j + B_{jk} x_{kF} y_k)}{\bar{y}<em>j} \left(\frac{p</em>{jF} - p_{jP}}{p_{j0}}\right)$</td>
</tr>
<tr>
<td>Organic component 2</td>
<td>$J_k = \frac{D_{k0} \exp(A_{kk} x_{kF} y_k + B_{jk} x_{jF} y_j)}{\bar{y}<em>k} \left(\frac{p</em>{kF} - p_{kP}}{p_{k0}}\right)$</td>
<td></td>
</tr>
</tbody>
</table>

Table 24 Suggested mass-transport models for the dehydration of binary and ternary mixtures with pervaporation (i: water, j: organic component 1, k: organic component 2)
5.3 Conclusion

The proposed mass-transport model for the pervaporative dehydration of ternary mixtures is a semi-empirical one, eliminating the properties of the polymer material. Therefore, as is the case with most pervaporation models, experiments are essential to estimate parameters for the given system comprising of the liquid mixture and the polymer membrane. The model takes into account the strong non-ideality of the investigated ternary mixtures by incorporating the activity coefficients as well as concentrations into the exponential term. Simplifications were also suggested, without the significant reduction of model accuracy, and describing component permeation reasonably well.
6 Major new results

Thesis 1 [II]

I determined that the generally accepted solution-diffusion pervaporation model of Rautenbach is not applicable in a wide feed water concentration range. Based on dehydration experiments with the binary aqueous mixtures of ethanol, isobutanol and n-butanol with PVA/PAN composite membranes, I developed a new model that is more accurate in extended – up to 14.3-21.1 wt% – concentration ranges of water in the feed mixture. My development is based on the supplement of the mass transport coefficient with an exponential term, thus proving its concentration dependence.

Thesis 2 [I, III, IV]

I proved on the basis of process simulations of real case studies of alcohol dehydration with hybrid separation techniques that the utilization of my new pervaporation model delivers more reliable results than those of the original Rautenbach model. Thus, I verified the applicability of my model for industrial separation problems, the scope of which typically involves wider concentration ranges.

Thesis 3 [V]

I demonstrated the successful pervaporative dehydration of the ternary mixtures of ethanol/n-butanol/water and ethanol/ethyl acetate/water with a PVA/PAN composite membrane on an experimental basis, between 60-90°C and with feed water concentrations increased up to ~16 wt%. Permeate water concentrations exceed 94 mol% at every experimental point for both ternary mixtures. I detected that the partial flux and permeance values for both mixtures varied significantly depending on the concentration of the components in the feed mixture. I also showed that the permeation order of the studied components can be qualitatively determined based on the solubility parameter distances between the components and the membrane polymer.
Thesis 4 [V]

Based on the dehydration experiments with the ternary mixtures I determined considerable mutual interactions between the permeating components and between the components and the membrane, which significantly influence the mass transfer characteristics of the permeating species. Consequently, I determined that the exponential extension of my novel pervaporation model should include not only the compositions of the permeating compounds, but the average of their activity coefficients at the two sides of the membrane as well, constituting the complete model. I also determined simplification options for my new model in the case of the ternary mixtures, thus decreasing model complexity while preserving model accuracy.

Thesis 5

I detected that in the case of binary mixtures, the application of the complete model, with both components and their average activity coefficients as weighting factor, also improves the accuracy of the model. However, the relative improvement compared to the model of Thesis 1 is negligible; therefore the model extension can be omitted in the binary cases without significantly compromising model accuracy.
List of Publications

Publications related to the thesis


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Presentation


Posters


Other publications

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Appendices

Appendix A. Cost equations

Investment costs of a distillation column

- Investment costs of column and decanter externals:

\[
\text{Installed Cost (\$)} = \frac{M&S}{280} \cdot 101.9 \cdot D^{1.066} \cdot H^{0.802} \cdot (2.18 + F_c)
\]

where

- \(M&S\) Marshall-Swift index
- \(D\) diameter [ft]
- \(H\) height [ft]

Correction factor for columns:

\[F_c = F_m F_p\]

- \(F_m\) shell material: 2.25 (SS)
- \(F_p\) pressure: 1 (up to 50 psi)

- Investment cost of column trays:

\[
\text{Installed Cost (\$)} = \frac{M&S}{280} \cdot 4.7 \cdot D^{1.55} \cdot H \cdot F_c
\]

where

- \(M&S\) Marshall-Swift index
- \(D\) diameter [ft]
- \(H\) tray stack height [ft]

Correction factor for column trays:

\[F_c = F_s + F_t + F_m\]

- \(F_s\) tray spacing [in]: 1.0 (24)
- \(F_t\) tray type: 0.4 (Valve)
- \(F_m\) tray material: 1.7 (SS)
- **Investment costs of heat exchangers:**

\[
Cost (\$) = \frac{M&S}{280} \cdot 101.3 \cdot A^{0.65} \cdot (2.29 + F_c)
\]

where

- **M&S** Marshall-Swift index
- **A** surface area [ft²]

Correction factor for heat exchangers:

\[
F_c = (F_d + F_p) F_m
\]

- **F_d** design type: 1.35 (Kettle, reboiler)
- **F_p** design pressure: 0 (up to 150 psi)
- **F_m** shell and tube material: 3.75 (SS/SS)

- **Investment costs of permeate cooling:**

\[
Cost (\$) = \frac{M&S}{280} \cdot 517.5 \cdot bhp^{0.82} \cdot (2.11 + F_c)
\]

where

- **M&S** Marshall-Swift index
- **bhp** efficiency in brake horsepower

Correction factor for deep-freezer:

- **F_c = F_d**
- **F_d** design type: 1.0 (Centrifugal, motor)

\[
COP = 2
\]

- **Investment costs of membrane modules:**

\[
Cost (\$) = 51191 \cdot A^{0.562}
\]

Membrane replacement cost:

\[
Cost (\$) = 500 \cdot A
\]

where

- **A** membrane surface area [m²]
Appendix B. Pervaporation dehydration results of ethanol-water binary mixture

Partial flux and permeance results:

Figure B-1 Effect of water concentration and temperature on partial water flux (a), partial ethanol flux (b), water permeance (c) and ethanol permeance (d) at 60, 75 and 90°C for E/W binary mixture.
Permeate water content and selectivity:

**Figure B-2** Effect of feed water concentration on permeate water content (a) and selectivity (b) for E/W binary mixture at 60, 75 and 90°C
Table B-1 Modelling results for the ethanol/water binary mixture based on Eq. (5.1) changing the exponential term of the transport coefficient. $D_{i0}^*$, $E_i$, $A_i$, $B_{ij}$, are regressed parameters of the pre-exponential factor of the transport coefficient, the activation energy (Eq. (2.32)), and the constants for each component of the mixture, respectively. OF represents the objective functions of the regression. Subscript 1 stands for the feed side of the membrane.

<table>
<thead>
<tr>
<th>Model</th>
<th>$D_{i0}^*$</th>
<th>$E_i$</th>
<th>$A_i$ ($A_{ii}$)</th>
<th>$B_{ij}$</th>
<th>OF</th>
<th>R</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\exp(A_w \cdot x_{w1})$</td>
<td>2.09E-03</td>
<td>52392</td>
<td>2.07</td>
<td></td>
<td>0.1483</td>
<td>0.9845</td>
<td>0.9692</td>
</tr>
<tr>
<td>$\exp(A_w \cdot x_{w1} \cdot \bar{y}_w)$</td>
<td>1.94E-03</td>
<td>52987</td>
<td>1.58</td>
<td></td>
<td>0.1632</td>
<td>0.9817</td>
<td>0.9638</td>
</tr>
<tr>
<td>$\exp(A_{ww} \cdot x_{w1} \cdot \bar{y}<em>w + B</em>{we} \cdot x_{e1} \cdot \bar{y}_e)$</td>
<td>3.00E-02</td>
<td>49326</td>
<td>0.17</td>
<td>-1.19</td>
<td>0.1512</td>
<td>0.9913</td>
<td>0.9827</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\exp(A_e \cdot x_{e1})$</td>
<td>2.43E-02</td>
<td>44862</td>
<td>-6.78</td>
<td></td>
<td>0.2740</td>
<td>0.9344</td>
<td>0.8731</td>
</tr>
<tr>
<td>$\exp(A_e \cdot x_{w1} \cdot \bar{y}_w)$</td>
<td>2.17E-05</td>
<td>46493</td>
<td>5.26</td>
<td></td>
<td>0.2787</td>
<td>0.9221</td>
<td>0.8503</td>
</tr>
<tr>
<td>$\exp(A_{ee} \cdot x_{e1} \cdot \bar{y}<em>e + B</em>{ew} \cdot x_{w1} \cdot \bar{y}_w)$</td>
<td>2.55E-01</td>
<td>34043</td>
<td>-4.07</td>
<td>0.49</td>
<td>0.1149</td>
<td>0.9840</td>
<td>0.9683</td>
</tr>
</tbody>
</table>
Appendix C. Hansen solubility parameters and solubility parameter distances of the E/B/W and E/A/W ternary mixtures

Table C-1 Hansen solubility parameters and solubility parameter distances of the ethanol/n-butanol/water mixtures at 2:1, 1:1 and 1:2 EtOH to BuOH ratios

<table>
<thead>
<tr>
<th>Organic ratio</th>
<th>Water conc. [wt%]</th>
<th>Solubility parameters [MPa$^{1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{\delta}_d$</td>
</tr>
<tr>
<td>2:1</td>
<td>2</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16.2</td>
</tr>
<tr>
<td>1:1</td>
<td>2</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16.2</td>
</tr>
<tr>
<td>1:2</td>
<td>2</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Table C-2  Hansen solubility parameters and solubility parameter distances of the ethanol/ethyl acetate/water mixtures at 2:1, 1:1 and 1:2 EtOH to EtAc ratios

<table>
<thead>
<tr>
<th>Organic ratio</th>
<th>Water conc. [wt%]</th>
<th>( \delta_d )</th>
<th>( \delta_p )</th>
<th>( \delta_h )</th>
<th>( \delta_t )</th>
<th>( R_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>3</td>
<td>15.9</td>
<td>7.9</td>
<td>15.4</td>
<td>23.5</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>15.9</td>
<td>8.2</td>
<td>15.4</td>
<td>23.7</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.0</td>
<td>8.6</td>
<td>15.5</td>
<td>23.9</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16.1</td>
<td>9.1</td>
<td>15.6</td>
<td>24.2</td>
<td>5.0</td>
</tr>
<tr>
<td>1:1</td>
<td>3</td>
<td>16.0</td>
<td>7.4</td>
<td>13.5</td>
<td>22.3</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>16.1</td>
<td>7.7</td>
<td>13.6</td>
<td>22.5</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.0</td>
<td>8.1</td>
<td>13.7</td>
<td>22.5</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16.1</td>
<td>8.6</td>
<td>13.8</td>
<td>22.9</td>
<td>5.7</td>
</tr>
<tr>
<td>1:2</td>
<td>3</td>
<td>16.0</td>
<td>6.9</td>
<td>11.6</td>
<td>20.9</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>16.1</td>
<td>7.2</td>
<td>11.7</td>
<td>21.2</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16.0</td>
<td>7.5</td>
<td>11.8</td>
<td>21.3</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>16.1</td>
<td>8.1</td>
<td>12.1</td>
<td>21.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>
Appendix D. Modelling results for the acetone-isopropanol-water ternary mixture

Table D-1 Modelling results for the acetone-isopropanol-water ternary mixture based on the experimental results of Koch and Górak [130]. Model column lists the variations of the exponential term of the transport coefficient in Equation (5.1). $D_{i0}$, $E_{i0}$, $A_{ii}$, $B_{ij}$, $C_{ik}$ are regressed parameters of the pre-exponential factor of the transport coefficient, the activation energy (Equation (2.32)), and the constants for each component of the mixture, respectively. OF represents the objective functions of the regression.

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>$D_{i0}$</th>
<th>$E_{i0}$</th>
<th>$A_{ii}$ (A_{ij})</th>
<th>$B_{ij}$</th>
<th>$C_{ik}$</th>
<th>OF</th>
<th>R</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>exp($A_w \cdot x_{w1}$)</td>
<td>2.82E-03</td>
<td>44499</td>
<td>2.56</td>
<td></td>
<td></td>
<td>0.1583</td>
<td>0.9893</td>
<td>0.9787</td>
</tr>
<tr>
<td></td>
<td>exp($A_w \cdot x_{w1} \cdot \bar{Y}_w$)</td>
<td>1.53E-03</td>
<td>45980</td>
<td>2.90</td>
<td></td>
<td></td>
<td>0.1075</td>
<td>0.9933</td>
<td>0.9866</td>
</tr>
<tr>
<td></td>
<td>exp($A_{ww} \cdot x_{w1} \cdot \bar{Y}<em>w$+B</em>{wa} \cdot x_{a1} \cdot \bar{Y}<em>a$+$C</em>{wa} \cdot x_{i1} \cdot \bar{Y}_i$)</td>
<td>8.73E-08</td>
<td>68518</td>
<td>9.52</td>
<td>2.06</td>
<td>1.84</td>
<td>0.0334</td>
<td>0.9964</td>
<td>0.9928</td>
</tr>
<tr>
<td>Acetone</td>
<td>exp($A_a \cdot x_{a1}$)</td>
<td>4.29E-03</td>
<td>45126</td>
<td>-27.84</td>
<td></td>
<td></td>
<td>8.2705</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>exp($A_a \cdot x_{w1}$)</td>
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<td>Diffusion coefficient</td>
<td>$[m^2/s]$, $[m^2/h]$</td>
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<td>$f$</td>
<td>Fugacity</td>
<td>$[kPa]$, $[bar]$</td>
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<td>$F$</td>
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<td>$R_0$</td>
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<tr>
<td>$R_a$</td>
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\begin{itemize}
\item \( t \) \hspace{1cm} Time \hspace{1cm} \text{[h], [s]}
\item \( T \) \hspace{1cm} Temperature \hspace{1cm} \text{[°C], [K]}
\item \( T^* \) \hspace{1cm} Reference temperature \hspace{1cm} 293 K
\item \( V \) \hspace{1cm} Molar volume \hspace{1cm} \text{[cm}^3\text{/mol]}
\item \( w \) \hspace{1cm} Component concentration \hspace{1cm} \text{[wt\%]}
\item \( x \) \hspace{1cm} Mole fraction of a component in a liquid phase/feed \hspace{1cm} [-]
\item \( y \) \hspace{1cm} Mole fraction of a component in the vapour/permeate phase \hspace{1cm} [-]
\end{itemize}

\textbf{Superscripts}

\begin{itemize}
\item \( C \) \hspace{1cm} Combinatorial part
\item \( F \) \hspace{1cm} Feed
\item \( FV \) \hspace{1cm} Free volume
\item \( HB \) \hspace{1cm} Hydrogen bond
\item \( l \) \hspace{1cm} Liquid phase
\item \( P \) \hspace{1cm} Permeate
\item \( R \) \hspace{1cm} Residual part
\item \( T \) \hspace{1cm} Temperature dependency
\item \( v \) \hspace{1cm} Vapour phase
\end{itemize}

\textbf{Subscripts}

\begin{itemize}
\item \( b \) \hspace{1cm} Butanol
\item \( d \) \hspace{1cm} Dispersion component of the solubility parameter in Equation (2.6)
\item \( e \) \hspace{1cm} Ethanol
\item \( F \) \hspace{1cm} Feed
\item \( h \) \hspace{1cm} Hydrogen-bonding component of the solubility parameter in Equation (2.6)
\item \( i \) \hspace{1cm} Component \( i \)
\item \( ibu \) \hspace{1cm} Isobutanol
\item \( I \) \hspace{1cm} Interface
\item \( j \) \hspace{1cm} Component \( j \)
\item \( k \) \hspace{1cm} Solubility parameter component in Equation (2.11)
\item \( l \) \hspace{1cm} Liquid phase
\item \( obs \) \hspace{1cm} Observed (measured) value
\end{itemize}
\( p \) Polar component of the solubility parameter in Equation (2.6)

\( P \) Polymer in Equations 2.10, 2.12, 2.19

\( \text{pred} \) Predicted value

\( s \) Porous support layer of a membrane

\( S \) Solvent

\( t \) Total solubility parameter in Equation (2.6)

\( v \) Vapour phase

\( w \) Water

\( W \) Water

**Greek symbols**

\( \alpha \) Selectivity

\( \beta \) Separation factor

\( \gamma_i \) Activity coefficient of component \( i \)

\( \overline{\gamma}_i \) Mean activity coefficient

\( \delta \) Solubility parameter \([\text{MPa}^{1/2}]\)

\( \varepsilon \) Weight fraction in Equation (2.11)

\( \lambda \) Heat of evaporation \([\text{J/mol}]\)

\( \mu \) Chemical potential

\( \Phi \) Volume fraction

\( \chi \) Binary interaction parameter

**Abbreviations**

ABE Acetone-Butanol-Ethanol

BTESE 1,2-(bistriethoxysilyl)ethane

BuOH Butanol (iBuOH - isobutanol; n-BuOH – n-Butanol)

B/W Butanol/Water mixture

C1-C5 Distillation columns 1-5

CA Cellulose acetate

CMC- sodium carboxymethyl cellulose

Na

CNTs carbon nanotubes
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<td>COP</td>
<td>Coefficient of performance</td>
</tr>
<tr>
<td>CS</td>
<td>chitosan</td>
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<td>E/A/W</td>
<td>Ethanol/Ethyl Acetate/Water mixture</td>
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<td>E/B/W</td>
<td>Ethanol/n-Butanol/Water mixture</td>
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<td>ED</td>
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<td>Ethyl Acetate</td>
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<td>Ethanol</td>
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<td>E/W</td>
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<td>GC</td>
<td>Gas chromatograph</td>
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<td>Mass spectrometer</td>
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<td>graphene oxide</td>
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<td>NF</td>
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<td>Pervaporation</td>
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<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
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</tbody>
</table>

**Note:** PSI is represented as [mol/(m²h)].
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>poly(vinyl acetate)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>QP4VP</td>
<td>quaternized poly(4-vinylpyridine)</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>TAC</td>
<td>Total annual cost</td>
</tr>
<tr>
<td>TMC</td>
<td>trimesoyl chloride</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>VP</td>
<td>Vapour permeation</td>
</tr>
<tr>
<td>Zeolite</td>
<td>zeolite Linde Type A</td>
</tr>
<tr>
<td>LTA</td>
<td></td>
</tr>
<tr>
<td>ZIF-8</td>
<td>zeolitic imidazolate frameworks</td>
</tr>
</tbody>
</table>
DECLARATION

I, Nora Valentinyi, declare that the present doctoral thesis is my own work, and only contains references to sources specified within its bibliography. All segments quoted or paraphrased from other studies have been noted with a clear indication of the original work.

Budapest, 22.05.2019

..........................................
Nora Valentinyi

NYILATKOZAT

Alulírott Valentinyi Nóra kijelentem, hogy ezt a doktori értekezést magam készítettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egyértelműen, a forrás megadásával megjelölttem.

Budapest, 2019.05.22.

..........................................
Valentinyi Nóra