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

Ph.D. Theses

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1 Introduction

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. However, an increasing number of researchers view biofuels as an outworn conception as the majority of current biofuel producing technologies use food crops as feedstock which raises ethical questions. Besides, there are signs that electric vehicles replace internal combustion vehicles in the short to midterm future [1].

Bioethanol and biobutanol are also 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. The co-manufacture of biofuels and commodity chemicals is possible in bio-refineries, where bioethanol as potential platform chemical and bio-based n-butanol and isobutanol can all be produced. 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 and highly diluted aqueous mixtures, the separation of which generates huge challenges for the bio-industry. The conventional downstream processes 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. Although pervaporation 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.

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,

[1] D. Sperling, Electric vehicles: Approaching the tipping point, Bull. At. Sci. 74 (2018) 11–18.

hopefully, increasing the willingness for its industrial application.

2 Literature review

2.1 Pervaporation

Pervaporation is a membrane separation technique, which has established itself as an energy-efficient and highly selective liquid separation method having 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. 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 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. The permeate vapour is condensed and collected as a liquid phase. The liquid mixture enriched in the retained component(s) is called the retentate [2].

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 [3]. 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.

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. 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 evaluation of pervaporation efficiency requires common performance indicators applied in the membrane industry, such as flux, permeance, selectivity, and separation factor.

[2] J. Néel, Chapter 5 Pervaporation, in: Richard D. Noble and S. Alexander Stern (Ed.), Membr. Sci. Technol., Elsevier, 1995: pp. 143–211. doi:10.1016/S0927-5193(06)80007-0.
[3] R. Rautenbach, R. Albrecht, Membrane Processes, 1., John Wiley & Sons, Chichester, England, 1989.

The pervaporation flux is defined as the amount of material permeating through a unit of membrane area in a unit of time.

$$J_i = \frac{n_i}{A \cdot t} = P_i(x_i \gamma_i p_i^0 - y_i p^P) \tag{1}$$

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

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 [4], stating that components with similar solubility parameters are more likely to be soluble in one another. Pervaporation results were evaluated according to the Hansen solubility theory as well.

2.2 Distillation-pervaporation hybrid separation system

Pervaporation is rarely applied as a standalone process, either because its products might not be pure enough for subsequent processing or waste disposal [5]; or because of the high investment and replacement costs of the membranes [6]. 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.

2.3 Modelling and process simulation

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.

Three different modelling approaches can be identified: pure empirical models, semi-

[4] C.M. Hansen, Hansen solubility parameters: A User's Handbook, Second Edition, CRC Press, 2007
[5] F. Lipnizki, R.W. Field, P.-K. Ten, Pervaporation-based hybrid process: a review of process design, applications and economics, J. Membr. Sci. 153 (1999) 183–210.
[6] A. Koltuniewicz, Integrated Membrane Operations in Various Industrial Sectors, in: Compr. Membr. Sci. Eng., Elsevier, 2010: pp. 109–164.

empirical or phenomenological models and theoretical models [7]. The analytical depth determines the applicability of the models (membrane development or process design).

The solution-diffusion model is one of the most popular models for the description of mass transport in membranes is due to its simplicity and good description of experimental results. Rautenbach et al. [8] proposed a semi-empirical model based on the solution-diffusion theory which serves as the basis of the model development in the present thesis. Based on the semi-empirical nature of the models, pervaporation experimental results are required based on which the model parameter estimation process can be carried out.

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. 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 [9]. Therefore, my developed semi-empirical model was built into the ChemCAD flowsheeting software environment as a user added module, to be able to simulate the pervaporation and hybrid separation processes of this work.

[7] F. Lipnizki, G. Trägårdh, Modelling of pervaporation: Models to analyze and predict the mass transport in pervaporation, Sep. Purif. Methods. 30 (2001) 49–125.

[8] R. Rautenbach, C. Herion, U. Meyer-Blumenroth, Engineering aspects of pervaporation: calculation of transport resistances, module optimization and plant design, in: Pervaporation Membr. Sep. Process., Elsevier, Amsterdam, 1991: pp. 181–223.

[9] M. Skiborowski, A. Harwardt, W. Marquardt, Conceptual Design of Distillation-Based Hybrid Separation Processes, Annu. Rev. Chem. Biomol. Eng. 4 (2013) 45–68.

3   Methods

The studied mixtures were selected based on their current and future importance in the bio-industry as bio-based fuels or commodity chemicals. The binary alcohol-water systems of ethanol-water, n-butanol-water and isobutanol-water exhibit azeotrope compositions in which water is the minor component. Ethanol-n-butanol-water mixture (E/B/W) was studied due to its relevance in processing renewable biofuels, bioethanol and biobutanol (e.g. as a product of the so-called Acetone-Butanol-Ethanol (ABE) fermentation process) [10]. The ethanol-ethyl acetate-water (E/A/W) mixture was chosen as 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 [11].

The composite membranes (provided by DeltaMem AG) 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.

Table 1 Applied temperatures, concentration ranges and membranes for the laboratory experiments with the studied mixtures

Alcohol-water mixture	Temperature	Range of feed water concentration		Membrane
	(°C)	(mol/mol)	(wt%)	
Isobutanol - Water	70, 80, 90	0.05-0.4	1.5-14.3	PERVAP 1510
Ethanol -Water	60, 80	0.1-0.5	5.9-21.1	PERVAP 2210
n-Butanol – Water	60, 75, 90	0.05-0.4	2-16.6	PERVAP 1210
E/B/W	60, 75, 90	0.08-0.41	1.7-15.8	PERVAP 1210
E/A/W	60, 75, 90	0.05-0.39	3-15.9	PERVAP 1210

The experiments were carried out with a multi-purpose P-28 membrane unit provided by CM-Celfa Membrantechnik AG (shown in **Figure 1**) with a membrane area of 28 cm^2. The capacity of the double-jacketed feed tank is 500 cm^3. The permeate vacuum was achieved by a Vacuubrand PC 2003 VARIO vacuum pump. The desired feed temperature was adjusted and maintained by a thermostat, while the permeate vapour was collected in two cold

[10] S.J.M. Algayyim, A.P. Wandel, T. Yusaf, I. Hamawand, Production and application of ABE as a biofuel, Renew. Sustain. Energy Rev. 82 (2018) 1195–1214.
[11] Y.T. Ong, S.H. Tan, Pervaporation separation of a ternary azeotrope containing ethyl acetate, ethanol and water using a buckypaper supported ionic liquid membrane, Chem. Eng. Res. Des. 109 (2016) 116–126.

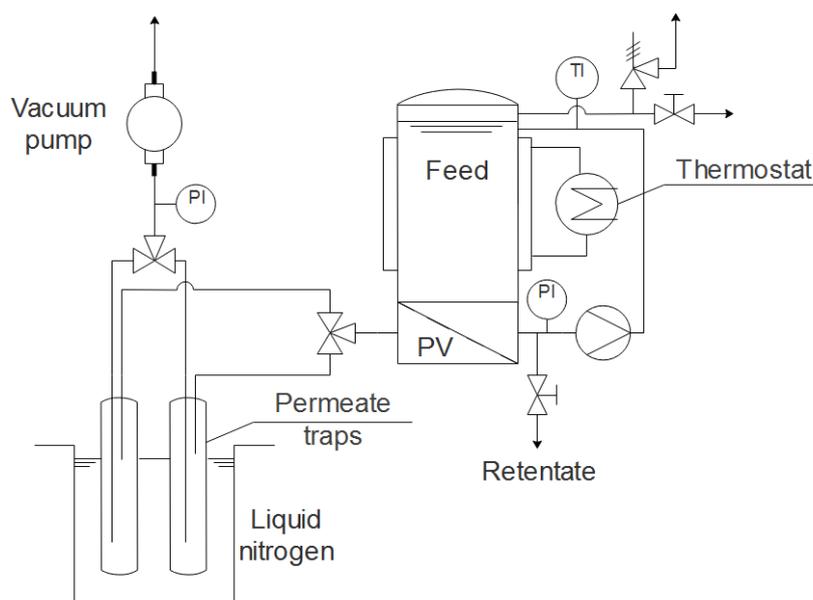traps connected in parallel and cooled with liquid nitrogen in a Dewar vessel.

Figure 1 Schematic figure of CM-Celfa P-28 membrane unit

In the case of the binary mixtures the alcohol content of the feed was measured with GC-14B gas chromatograph provided by Shimadzu, whereas for the ternary mixtures a Shimadzu GCMS-QP2010 SE gas chromatograph coupled with a mass spectrometer was used to analyse the organic solvent content of the feed mixture, the retentate and the permeate samples. 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.

During the modelling procedure STATISTICA® program was applied for parameter estimation. Process simulations were carried out with the help of a user added membrane module in the ChemCAD 6.4.3 software environment. Operational and investment cost were calculated based on the simulation results with the help of the Douglas equations [12].

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[12] J. Douglas, Conceptual Design of Chemical Processes, McGraw-Hill Science: New York, 1988.

4 Results

4.1 Dehydration of binary mixtures

Experimental results of ethanol-water and n-butanol-water dehydration were used solely for modelling purposes, while the pervaporative dehydration of isobutanol-water was investigated in detail in the thesis work.

Pervaporation measurements were carried out at 70, 80, and 90°C at various feed water concentrations. With the applied PERVAP 1510 membrane the mixture was successfully dewatered. An increase of partial fluxes of both water and isobutanol with the feed water content and the temperature was observed, which is in good accordance with the literature [13].

The applicability of a simplified form of the solution-diffusion model of Rautenbach (Model I) was tested for all three of the binary alcohol-water mixtures:

$$J_i = \frac{\overline{D_{i0}}}{\overline{\gamma_i}} \cdot \left(\frac{p_{iF} - p_{iP}}{p_{i0}}\right) \tag{2}$$

where J_i is the partial flux of component i, $\overline{D_{i0}}$ is the transport coefficient, $\overline{\gamma_i}$ is the average activity coefficient between the feed and permeate side, p_{iF} and p_{iP} are the partial pressures of the component at the feed and the permeate side, respectively, and p_{i0} is the vapour pressure of the pure i component. The transport coefficient is calculated as:

$$\overline{D_{i0}} = D_{i0}^* exp\left[\frac{E_i}{RT} \cdot \left(\frac{1}{T^*} - \frac{1}{T}\right)\right] \tag{3}$$

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

The average activity coefficient is calculated as the geometric mean of the activity coefficient at the feed and permeate sides:

$$\overline{\gamma_i} = \sqrt{\gamma_{iF} \cdot \gamma_{iP}} \tag{4}$$

It was found that 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 the alcohols. One of the aims of my work was the improvement of Model I, to widen its application range to higher water concentration regions, up to 0.5 mol fraction.

The tendency of measured fluxes suggests that partial fluxes depend on the feed

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[13] W.F. Guo, T.-S. Chung, T. Matsuura, Pervaporation study on the dehydration of aqueous butanol solutions: a comparison of flux vs. permeance, separation factor vs. selectivity, J. Membr. Sci. 245 (2004) 199–210.

concentration of the permeating compound in an exponential way; caused by the concentration dependence of the transport coefficient. The exponential tendency is enhanced in the improvement of Model I by complementing it with an exponential term. The exponential factor of my developed model (Model II) 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.:

$$J_i = \frac{\overline{D_{i0}} \exp(B_i x_{iF})}{\overline{\gamma_i}} \cdot \left(\frac{p_{iF} - p_{iP}}{p_{i0}} \right) \tag{5}$$

Since the model is semi-empirical, D_{i0}^*, E_{i0}, and B_i are fitted to the experimental results performed with the given membrane and liquid mixture. **Figure 2** presents that with Model II more accurate results can be obtained regarding the investigated systems for a wider concentration range, i.e. an extended operational window.

Process modelling, design and optimization of pervaporation and PV based hybrid separation methods in flowsheeting software packages were tested with case studies.
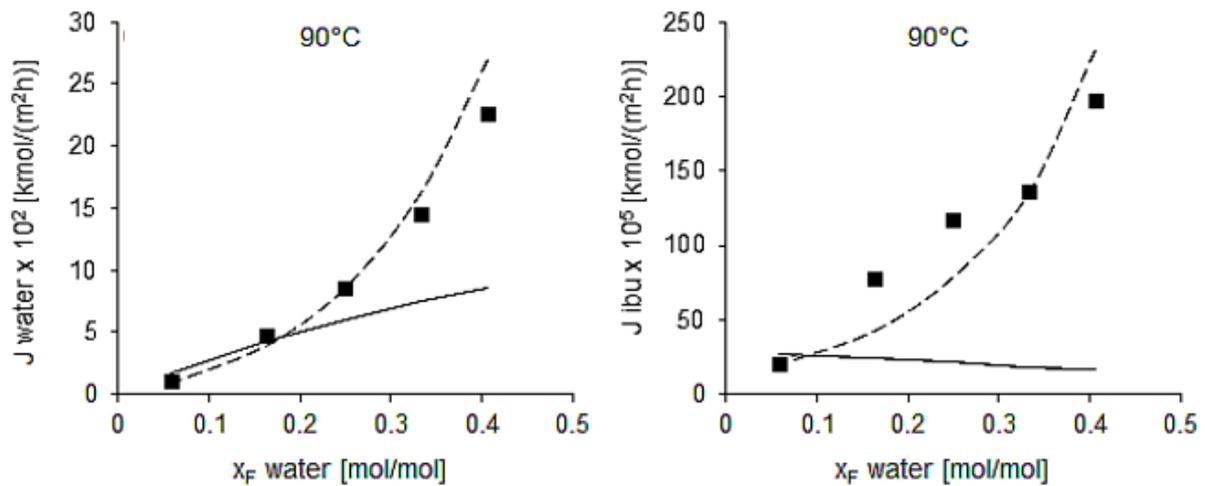

Figure 2 Measured partial fluxes (■) of water and isobutanol (ibu) compared to fluxes calculated with Model I (—), Model II (- - -) at 90°C in a function of the feed water content in molar fraction

4.2 Case studies

Model comparison through simulations of alcohol dewatering hybrid separation systems

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 my improved solution-diffusion model (Model II). The

studied separation systems were distillation-pervaporation hybrid systems processing a 800 kg/h feed stream with 15wt% alcohol content. Pervaporation was applied after the distillation columns for the final dehydration of the azeotrope mixtures of ethanol-water and isobutanol-water to produce 99.7 wt% alcohol and 99.95wt% water. Simulations performed with both Model I and II showed notable differences.

Simulation results of the hybrid separation process show that Model II gives greater pervaporation membrane area in both cases, therefore higher estimated costs. 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.

Separation alternatives for the dehydration of isobutanol

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. Here 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.

Simulations resulted in a significantly (more than 3.3 times) higher capital cost for the hybrid system 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 heteroazeotropic alternative. 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 $/m^2) 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 $/m^2 would result in a competitive option, causing a 20% decrease in the total annual cost compared with the heteroazeotropic distillation.

Investigation of process alternatives for the separation of ethanol/n-butanol/water ternary mixture

A feed stream of 800 kg/h consisting of ethanol (2 wt%), n-butanol (2 wt%), and water (96 wt%) was studied, modelling the dilute product mixture of ABE fermentation. Different separation alternatives were investigated. Primarily, the dilute stream was fed into a distillation column separating the ternary mixture to two binary ones: ethanol-water (E/W) and n-butanol-water (B/W). For the E/W mixture extractive distillation and a distillation-pervaporation hybrid system were compared, while the B/W mixture was separated either by heteroazeotropic distillation or a distillation-pervaporation hybrid system. The options were optimized and evaluated based on their total annual cost (TAC).

It was found that the hybrid system should be applied for ethanol production, as 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, therefore n-butanol can be produced more economically with heteroazeotropic distillation in the case of such a highly diluted feed stream of bioalcohols.

4.3 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 studied 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. In the case of the ternary mixtures (ethanol/n-butanol/water and ethanol/ethyl acetate/water), one of the main goals was to investigate if the concentration of the organic components affects the permeation. 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 pervaporation membrane.

Fluxes, permeances, selectivities and separation factors were examined as a function of temperature and water concentration (or water activity) in the feed. All fluxes follow an exponential increase with the feed water content, also increasing with elevated temperatures. Also, the experimental results showed that in the case of E/B/W and E/A/W ternary mixtures,

the ratio of the two organic compounds was an important factor regarding the permeation behaviour of the components. The permeation order of the pure components can be qualitatively predicted with Hansen solubility parameters.

To address the interdependence of the molecules, a further development of my 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:

$$J_i = \frac{\overline{D_{i0}}\exp(A_{ii}x_{iF}\overline{\gamma_i}+B_{ij}x_{jF}\overline{\gamma_j}+C_{ik}x_{kF}\overline{\gamma_k})}{\overline{\gamma_i}}\left(\frac{p_{iF}-p_{iP}}{p_{i0}}\right),$$ (6)

where 5 parameters are to be fitted to experimental results: D_{i0}^*, E_i, A_{ii}, B_{ij}, and C_{ik}.

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 [14].

Regression of various model options was tested, and the complete mass transport model of Equation (6) resulted in the best fit to measured data. The comparison of the measured and predicted total fluxes is depicted in **Figure 4** (a) and (b) for the E/A/W and E/B/W mixtures, respectively.
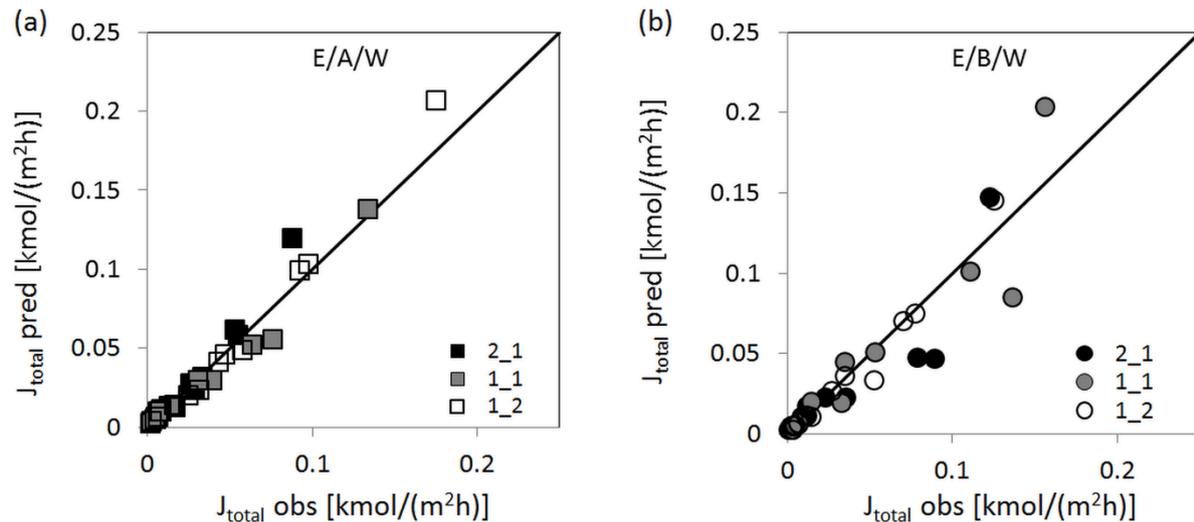

Figure 3 Measured and modelled total fluxes (Equation. (6)) for the E/A/W ternary mixture (a) and E/B/W mixture (b) for 2:1, 1:1, and 2:1 organic ratios at 60, 75 and 90°C on PERVAP 1210 membrane

[14] J. Brun, C. Larchet, R. Melet, G. Bulvestre, Modelling of the pervaporation of binary mixtures through moderately swelling, non-reacting membranes, J. Membr. Sci. 23 (1985) 257–283.

Model simplification options

To avoid redundancy, this extended model can be simplified with a minimal decrease accuracy. 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 the 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 must be included, though, in order to achieve the desired accuracy of the model, since their permeation is interdependent.

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

	Binary mixture	Ternary mixture
Water	$J_i = \dfrac{\overline{D_{i0}}\exp(A_i x_{iF})}{\overline{\gamma_i}}\left(\dfrac{p_{iF} - p_{iP}}{p_{i0}}\right)$	$J_i = \dfrac{\overline{D_{i0}}\exp(A_i x_{iF}\overline{\gamma_i})}{\overline{\gamma_i}}\left(\dfrac{p_{iF} - p_{iP}}{p_{i0}}\right)$
Organic component 1	$J_j = \dfrac{\overline{D_{j0}}\exp(A_j x_{jF})}{\overline{\gamma_J}}\left(\dfrac{p_{jF} - p_{jP}}{p_{j0}}\right)$	$J_j = \dfrac{\overline{D_{j0}}\exp(A_{jj} x_{jF}\overline{\gamma_J} + B_{jk} x_{kF}\overline{\gamma_k})}{\overline{\gamma_J}}\left(\dfrac{p_{jF} - p_{jP}}{p_{j0}}\right)$
Organic component 2		$J_k = \dfrac{\overline{D_{k0}}\exp(A_{kk} x_{kF}\overline{\gamma_k} + B_{kj} x_{jF}\overline{\gamma_J})}{\overline{\gamma_k}}\left(\dfrac{p_{kF} - p_{kP}}{p_{k0}}\right)$

5 Theses

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.

6 Potential application

Bio-based production of commodity chemicals is widely investigated in research laboratories and increasingly applied in the industry. The multicomponent aqueous products of these procedures are usually dilute, often forming several azeotropes. Thus, their downstream processing demands energy-intensive separation techniques to produce the chemicals with the desired purity at the end.

Pervaporation is a promising alternative to some conventional techniques, especially for dehydration of azeotrope mixtures. It offers highly selective, entrainer-free separation with a significantly lower energy demand than the conventional methods.

The developed pervaporation mass transport models of the present work are reliable tools for the description of the permeation processes of the studied binary and ternary mixtures. With these models integrated in ChemCAD software package it is possible to design and study the operation of pervaporation units and also pervaporation containing hybrid processes. The developed models may reduce scepticism towards membrane processes and provide a tool for chemical engineers to consider and thoroughly analyse the possibility of applying pervaporation in the chemical and bio-chemical industries.

7 Publications

<u>Publications related to the thesis</u>

<u>Journal publications</u>

I. **Valentínyi, N.**, Mizsey, P., Comparison of pervaporation models in flowsheeting environment, Procedia Engineering, 44: pp. 2098-2101. (2012),
doi: 10.1016/j.proeng.2012.09.059, I:1; FI:0

II. **Valentínyi, N**, Cséfalvay, E, Mizsey, P, Modelling of pervaporation: Parameter estimation and model development, Chemical Engineering Research and Design, 91:(1) pp. 174-183. (2013), doi: 10.1016/j.cherd.2012.07.001, IF:1.968; I:24; FI:17

III. **Valentínyi, N**, Mizsey, P, Comparison of pervaporation models with simulation of hybrid separation processes, Periodica Polytechnica-Chemical Engineering 58:(1) pp. 7-14. (2014), doi: 10.3311/PPch.7120, IF:0.269; I:12; FI:7

IV. **Valentínyi, Nóra**, Márton, Gáspár, Tóth, András József, Haáz, Enikő, André, Anita, Mizsey, Péter, Investigation of process alternatives for the separation of ethanol, n-butanol and water ternary mixture, Chemical Engineering Transactions 69: pp. 607-612. (2018), doi: 10.3303/CET1869102

V. **Valentínyi, Nora**; Andre, Anita; Haaz, Eniko; Fozer, Daniel; Toth, Andras Jozsef; Nagy, Tibor; Mizsey, Peter, Experimental investigation and modelling of the separation of ternary mixtures by hydrophilic pervaporation, Separation Science and Technology, (2019), doi: 10.1080/01496395.2019.1569692, IF:1.200

<u>Presentation</u>

1) **Valentinyi, N** (speaker), Cséfalvay, E, Mizsey P, Pervaporation model development based on experiments with isobutanol-water mixture (Pervaporációs modell fejlesztése izobutanol-víz elegyen végzett kísérletek alapján), 40. Műszaki Kémiai Napok, Conference of Chemical Engineering, Veszprém, Hungary, 24-26 April 2012, pp. 54-58.

Poster presentations

2) **Nóra Valentínyi**, Péter Mizsey, Comparison of pervaporation models in flowsheeting environment, Oláh György Doctoral Conference X., Budapest, 7 February 2013.

3) **N. Valentinyi**, P. Mizsey, Comparing process alternatives for isobutanol production, 16th Aachener Membran Kolloquium. Aachen, Germany, 2-3 November 2016, pp. 297-305. (ISBN:978-3-95886-120-6)

Other publications

Journal publications:

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