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Methodology for parameter estimation of modelling of pervaporation in flowsheeting environment

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Abstract

The rigorous modelling of pervaporation, especially in professional software environment, plays a high practical importance if hybrid separation processes containing membrane units are to be designed. In this work a methodology is recommended and presented for such design problems. This methodology consists of the following steps: laboratory pervaporation experiments, estimation of the parameters needed for the modelling of the pervaporation, and finally the double verification of the parameters. The parameter estimation is handled as a mixed integer nonlinear programming (MINLP) problem and professional flowsheeting simulator is also applied in the double verification step. Following this methodology, reliable parameters of the pervaporation needed for rigorous modelling can be determined. The pervaporation module with the reliable parameters in professional software environment enables the design of complicated separation processes, e.g., hybrid separation processes containing pervaporation.

Keywords: Membranes; Pervaporation; Mathematical modelling; Parameter estimation

1. Introduction

In the development of separation technologies there is a clear incentive to design and realise effective and, on the other hand, also environmental conscious separation processes. A possible solution alternative to realise this goal is the design and application of hybrid separation processes where different kinds of unit operations are combined to strengthen each other's advantages to make efficient separation processes. A significant step in the separation process development is the application of different membrane technologies. The application of the membrane separation technologies also has an important contribution to the successful realisation of environmental expectation that has been to build up the so-called clean technologies and also to contribute to the sustainable development and consumption [1–3].

The pervaporation is a rapidly developing membrane technology and has the advantage that it can be used for special separation tasks. The separation of liquid mixtures by pervaporation is not limited by the vapour–liquid equilibrium, and azeotropic mixtures can be simply separated with pervaporation then to apply classical distillation techniques like azeotropic distillation. Depending on the type of membrane applied, the pervaporation could be also successful separation alternative for the solution of different complicated separation processes, e.g., dehydration of organic solvents, the recovery of organic compounds, and the separation of organic mixtures even azeotropic ones [4–9].

In recent years, pervaporation has established itself as one of the most promising membrane technologies [3,10]. Generally, in many cases pervaporation alone could not supply products suitable for further processing or waste disposal [6,10]. Hence pervaporation has been usually combined with other separation processes like distillation, liquid–liquid extraction, adsorption and stripping. The advantages of a pervaporation process can even be increased with such a co-ordinated combination. Such combinations belong to the group hybrid separation process alternatives.

The design of hybrid separation processes needs comprehensive engineering knowledge and design tools. An important design tool is the rigorous modelling of the individual units of the hybrid separation process. There have been several attempts for comprehensive modelling of different membrane

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Nomenclature

A	area (m^2)
A_{ij}	parameter of the Wilson activity coefficient equation ($cal\,g^{-1}\,mol^{-1}$)
c	total molar concentration ($mol\,mol^{-1}$)
c_i	concentration of component i ($mol\,m^{-3}$)
c_p	specific heat on constant pressure (J/mol)
D_i	diffusivity coefficient ($m^2\,s^{-1}$)
D_{i0}	diffusivity coefficient of component i ($mmol\,m^{-2}\,h^{-1}$)
$\overline{D_i}$	transport coefficient, theoretically: among the two layers of the active surface of the membrane for component i ($mmol\,m^{-2}\,h^{-1}$)
$\overline{D_i^*}$	relative transport coefficient of component i ($mol\,m^{-2}\,h^{-1}$)
E_i	activity coefficient of component i (kJ/kmol)
F	feed stream (mol/h)
f_{i0}	fugacity of pure i component (mbar, kPa)
f_{iF}	fugacity of component i in the feed (mbar, kPa)
f_{iP}	fugacity of component i in the permeate (mbar, kPa)
J	total flux ($mmol\,m^{-2}\,h^{-1}$) in Fig. 2A; in Fig. 3A–D flux ($kg\,m^{-2}\,h^{-1}$)
J_i	partial flux ($mol\,m^{-2}\,h^{-1}$) in Eq. (8)
J^P	permeance ($mol\,m^{-2}\,h^{-1}\,kPa^{-1}$) in the Appendix A
l	distance of diffusion (m); in the Appendix A: membrane thickness (m)
n	number of intervals and also number of optimizable parameters
n_i	weight of component i (mol)
p_P	pressure on the permeate side of the membrane (kPa)
p_{i0}	pure i component tension (mbar, kPa)
p_{i1}	partial pressure of component i on the liquid phase membrane side (mbar, kPa)
p_{i2}	partial pressure of component i on the vapour phase membrane side (mbar, kPa)
p_{i3}	partial pressure of component i between the active and porous layer of the membrane (mbar, kPa)
$[P_i/l]$	permeance ($mol\,m^{-2}\,h^{-1}\,kPa^{-1}$) in the Appendix A
R	universal gas constant ($8.31\,J\,mol^{-1}\,K^{-1}$)
T	temperature (K), temperature on diagrams (°C)
T^*	293 K reference temperature
V_{Vi}	Wilson molar volume coefficient ($ml\,mol^{-1}$)
x	composition of the liquid phase (mass fraction)
x_w	mass fraction of water in retentate
x_a	mass fraction of alcohol (ethanol) in retentate
y	composition of vapour phase (mass fraction)
y_w	mass fraction of water in permeate
y_a	mass fraction of alcohol (ethanol) in permeate

Greek letters

α	separation factor
β	selectivity
γ_{i1}	activity coefficient of component i in the feed
γ_{i2}	activity coefficient of component i in the permeate
$\overline{\gamma_i}$	average activity coefficient of component i
δ	thickness of the membrane (m)
λ_i	heat of evaporation of component i ($J\,mol^{-1}$)

separation processes, e.g., Han et al. [11], Mariott and Sørensen [12]. Rigorous modelling can be completed with professional flowsheeting software packages like ASPEN Plus® (Aspen Technology Inc., USA) or ChemCAD© (Chemstations Inc., 1998–2004). These engineering software tools contain reliable physical property data bank and also rigorous models for several chemical engineering units. With the help of the flowsheeting software packages, the design parameters of the unit operations can be determined with exhaust and reliable modelling and optimization according to a defined objective function. Since the pervaporation is a relatively new separation method its rigorous model is not yet included in the flowsheeting packages. However, a rigorous model of the pervaporation is badly needed for the proper design of the hybrid separation processes if they include pervaporation belonging to the group of clean technologies.

2. Background

2.1. Rigorous modelling of pervaporation

Pervaporation is such a membrane separation process where components of a liquid mixture are separated according to the following mechanism [13,14]:

- selective sorption in the membrane of the key component;
- diffusion through the membrane where the membrane itself represents the barrier between the two phases (liquid and vapour);
- desorption of the key component into the vapour phase on the membrane's permeate side being under vacuum.

A fourth step can be inserted into this mechanism if a composite membrane is used and a support layer is also considered, that is, the entering and permeating through the support layer are accomplished by diffusive or pore flow. Further effect at pervaporation is the concentration polarisation, which means an additional diffusive layer in front of the feed side's active layer [15]. In technical literature it has been verified that pervaporation membranes has no propensity for this phenomena because of membrane material and the cross-flow filtration circumstances [16].

The operation of the pervaporation membrane is usually characterised with e.g., the separation factor:

$$\alpha = \frac{y_w/y_a}{x_w/x_a} \tag{1}$$

The separation factor depends, among other influential factors, also on the composition of the liquid mixture to be separated as well as on the temperature.

Other important feature for the characterisation of pervaporation is the transmembrane flux that formally is the permeate. An obvious mathematical description to describe this material transport generally is to use Fick's law (Eq. (2)):

$$J_i = \frac{\mathrm{d}n_i}{A\,\mathrm{d}t} = -D_i\frac{\mathrm{d}c_i}{\mathrm{d}l} \tag{2}$$

The advantage of the Fickian equation is its simple mathematical form but it is not convenient to apply since when dealing with non-ideal systems the diffusion coefficient depends on the concentration in a very complicated form. Hence several authors have dealt with the developing of different models for the pervaporation. The major models are the following (without completeness) [12,14–17]:

- solution–diffusion model;
- total solvent volume fraction model (an alternative of the solution–diffusion model);
- pore-flow model.

In the case of anisotropic membranes, the chemical potential decreasing variation as a function of place is the same in these models. The solution–diffusion model assumes that chemical potential gradient is expressed only as a concentration gradient whilst in pore-flow model driving force is expressed as pressure gradient. In solution–diffusion concept membranes transmit pressure in the same way as liquids. It is implicit that across the membrane section pressure is uniform and equal to the higher pressure solution. Pore-flow model is modified with the assumption that pressure is smoothly descending along the membrane active layer section and the solvent activity has not change across the membrane. Models are agreed in the mechanism written above and in assuming that the porous layer of anisotropic membranes has negligible pressure gradient.

Model with subsequent observation has been recommended by Stephan and Heintz [15,16]. They investigated seven binary systems relying on the solubility of each component in the active layer of the membrane. The authors even studied the effect of concentration polarisation and swelling rate of the membrane material. Atra et al. investigated the behaviour of binary alcohol–water liquid transport through organophilic membrane [4].

Effective and comprehensive information about mathematical implementation of models was found in review sources containing a broad region of assumptions and approaches for diffusive transport among others irreversible thermodynamics and kinetics of liquid transport [14,18–20].

From the viewpoint of the membrane material which is decisive of transport through the permselectivity, the interaction of membrane and particle was studied by several authors. A characteristic study of the polar membrane systems in vapour permeation process, the transport had both kinetically (diffusivity) and thermodynamically (sorption) attendance in examination by Modesti et al. [21]. Polarity of liquid mixture and membrane decisively affect the transportation.

The "solution–diffusion" model based on observations has been recommended and derived originally by Rautenbach et al. [13]. Rautenbach et al.'s model belongs to the group of "solution–diffusion" approaches. It corresponds to the physical occurrence of pervaporation. The model is capable of describing the behaviour of pervaporation if a composite membrane is applied. The composite membranes have two definite layers: a permselective active layer and a porous support. The model expresses the molecular transport practically with the gradient of chemical potential because in this case the transport coefficient, $\overline{D_i}$can be applied to describe the pervaporation. The transport coefficient has the advantage that it depends on the concentration only in a negligible way [25].

The original flux equation of the model used in this work is given by Rautenbach et al. [13] Eq. (3) is an integration of a one-dimensional differential equation, according to the analogous form for transport of Fick's law (Eq. (2)):

$$J_i = \frac{cD_{i0}}{\delta\overline{\gamma_i}}\left(\frac{f_{i\mathrm{F}}-f_{i\mathrm{P}}}{f_{i0}}\right) = \frac{cD_{i0}}{\overline{\gamma_i}}\left(\frac{f_{i\mathrm{F}}-f_{i\mathrm{P}}}{f_{i0}}\right) \tag{3}$$

with the gradient of pressure difference derived from the chemical potential difference as driving force (Eq. (3)). Eq. (3) can be rearranged and written for each component assuming that fugacity and partial pressure are equal at low pressure:

$$J_i = \frac{1}{1+(\bar{D}_i/Q_0 p_{i0}\bar{\gamma}_i)}\,\frac{\bar{D}_i}{\bar{\gamma}_i}\left(\frac{p_{i1}-p_{i2}}{p_{i0}}\right), \quad i=(1,\ldots k) \tag{4}$$

Rautenbach et al. [13] defined Q_0 as the permeability coefficient of the porous support layer of the membrane (Eq. (5)):

$$J_i = Jy_i = Q_0(p_{i3}-p_{i1}) \tag{5}$$

The item p_{i3} is the porous layer input pressure and describes the pressure between the membrane active and porous layers, and it can be mathematically eliminated. Partial pressures in Eqs. (4) and (5) indicate saturated states of components and were calculated by Antoine equation [23]. The Q_0 parameter is independent from the temperature.

The $\overline{\gamma_i}$ is the geometric average of the activity coefficients of the feed side and the permeate side of the membrane:

$$\bar{\gamma}_i = \sqrt{\gamma_{i1}\gamma_{i2}} \tag{6}$$

The activity coefficient can be calculated with any known activity vapour–liquid equilibrium model.

The transport coefficient shows an Arrhenius type temperature dependency:

$$\overline{D_i} = \overline{D_i^*}\exp\left[\frac{E_i}{R}\left(\frac{1}{T^*}-\frac{1}{T}\right)\right] \tag{7}$$

E_i is for the activation energy for each component and $T^* = 293\,\mathrm{K}$ is the reference temperature. Eq. (7) represents that the pervaporation is strongly temperature dependent.

Based on this solution–diffusion model by Rautenbach et al. [13], Mizsey et al. [22] have developed a modelling algorithm and they have implemented it into the ChemCAD professional software environment as a user-added subroutine.

If the total membrane area is divided into infinitesimal sections then the iterative solution of equations distribute the result. Eqs. (4) and (7) can be solved for each section of a membrane module but they must be supplemented by the heat balance. The pervaporation model of Mizsey et al. [22] uses also the heat balance. Eq. (8) shows the heat balance for a membrane section:

$$\frac{c_p F \Delta T}{A} = \sum_{i=1}^{k} \lambda_i J_i \quad i = (1, \dots k) \tag{8}$$

On the basis of the material and heat balance equations (Eqs. (4), (7) and (8)) the material flows and temperatures of the pervaporation can be determined.

Eqs. (3)–(8) assume a constant composition on the feed side. In practical cases it is not always the situation, but by applying sufficient velocity of circulation this condition can be evaluated. For more exact formulation the equations should be rewritten into a differential equation form to consider the dependency on the area of the membrane and correctly accounting for the changing compositions. Since the professional flowsheeting softwares are usually not prepared for such a situation the problem of modelling has to be solved in a different way. Instead of solving a differential equation system a difference equation system can be considered supposing several membrane sections having such a small piece of area where constant feed composition and temperature can be supposed [22].

The practical application of the pervaporation subroutine needs system (mixture to be separated and membrane)-dependent input data. In terms of a binary mixture, the transport coefficient and its temperature-dependent term, namely the activation energy, ($\bar{D}_i$; $\bar{E}_i$) for each component and the permeability coefficient of porous support layer (Q_0) are the inputs. Parameter Q_0 is influenced by the real physical composition of the membrane. All input parameters are to be determined with measurement. Thus, the experimental determination at least five parameters (binary mixture) is necessary. These parameters are used in the user-added pervaporation subroutine. The accuracy of the parameters have a paramount importance since if the exact design of a pervaporation module is targeted, e.g., as a part of a hybrid separation process, only accurate parameters can give reliable results for the size and the properties of the pervaporation unit to be designed. This explains why the double verification of the parameters is needed.

2.2. *Recommended methodology for the rigorous modelling of pervaporation*

The rigorous, reliable modelling of pervaporation is greatly needed for example at the design of hybrid separation processes including this kind of unit as well. The tool is already given in the form of a user-added subroutine of a professional flowsheeting software package. The "solution–diffusion" model by Rautenbach et al. [13] and Mizsey et al. [22] is selected (see also Appendix A). The reliable calculations with the pervaporation subroutine need reliable input data as well, which are the parameters of the pervaporation system. These parameters are the transport coefficients and their temperature dependency for each component and the permeability coefficient of the porous support layer of the composite membrane selected for the separation.

To supply reliable data for the pervaporation subroutine, the data should be verified and tested. For this task the following methodology is recommended:

- Step 1: Selection of the proper membrane for the pervaporation problem;
- Step 2: Measurements on test equipment at the composition range expected and at different temperatures;
- Step 3: Parameter estimation for the mathematical model of the pervaporation;
- Step 4: Double verification of the parameters: both with the parameter estimation program and the user-added subroutine.

Following this methodology it becomes possible to determine the parameters for the rigorous modelling of pervaporation in flowsheeting environment.

3. Experimental, mathematical evaluation, result and discussion

In the experimental part the recommended methodology for pervaporation modelling is presented. This includes both laboratory experiments and computer modelling. For the practical presentation of the methodology such a system is selected where there are enough empirical data and practical experiences to detect possible discrepancies of the methodology. One of the most investigated mixtures with practical examples is the separation of the ethanol–water azeotrope system and therefore this system is selected for the presentation of our methodology.

3.1. *Step 1: Selection of proper membrane for the pervaporation*

According to membrane suppliers (e.g., SULZER Chemtech GmbH) the PERVAP 2210 hydrophilic PVA/PAN (0.5–2 μm thick polyvinyl alcohol as permselective and polyacrylonitrile as micro-porous support layer) composite membrane is a suitable one for such a separation, thus it is selected for the solution of the separation problem and further investigation. The membrane was conditioned at current measurement temperature (50, 70, 80, 90 °C) for about 1 h using 5 wt.% water/alcohol mixture before pervaporation.

3.2. *Step 2: Measurements on test equipment*

The laboratory pervaporation experiments are worked out on CM-CELFA Membrantrenntechnik AG P-28 multifunctional membrane unit. Fig. 1 shows the schematic picture of the apparatus. The membrane is laid on a sintered disc that separates the membrane test cell into two compartments: feed and permeate sides. The volume of the feed tank is up to 500 ml, the concentration of the feed is kept constant with

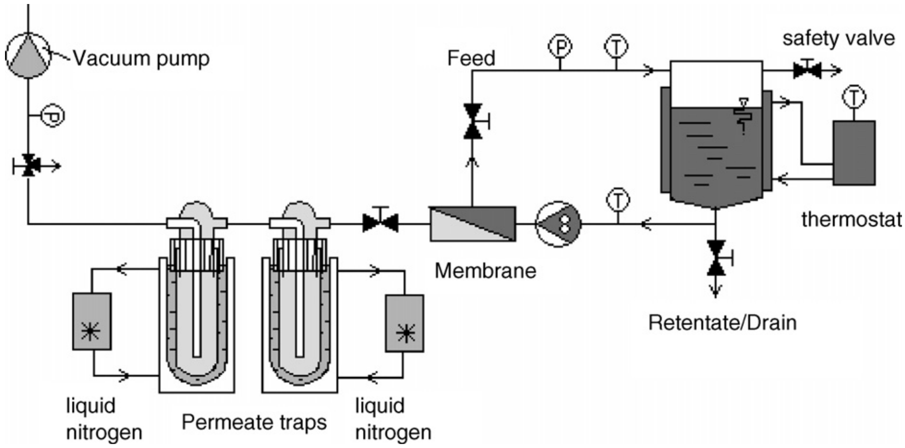

Fig. 1. Schematic figure of experimental apparatus for pervaporation.

permanent cross-flow circulation at a circulation velocity of ~182 l/h. The effective membrane area is 28 cm^2. Since the permeate quantity was practically negligible to the feed quantity (approximately 1:200), the composition on the feed side can be considered as constant, and considered as perfectly mixed. The applied vacuum was 0.267 kPa (2.7 mbar) and maintained with a Vacuubrand PC 2003 VARIO controlled vacuum pump. The experiments were carried out under isotherm conditions. Two monitoring thermometers were placed in the inlet and outlet of the membrane cell. The outlet from the permeate side was directly connected to a liquid nitrogen cooled glass trap. To avoid material loss, the equipment and the measurements were also tested using a second trap in series, also cooled with liquid nitrogen, and no material loss was observed. The mass balances of the experiments showed also that there was less than 2% material loss during the experiments. Retentate water content was analysed with Karl–Fisher titration, the ethanol was measured by Schimatzu gas chromatograph-14B equipped with CP-SIL-5CB WCOT column (column dimensions are: 0.32 mm × 0.45 mm × 1.2 μm) and with FID detector.

The composition interval investigated ranges between 0.5 and 14 wt.% water content in the feed. Since the pervaporation has exponential dependency on the temperature, hence the measurements were taken at four temperature values: 50, 70, 80 and 90 °C. The temperature values are determined according to the physical property (boiling temperatures) of the system and the membrane temperature durability (~95 °C).

The measured data are evaluated and presented in Fig. 2. The measured data show good tendency and the system behaves according to expectations. The measured data can be converted into permeance and evaluated (see Appendix A). At less than 4 wt.% water they show strange dependency that can be, however, explained. Although the presentation of experimental data in permeance has several advantages, since the model of [13] is based on Eqs. (3)–(7) using fluxes, this form of presentation of the measured data should be kept.

The pervaporation separation index (PSI), that is the product of the separation factor and total permeation rate, can be also used to evaluate and check experimental data. The temperature dependency of PSI can be clearly seen in Fig. 2D.

3.3. Step 3: Parameter estimation for the mathematical model of the pervaporation

The core of the whole methodology is the parameter estimation by means of the measured data. According to fluxes and permeate purity data, the transport coefficient and its activation energy showing the temperature dependency for each of the two compounds and the permeability coefficient for the membrane are estimated. For the estimation a program is written based on Eqs. (4), (6) and (7) in a general algebraic modelling system (GAMS) mathematical optimizing program environment. The description of the non-ideality of activity coefficient can be completed with different models, e.g., UNIQUAC, Wilson. In the given concentration and temperature ranges both equilibrium models are tested and give the same results. Finally, the Wilson model is selected for the sake of simplicity. Table 1 presents the Wilson-coefficients used for the calculation.

Mathematically a finite difference approach is applied for this optimization thus solving the NLP problem. The problem is tailored to handle binary, ternary and – at will – more component mixtures, since the coefficients in binary interaction parameters are usable in appropriate pairs to generate the activity coefficients of multicomponent mixtures. GAMS program provides a great variety of solvers of industrial, mathematical and economical problems with comment on the problem's emergence circumstances and recommended solving type.

Parameter estimation problem is constructed as a MINLP problem. Originally, the model requires a NLP problem, but the possibility of finding a global optimum of a five parametric equation with NLP is low. Using MINLP the convergence way to optimality is directional. The procedure for solving has the following steps:

Table 1
WILSON parameters used in the GAMS model [24]

A_{12}	975.49
A_{21}	276.76
V_{L1}	18.069
V_{L2}	58.69

1, water; 2, ethanol.

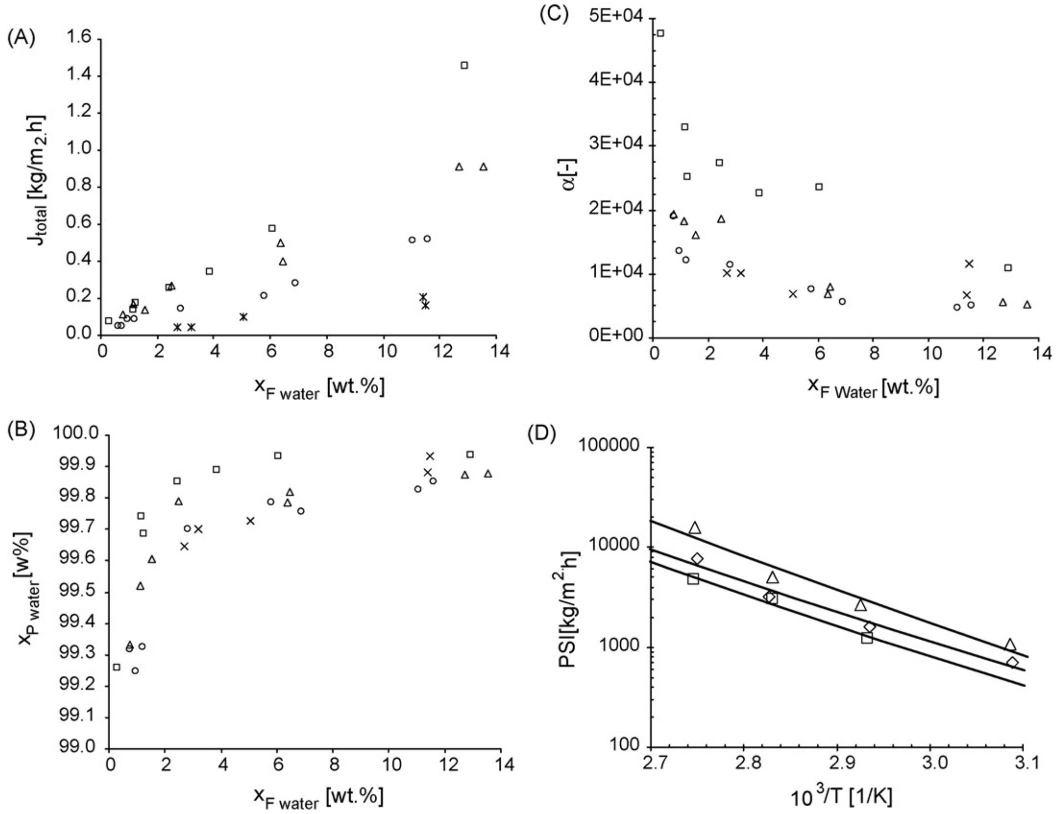

Fig. 2. Measurement results vs. feed water concentration (wt.%): A, total flux; B, permeate water content (wt.%); C, separation factor; D, pervaporation separation index. Membrane is PERVAP 2210, displayed measurement data (×) $T = 50\,°C$, (◯) $T = 70\,°C$, (△) $T = 80\,°C$, and (□) $T = 90\,°C$.

- In the first step the program computes a normal solution from the initial values between the given boundaries. As a first approximation, upper and lower bounds are set as wide as possible, in the next step each appropriate bound is substituted with computed non-optimal value according to the relaxed solution. The technique separates continuous and binary variables.
- When the mixed integer linear programming (MILP) problem finds a local optimum for each parameter within their given upper and lower boundaries, then boundaries become equal and the flag of the parameter is set to +1 integer value. This +1 indicates that the interval presumably contains the optimal value of the parameter. Otherwise the flags are not integer values.
- The intervals of the parameters are substituted into nonlinear programming (NLP) (with “Conopt”) problem and optimization takes place. If it has the same solution like the MILP problem then the solution is accepted. If it has no solution then a new solution of the MILP problem is presented offering new intervals for the optimization.
- If both problems, MILP and NLP, are not in contradiction and all requirements are fulfilled then the objective function’s optimum is found.

It is evident that parameter boundaries are to be set to rational values according to engineering considerations. “Conopt” solves the MIP problem using simplex algorithm with using outer approximation, considering the fact that the mixed integer problem increases the computational time. The objective function is the deviation of the measured and modelled data. The parameter estimation is made for Q_0 $\bar{D}_i$; $\bar{E}_i$ via the minimisation of the objective function.

Table 2 presents the parameters of the water–ethanol–PERVAP 2210 system determined with GAMS according to the method described here.

3.4. Step 4: Double verification of the parameters

This verification of the parameters is necessary since the parameter estimation may find a minimum standard deviation of the measured and the calculated data where the parameters found are not accurate enough and/or do not describe properly the system’s behaviour for each feature. Sometimes it can be difficult to find good parameters for the description of the system, which parameter describes well both the total flux and

Table 2
Determined parameters for ethanol dehydration using PERVAP 2210 hydrophilic membrane

	System PERVAP 2210	
	Water	Ethanol
$Q_0 = \frac{\text{kmol}}{\text{m}^2\,\text{h}\,\text{bar}}$	3.0	
$\overline{D_i^*} = \frac{\text{kmol}}{\text{m}^2\,\text{h}}$	4.49×10^{-3}	4.63×10^{-6}
$E_i = \frac{\text{kJ}}{\text{kmol}}$	46 165	22 614

composition of permeates at four temperatures simultaneously. In this manner the objective function used in the parameter estimation should consider both these features of the system.

The most suitable verification of the parameters is the recalculation of the data measured on the laboratory equipment with another tool. The estimated parameters (Table 2) are substituted both into the mathematical model written in the GAMS environment and into the user-added subroutine written in the professional flowsheeting software environment (ChemCAD). The user-added subroutine working in ChemCad environment contains Eqs. (4), (7) and (8). This is a double verification and it might seem to be unnecessary but functionally if a problem occurs it is easier to detect it with the evaluation of the simulation results and the measured data (Fig. 3).

Since the permeate quantity is practically negligible compared to the feed quantity and the feed side is perfectly mixed; therefore, the composition on the feed side could be considered as constant. This means that at the modelling of measured data

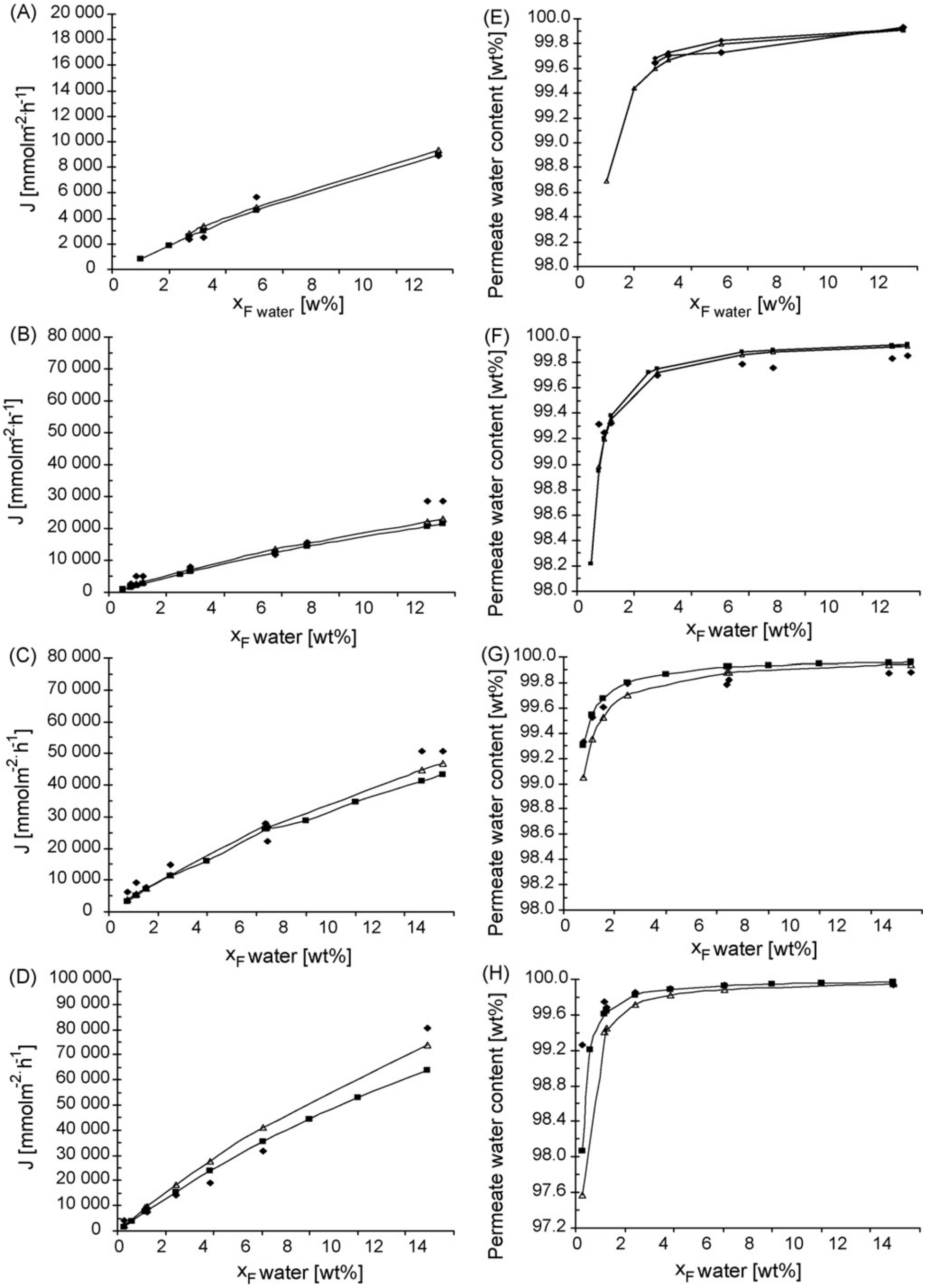

Fig. 3. Ethanol–water dehydration by pervaporation, PERVAP 2210 measured data, GAMS parameterized functions, and ChemCAD modelled data. Figures presenting total flux (summarized of Eq. (4). partial flux) are A, $T = 50\,^{\circ}$C; B, $T = 70\,^{\circ}$C; C, $T = 80\,^{\circ}$C; D, $T = 90\,^{\circ}$C isothermal functions. Figures presenting permeate water content E, $T = 50\,^{\circ}$C; F, $T = 70\,^{\circ}$C; G, $T = 80\,^{\circ}$C; H, $T = 90\,^{\circ}$C. Symbols are respectively, (♦) measured data points, (△) GAMS parameterized functions, and (■) ChemCAD simulated data.

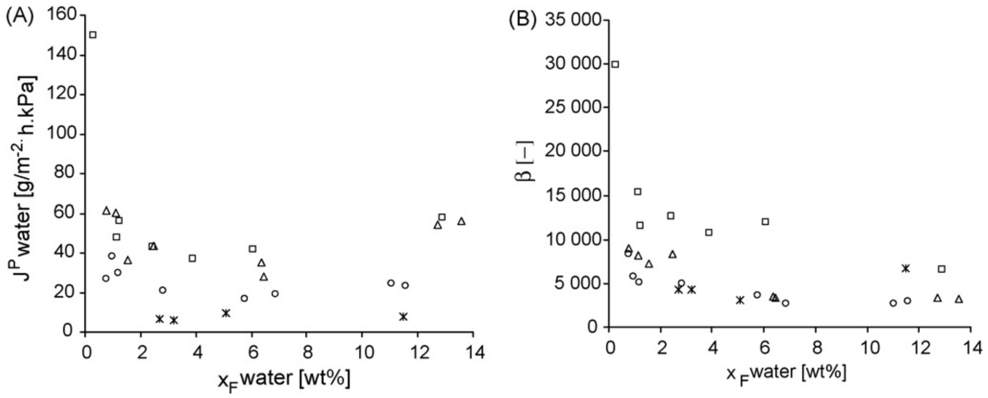

Fig. 4. (A) Permeance and (B) selectivity, ethanol dehydration PERVAP 2210. Symbols represents (×) $T = 50\,°\mathrm{C}$, (◯) $T = 70\,°\mathrm{C}$, (▲) $T = 80\,°\mathrm{C}$, and (□) $T = 90\,°\mathrm{C}$.

one membrane area section could be supposed that is equal to that of the experimental apparatus and there is no need to work with differential or difference equations.

The data calculated with the GAMS and with the ChemCAD user-added subroutine as well as the measured data for the total permeate flux and its water composition are presented in Fig. 3A–D and 3E–H, respectively.

The comparison of the measured and the calculated data proves that the methodology delivers reliable parameters for the model and its implementation is capable of describing the performance of a pervaporation unit. The estimated parameters show that the activation energy of the transport coefficient's temperature dependency of water is higher than that of the ethanol showing a higher temperature dependency of the membrane for this transport (see Eq. (7)). On the other hand, the relative transport coefficient of water is three orders of magnitude higher than that of the ethanol.

4. Conclusions

In this work a methodology is recommended and presented which gives a guideline of practical importance for the modelling and design of pervaporation units. After laboratory experimental investigation, also at low water content, of the pervaporation system, the application of the MINLP program technique proves to be a powerful tool for the estimation of the corresponding parameters of the system. The double verification, both with the GAMS program package and the user-added subroutine written in professional software environment (ChemCAD), helps to check the reliability of the system's parameters. Following the methodology reliable parameters of the pervaporation can be determined and supplied to the user-added subroutine. The application of the pervaporation model with the parameters estimated enables the user to work at any operating circumstances. Since the pervaporation subroutine works in professional flowsheeting environment, it becomes possible to design complex, hybrid separation processes as well.

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Appendix A

At the evaluation of pervaporation membrane features, it is possible to decouple the effect of operating conditions on membrane performance evaluation with using permeance and selectivity instead of flux and separation factor [24].

The definition equations are

$$J^{\mathrm{P}} = \left[\frac{P_i}{l}\right] = \frac{J_i}{x_i \gamma_i p_{i0} - y_i p^{\mathrm{P}}} \tag{8}$$

where J^{P} is the permeance and

$$\beta = \frac{P_i/l}{P_j/l} \tag{9}$$

where β is the selectivity and shows the ratio of the permeances of components of a binary mixture.

Fig. 4A and B shows the permeance for water and the selectivity of the membrane, respectively. It can be clearly seen that for PERVAP 2210 the water component shows strong dependence on temperature. As long as other authors [9,25] took measurements at higher feed water concentration (above 4 wt.%), we investigated at lower values, below 5 wt.% and especially around at 1 wt.%, since this concentration range is an important one for the dewatering of organic solvents. At such small compositions interesting phenomena can be observed: the permeance increases while approaching zero feed water concentration. This is due to the facts that the permeate purity sharply drops down and the denumerator of Eq. (8) decreases as well and these two facts results in increasing tendency of the permeance.

Since the solution–diffusion model of the pervaporation is based on the calculation of the fluxes, in our modelling work this type of description of pervaporation is followed.

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