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MODELLING OF PERVAPORATION: MODELS TO ANALYZE AND PREDICT THE MASS TRANSPORT IN PERVAPORATION

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MODELLING OF PERVAPORATION: MODELS TO ANALYZE AND PREDICT THE MASS TRANSPORT IN PERVAPORATION

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CONTENTS

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ABSTRACT

The modelling of the ma ss transfer in pervaporation is one of the fundamental aspects to understand and therefore improve the process performance. This paper reviews the different models to analyse and predict the mass transport through the selective layer in pervaporation. It therefore provides an overview combined with some guidance about the different models proposed in the literature and the applicability range of these models. The different models reviewed cover the two key mass transport steps in pervaporation: *(1)* sorption into the membrane, and *(2)* diffusion through the membrane. For the two different steps individual models will be proposed as well as models covering the mass transport across the membrane as a whole. The different models will be grouped with respect to the nature of the models: theoretical, semi-empirical or empirical. Further the applicability range of the different models regarding the different polymer classes such as glassy, semi-crystalline, or rubbery will be shown. Finally, it will be commented on the applicability of the models with regard to two main research fields in pervaporation: development of membranes and design of processes and modules. Inorganic and composite-material membranes involve additional models to analyse and predict the mass transport and have been excluded from this review.

Key Words: Pervaporation; Modelling; Polymeric membranes; Mass transport

1. INTRODUCTION

1.1 Background

Pervaporation is a separation process, which is based on the selective transport through a dense membrane combined with a phase change of the permeating components from liquid to vapour. During previous years pervaporation established itself as a potential process alternative for the dehydration of organic compounds, the recovery of organic compounds from water and the separation of organic-organic mixtures. Present research in pervaporation covers the development of new membrane materials and the improvement of the process designs. Fundamental for success in both areas is the understanding of the mass transfer through the selective layer of the membrane. The various models to analyse and predict the mass transport performance in pervaporation can play an important role to further apply and establish pervaporation as a separation technique.

The focus of this paper will be on the various models, which have been developed over the years to analyse and predict the mass transfer through the selective layer in pervaporation. The aim of this paper is to review these models published in the literature with regard to their applicability range and nature of the models used: theoretical, semi-empirical or empirical. It will therefore provide some guidance when the different models should be applied. The review will focus only on the mass transfer through polymeric membranes, the most widely used type of membranes in pervaporation. Inorganic and composite-material membranes, which are also applied in pervaporation, involve additional models to analyse and predict the mass transport. They are therefore excluded from this review. Further, the focus is only on the mass transfer through selective layer of the membrane, therefore additional influences on the overall mass transfer in pervaporation related to effects such as concentration polarisation, permeate pressure drop, flow pattern, and heat transfer are not covered by the proposed models. These effects are important to be considered in process and module design, but lead to more complex and specific models. However, a key feature in all models for process and module design is the mass transfer through the selective layer of membrane and thus the models proposed in this article can be used as a foundation to develop specific models for both areas. After classifying the nature of different models to analyse and predict the mass transfer in pervaporation, the different models for pervaporation found in the literature will be grouped with reference to the step in the mass transport they represent: sorption, diffusion or the overall process. The applicability range of these models will be discussed and examples of applications will be given.

1.2 Classification of Models for Mass Transfer in Pervaporation

The choice of an appropriate model for pervaporation depends on its application, i.e. membrane development or process and module design. Further, the selected model should on one hand include all the required parameters for development and optimisation, but on the other hand the number of parameters should be kept to a minimum to reduce the number of experiments required. In the literature three different classes of models for pervaporation can be found (see Figure 1):

1. empirical models,
2. theoretical models, and
3. semi-empirical / phenomenological models.

In the following these approaches to model pervaporation are briefly introduced. The analytical depth of the models can be used as a measure to determine the applicability range of the models – membrane development or process and module design. While for membrane development a high analytical depth with regard to the trans-membrane mass transfer is required, the main aim in process and module design is to have reasonable representation of all effects influencing the overall mass transfer in pervaporation. The mass transfer through the selective layer is only one of the steps in the overall mass transfer.

1.2.1 Empirical Models

Empirical models describe the process based on interpolation of data collected by measurements—input and output—without taking any physical / chemical relations into account. The advantage of these models is the low level of math-

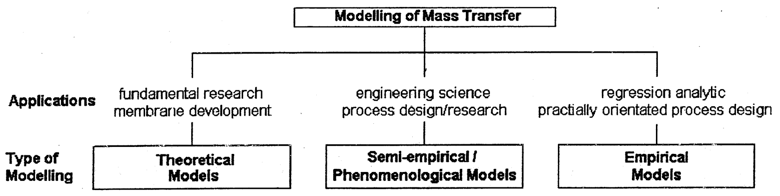

Figure 1. Overview of the different classes of models for pervaporation *(modified after [1])*.

ematics required while gaining a high accuracy based on an appropriate database. The disadvantage of this approach is the large number of experiments required to obtain this representative database. To explore new operation conditions it might also be dangerous to extrapolate results into areas where these process parameters have not been measured in advance. Applying empirical models is a simple way to obtain results but does not necessarily lead to deeper understanding of parameters influencing the process. Hence, empirical models are useful for initial comparisons of membranes, process designs, and module designs but their analytical depth is often not appropriate for optimisation, which is an important feature of design and development.

1.2.2 Theoretical Models

Theoretical models use the molecular parameters of the process including their physical relationships. These molecular parameters are derived from thermodynamic and physical/chemical relations. Theoretical models are, therefore, based on molecular processes. The intermolecular processes are described by the laws of physical chemistry and statistical thermodynamics. The advantage of these models is that the parameters involved are fundamental values, e.g. sorption, diffusion, and desorption coefficients, which are determined by independent measurements. Furthermore, isolating the different fundamental parameters, the theoretical approach leads to a fundamental understanding of the process and the parameters involved. Thus, the disadvantage is that transferring data from one system to another might include extrapolations into areas where these values have not been measured under given process conditions, since the determination of fundamental values often requires complex experiments. Further, the number of parameters in these models is generally large, which often leads to high mathematical complexity. Theoretical models should be applied for membrane development, when a high analytical depth of the model is required. For development and comparison of process and module designs these models are very complex and, therefore, require an often inappropriate amount of mathematical effort.

1.2.3 Phenomenological/Semi-empirical Models

Phenomenological/semi-empirical models combine features of theoretical with empirical approaches. Phenomenological models are commonly based upon a theoretical approved background. Consequently, the number of required experiments to get a quantitative reasonable model can be minimised without reducing the quality of the approach. The opportunity of extrapolating results is also improved compared to the empirical models. The disadvantage of this approach is

Table I. Models of the Mass Transfer in Pervaporation

Model	Classification of Model	Number of Permeating Components	Polymer Type Glassy	Semi-crystalline	Cross-linked	Rubbery	Co-polymers
Sorption ***(Section 2)***							
Langmuir and Henry's Law Isotherms	empirical	single	•	•	•	•	•
Solubility Parameter Theory	semi-empirical	binary	•		•	•	•
Flory-Huggins	semi-empirical	binary	•	•	•	•	
UNIQUAC	semi-empirical	multi	•		•	•	•
UNIFAC	theoretical	multi	•	•	•	•	
ASOG-FV	semi-empirical	multi	•				
Entropic-FV	semi-empirical	multi	•			•	•
modified NRTL	semi-empirical	binary	•			•	
ENSIC	semi-empirical	single				•	•
Molecular Simulations for Sorption	theoretical	binary	•			•	
Diffusion ***(Section 3)***							
Empirical Diffusion Coefficients	empirical	multi	•	•	•	•	•
Free Volume	theoretical	binary	•	•	•	•	•
Dual Sorption	theoretical	binary	•				
Molecular Simulations for Diffusion	theoretical	binary	•			•	
Trans-Membrane Mass Transfer ***(Section 4)***							
Empirical Model by Franke	empirical	multi	•	•	•	•	•
Solution-Diffusion Model	semi-empirical	multi	•	•	•	•	•
Semi-Empirical Model after Meyer-Blumenroth	semi-empirical	binary/ternary	•				
Q_i-Model	semi-empirical	binary	•			•	
Process-specific Permeability Functions	semi-empirical	binary	•				
Thermodynamic of Irreversible Processes (TIP)	semi-empirical	multi	•			•	
Stephan-Maxwell Theory	Theoretical	ternary	•	•	•	•	•
Pore Flow Model	semi-empirical	binary	•			•	
Pseudophase-Change Solution-Diffusion Model	theoretical	binary				•	

The table represents only present and potential applications of the different models, where either the relevant equations are given or experimental evidence is presented.

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that the model parameters compared to the theoretical models lost their character of being fundamental values. However, phenomenological models often cover all key parameters and are therefore suitable to give an understanding how these different parameters influence the process. These models can therefore be used as a foundation to develop models for process and module design by extending and combining the models to cover the effects of e.g. concentration polarisation, permeate pressure drop and heat transfer.

1.3 Applications of Models for Pervaporation

Apart from the classification of the models, the different models found in the literature can be distinguished regarding the mass transfer steps covered, their applicability for multi-component mixtures and the state of the polymers.

The trans-membrane mass transfer in pervaporation consists generally of three consecutive steps:

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

The mass transport in each of these steps might be influenced by the presence of more than one component in the feed. With an increasing number of components in the feed the complexity of the models increases since the effect of coupling in each of the steps has to be considered. Hence for each of the steps and for the overall trans-membrane mass transfer different models can be found in the literature depending on the number of permeating components. The influence of desorption is in most cases negligible, and can be covered by similar models as sorption. Consequently, desorption has been excluded from this review.

The selection of the model depends also to what extent the membrane polymer is in rubbery, glassy or semi-crystalline state, and its degree of cross-linking.

Table I provides a general overview over the different models covered in this paper. The models are tabled with regard to the mass transfer steps covered by the model, the classification of the model, number of permeating components and the applicability with regard to the state of the membrane polymer.

2. MODELS OF MEMBRANE SORPTION

The sorption step is along with diffusion the most important step in the pervaporation process by determining the mass transfer rates of components and, therefore selectivity of the membrane. Hence predicting and analysing sorption is important to select appropriate membranes for a predefined task.

A measure of sorption is the activity or the volume fraction of the component in the membrane. Both can be related to the sorption isotherm. In the following different models to determine the sorption behaviour as part of the mass transfer are presented.

2.1 Langmuir and Henry's Law Isotherms

One of the most accurate approaches to determine the sorption behaviour of the membrane are sorption measurements using the membrane material and the feed components. To determine the sorption isotherm approaches such as gravimetric methods[2] or the quartz crystal microbalance method[3], can be used to estimate the time-dependence of the sorption process as well as the sorption equilibrium and, consequently, to predict the sorption isotherm. For modelling the pervaporation process at low-pressure conditions the sorption data of non-saturated vapours of the pure components, as well as the mixtures, are useful in determining the overall solubilities and diffussivities[4]. It is, however, normally not possible to use the vapour sorption data to model the mass transport of the liquid feed at saturated conditions. As a result, some additional experiments have to be carried out[4]. To analyse the sorption data there are two common models. For rubbery membranes the sorption isotherm can be normally be fitted to Henry's Law isotherm:

$$C_{D,i} = k_{D,i} \cdot p_i \tag{1}$$

Alternatively, in case of glassy polymers a Langmuir type of isotherm is more applicable:

$$C_{H,i} = \frac{C'_{H,i} \cdot b_i \cdot p_i}{1 + b_i \cdot p_i} \tag{2}$$

Furthermore using sorption experiments it is possible to determine the activity of the solvent in the membrane polymer. At equilibrium the activity in the membrane is equal to that in the surrounding, and can be estimated using[5]:

$$a_i = \frac{p_i}{p_i^{sat}} \cdot \left[\frac{(B_i - \tilde{V}_i) \cdot (p_i^{sat} - p_i)}{R \cdot T} \right] \approx \frac{p_i}{p_i^{sat}} \tag{3}$$

Several researchers[6-11] determined the activity and sorption isotherm of various membrane-solvent systems. The single component isotherm can be used as a foundation to predict the sorption behaviour in multi-component systems using e.g. the UNIQUAC method *(Section 2.4)* or to predict fluxes of multi-component systems using the Maxwell-Stefan Theory *(Section 4.4)*.

Overall, the resulting single component isotherms can either be used to compare the sorption behaviour of different components-membrane systems directly for membrane development. Alternatively, it can be combined with the appropriate models to determine the sorption and mass transfer performance of the multi-component systems and can therefore be used in membrane development as well as in process and module design.

2.2 Solubility Parameter Theory

The solubility parameter theory is a semi-quantitative model. It describes the interactions between the solute and the polymer[12]. This theory was originally developed to describe the mixing behaviour of water, but it has been found to be useful when predicting the compatibility of solvents and polymers using one-dimensional solubility parameters. Later this approach was modified to three-dimensional solubility parameters and several approaches have been suggested to improve the predictions by this method.

Solubility parameters describe the energy required to overcome the intermolecular forces needed to separate molecules in a liquid. A solvent with a solubility parameter similar to the polymer will have high solubility[13]. Conversely, for the penetration of molecules through a polymer, it has been shown that too similar solubility parameters can lead to an immobilisation of the permeating component within the polymer. Consequently, the effective size of the transport corridor, through the polymer, would decrease[14].

2.2.1 One-Dimensional Solubility Parameters

A definition of the solubility parameter δ_i can be based on a theory developed by Scatchard and Hildebrand. For regular mixtures, the solubility parameter can be defined as:

$$\delta_i = \sqrt{\frac{\Delta E_{vap,i}}{\tilde{V}_i}} \tag{4}$$

This definition may be applicable for many non-polar solvents i.e. polymers, but not necessarily for all polar solvents and solid materials. Hence, the success of applying this theory depends very much on the system analysed. Huang and Lin[15] compared permeation rates of chlorinated methanes through polyethylene *(PE)* with the one-dimensional solubility parameter theory. It was revealed that it was not possible to rank the permeation of the components according to the order of the theory. Einax et al.[16] compared the permeabilities of benzene and different alcohols through PE, polyamide *(PA)*, and polydimetylsiloxane *(PDMS)* with the theory. In this study a reverse relationship between permeabilities and one-dimensional solubility parameters was observed. This was related to an increased cohesive force of the polymers, which lead to an increased energetic requirement to enlarge the temporary microvoids to the size required to take in the permeating components. In another study for systems of PDMS/toluene and PDMS/n-butanol, it was reported that according to the one-dimensional solubility parameters theory, toluene permeated faster than n-butanol[17]. Carter and Jagannadhaswamy[18] studied the four systems: polypropylene*(PP)*/benzene/methanol, PP/benzene/isopropanol, cellulose/water/isopropanol and cellulose/water/methanol. In case of the systems including PP the theory gave qualitative representation of the experimental results, while for cellulose the theory did not succeed. The work of Zhu et al.[14] showed for different membrane material combined with either chloroform, chlorobenzol or 1,2-Chloroethane and water that the separation factor increased when the one-dimensional solubility parameters became smaller. Further, in a study by Yamada and Hamaya[19] for systems with PE combined with benzene/aniline, benzene/benzyl alcohol, and benzene/phenol it was observed that the order of the separation factors was according to the differences of the one-dimensional solubility parameters between polymer and permeating components.

2.2.2 Three-Dimensional Solubility Parameters

Hansen[20] modified the one-dimensional theory to the improved description of the solubility parameters. In the modified theory the overall energy of vaporisation, $\Delta E_{vap,i}$, is the total energy required to remove a molecule from its neighbouring molecules[21]. This total energy can be considered as the sum of energies required to overcome dispersion forces $\Delta E_{df,i}$, dispersion polar interactions $\Delta E_{di,i}$ and breaking hydrogen bonds $\Delta E_{hb,i}$ [21].

$$\Delta E_{vap,i} = \Delta E_{df,i} + \Delta E_{di,f} + \Delta E_{hb},_{i} \tag{5}$$

Combining Equations *(4)* and *(5)* gives:

$$\delta_i = \sqrt{\delta_{df,i}^2 + \delta_{di,i}^2 + \delta_{hb,i}^2} \tag{6}$$

Based on this equation, the three components can be presented as vectors lying along the orthogonal axes of a 3-dimensional space, see Figure 2.

The solubility parameters are represented by the end-point of the radius vector. The three co-ordinates can, therefore, be used to represent each polymer and each solvent. Consequently, the distance between the vector end point of the solvent and the polymer can be calculated by[13]:

$$\Delta_{P,i} = [(\delta_{df,P} - \delta_{df,i})^2 + (\delta_{di,P} - \delta_{di,i})^2 + (\delta_{hb,P} - \delta_{hb,i})^2]^{1/2} \tag{7}$$

In the cases where $\Delta_{P,i}$ decreases the interactions between the solvent and the polymer increase. This would, therefore, indicate an increase in the swelling be-

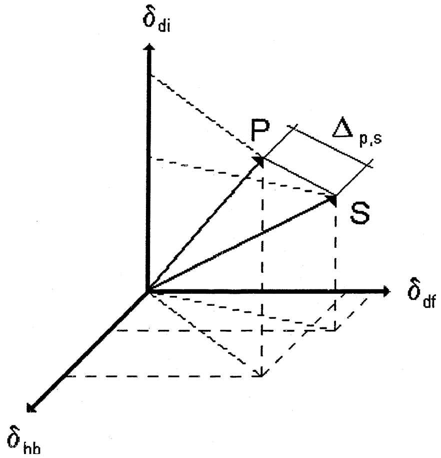

Figure 2. Representation of solubility parameters of a solvent and a polymer in a 3-dimensional phase space *(adapted from [22]).*

haviour of the polymer[22]. Kucharski and Stelnasezek[23] applied this theory to analyse the pervaporation of a cyclohexane/benzol mixture through a polyisoprene *(PIP)* membrane. In accordance to predictions of the model it was found that the benzene was enriched. Uragami et al.[24] studied the permeation of n-alcohols, isoalcohols and n-hydrocarbons through Nylon 12 membranes. While in case of the alcohols a reverse relationship between three-dimensional solubility parameters theory and permeation rate was observed, no relationship was observed in case of the hydrocarbons. Mulder et al.[25] studied the pervaporation of three isomeric xylenes, o-xylene, m-xylene and p-xylene, through six different types of cellulose esters. Comparing the three-dimensional solubility parameters with solubility and swelling experiments it was revealed, that experimental results were in accordance with the theory. However, comparing the theory with results from pervaporation experiments of a binary mixture of o-xylene/p-xylene through cellulose ester membranes, in all cases an enrichment of p-xylene in the permeate was observed. This result was not in accordance with the theory and related to immobilisation of o-xylene in cellulose ester due to differences in molecular shape and solvent-polymer interactions. Hence it was concluded that selectivity cannot be predicted using this theory. Bell[26] compared the permeabilities of water, acetone and different alcohols through cellulose and PDMS using three-dimensional solubility parameters. In this work it was possible to predict the qualitative order of permeabilities for the PDMS systems but not for the cellulose systems. Nijhuis[27] used this theory to explain the hydrophobic nature of twelve different polymers by relating a low ability of polar interactions and hydrogen bondings to low water sorption. In this work it was, however, pointed out, that the sorption behaviour of the organic components *(toluene and trichloroethylene)* was independent from the predictions by the solubility parameter theory.

In order to improve the predictive capability of the solubility parameters several authors[28-30] suggested the introduction of W_1, W_2 and W_3 as weight factors:

$$\Delta^{W}_{P,i} = [W_1(\delta_{df,P} - \delta_{df,i})^2 + W_2(\delta_{di,P} - \delta_{di,i})^2 + W_3(\delta_{hb,P} - \delta_{hb,i})^2]^{1/2} \tag{8}$$

It has been generally suggested to use the weight factors[30] $W_1 = 4$, and $W_2 = W_3 = 1$, or alternatively[31] $W_1 = 1$, and $W_2 = W_3 = 0.25$. However, the nature of these parameters is purely empirical. Zeller[29] therefore suggested relating the weight factors to chemical classes of the solvents. Applying this theory to predict the solubility of different chemical solvent classes into Viton®, improved predictions were achieved by using these group related weight factors[29].

In order to apply the solubility parameters on ternary systems, the interactions of the membrane with the binary mixture have to be taken into account. In the case the two liquid solvents have no strong interactions, Froehling et al.[32] suggested to calculate the solubility parameters δ_{df}, δ_{di} and δ_{hb} through combination of the parameters of the two solvents based on their volume fractions in the mixture. Hence for each of the solubility parameters, represented by k, the following equation can be used:

$$\delta^{mix}_{k,ij} = \Phi_i\delta_{k,i} + \Phi_j\delta_{k,j} \qquad k = df, di, hf \tag{9}$$

Using this theory for poly*(vinyl chloride) (PVC)*, and three solvent pairs *(toluene/methanol, trichloroethylene/nitromethane, n-butyl acetate/nitromethane)* it was observed that for the first two pairs without any interactions it was possible to apply the theory successfully, while for the third pair with interactions it failed[32].

Use of the ratio $\Delta_{P,i}/\Delta_{P,j}$ as a measure of preferential sorption in ternary systems is recommended by Lloyd and Meluch[33]. In cases where the transport of component i is desired and component j is rejected by the polymer, a polymer should be selected to minimise the ratio $\Delta_{P,i}/\Delta_{P,j}$ by minimising $\Delta_{P,i}$ and/or maximising $\Delta_{P,\mathrm{j}}$. This can be achieved through selection of a polymer with a strong affinity for component i and a low affinity for component j. However, applying this theory for quantitative prediction of selectivities for ethanol/water and chloroform/water using eight different membrane polymers, Lee et al.[22] concluded this theory is not suitable.

Finally, Sferrazza and Gooding[34] suggested combination of the conventional two-component solubility parameters to define a predictive parameter, which takes the interactions of component i and j into account:

$$\Delta^{mix}_{P,ij} = \Delta_{P,j} + \Delta_{i,j} - \Delta_{P,i} \tag{10}$$

This modified approach to solubility parameters was applied to estimate sorption selectivities for polybenzimidazole *(PBI)*, polyvinyl alcohol *(PVA)* and low density polyethylene *(LDPE)* regarding 24 different organic components diluted in water. For each membrane it correctly predicted that chlorobenzene has the highest selectivity, while the predictions for the other organic components were scattered[34].

Overall, the different available approaches to solubility parameters outlined above do not overcome the restrictions of the overall solubility parameters theory[13]. Namely:

- The theory takes only the energetic contribution of the mixing process into account and neglects entropic effects.
- Specific interactions between solvent and polymer are neglected as the theory is based on the properties of pure components. Thus, theory should be restricted to hydrophobic components as hydrophilic components like water or alcohols give rise to strong specific interactions, i.e. hydrogen bondings.

Based on these restrictions, and the varying successes of applying the solubility parameter, this theory should be restricted to qualitative predictions of sorption for various components in membrane development. Since predictions of fluxes are not possible based on the results gained from the solubility parameter theory, this approach is not suitable for process and module design.

2.3 Flory-Huggins Theory

The Flory-Huggins theory is a general method used to predict concentration profiles and to explain sorption selectivity of membranes and real fluid mixtures.

This theory was originally developed for binary systems and then extended to ternary systems with non-cross-linked membrane polymers. Subsequently, the theory has been extended to cover cross-linked, semi-crystalline and glassy polymers. The criterion of solubility and membrane swelling is the Gibbs free energy of the interacting components. This is represented by the dimensionless binary Flory-Huggins interaction parameters. The Gibbs free energy of a ternary system consists of a binary mixture and a non-cross-linked high molecular weight polymer membrane. It can generally be described by the Flory-Huggins thermodynamics using the following equation[21]:

$$\begin{aligned}\frac{\Delta G^{mix}}{RT} &= x_i \ln \Phi_i + x_j \ln \Phi_j \\ &\quad + x_p \ln \Phi_P + \mathrm{X}_{i,j} x_i \Phi_j + \mathrm{X}_{i,P} x_i \Phi_P + \mathrm{X}_{j,P} x_2 \Phi_P \end{aligned} \qquad (11)$$

Assuming that only the binary interaction parameter $\chi_{i,j}$ of the two components in the mixture is dependant on the concentration and assuming $\chi_{i,P}$ and $\chi_{j,P}$ remain constant, a general form of the Flory-Huggins theory, used to calculate the activity for each component with respect to x_i and x_j, can be derived. This is achieved through differentiating Equation *(11)*, so developing Equations *(19)* and *(20)* see Table II.

In all cases of the Flory-Huggins equation two boundary cases can be further analysed[27]:

1. The molar volume of the polymer $\widetilde{V}_p$ is generally much larger than the molar volumes of the liquid solvents $\widetilde{V}_i$ and $\widetilde{V}_j$. Hence, if $\widetilde{V}_i / \widetilde{V}_p$ or $\widetilde{V}_j / \widetilde{V}_p \rightarrow 0$ the related terms may be neglected.
2. For pure liquid sorption, or if the sorption for one component is very low *($\Phi_i \cong 0$ or $\Phi_j \cong 0$)*, the Flory-Huggins equations for ternary systems reduces to a binary system.

The binary Flory-Huggins interaction parameter $\chi_{i,j}$ describing the interactions between the two liquid solvents is a function of the concentrations. The parameter determined is, therefore, based on the excess free energy of mixing ΔG^E by[35]:

$$\chi_{i,j} = \frac{1}{M_i \cdot \widetilde{V}_j} \cdot \left(M_i \cdot \ln \frac{M_i}{\widetilde{V}_i} + M_j \cdot \ln \frac{M_j}{\widetilde{V}_j} + \frac{\Delta G^E}{RT} \right) \tag{12}$$

These aforementioned models of the Flory-Huggins theory are limited since they require data from ΔG^E. In cases where the data for ΔG^E is unavailable, $\chi_{i,j}$ can alternatively be calculated based on the Flory-Huggins thermodynamics for binary mixtures[27] using the following equation:

$$\chi_{i,j} = \frac{\ln a_i - \ln \Phi_i + (\widetilde{V}_i / \widetilde{V}_j - 1) \cdot \Phi_j}{\Phi_j} \tag{13}$$

The activity coefficient a_i, required in Equation *(13)*, can be estimated through an appropriate model, such as NRTL, UNIQUAC or UNIFAC.

To determine the interaction parameters $\chi_{i,P}$ and $\chi_{j,P}$ between the components of the binary mixture, two experimental approaches can be applied: either swelling experiments of the pure solvents with the polymer or using inverse gas chromatography. Of these two approaches the inverse gas chromatography approach is the less favourable one as the interaction parameters are determined at infinite polymer concentration at a specified increased temperature. As the interaction parameters are temperature and concentration dependent, extrapolation might cause difficulties while the swelling experiments can be carried out at any temperature. Using swelling experiments of the pure solvent, the interaction parameters can be determined by the following equation[35]:

$$\chi_{i,P} = -\left(\frac{\ln(1 - \Phi_P) + \Phi_P}{\Phi_P^2} \right) \tag{14}$$

Alternatively, Bristow and Watson[36] suggested a semi-empirical model based on the solubility parameter theory:

$$\chi_{i,P} = \chi_i + \frac{\widetilde{V}_i}{RT} \cdot (\delta_i - \delta_P)^2 \tag{15}$$

Here χ_i is defined as constant with a value of 0.35. For some systems it is found that this value might change significantly depending on the polymer mole fraction[37].

Koningsveld and Kleinjtens[38] introduced a variable interaction parameter $\chi_{i,P}$, which accounts for interacting contact surfaces. This method leads to the following equation:

$$\chi_{i,P} = c_1 + \frac{c_2 \cdot (1 - c_3)}{(1 - c_3 \cdot \Phi_P)^2} \tag{16}$$

The three adjustable parameters c_1, c_2, and c_3 can be determined by a non-linear curve based on experimental sorption data.

An exponential approach to describe the variation of the interaction parameter was introduced by Jonquiéres et al.[39]:

$$\chi_{i,P} = c_4 \Phi_1^{c_5} \tag{17}$$

The two parameters c_4, and c_5 are of empirical nature and have to be adjusted for the solvent-polymer system.

The Flory-Huggins thermodynamic was successfully applied by Mulder[35] to predict concentration profiles and sorption behaviour of cellulose acetate membranes for ethanol-water mixtures. More recent Favre et al.[40, 41] applied the Flory-Huggins theory to several ternary systems. The predictions achieved by the theory in the case of rubbery polymers swelled by apolar mixtures had a precision within the range of 10 % compared to experimental data. However, it was also revealed[40] that in case of apolar liquids and thermoplastics significant differences between experimental data and the isotherm pattern predicted were observed. Even though, it was possible to predict the basic trends. In the cases of both homogeneous polymers and copolymers with polar liquids it was found that only poor predictions could be achieved by using the Flory-Huggins theory.

2.3.1 Modified Flory-Huggins

For specific polymers the Flory-Huggins Theory *(Equations (20) and (21))* can be easily modified. The activities for a ternary system of cross-linked membranes and binary liquid mixture can be calculated. This is achieved through addition of a term, in these equations, that describes the energy change due to the elastic strain[27], see Equations *(22)* and *(23)* in Table II. In these modified equa-

Table II. Basic and Modified Flory-Huggins Equations for Ternary Systems

Basic Flory-Huggins Equation:

$$\ln a_i = \ln \Phi_i + \Phi_j\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_j}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_P}\right) + (\chi_{i,j}\cdot\Phi_i + \chi_{i,P}\cdot\Phi_P)\cdot(\Phi_j + \Phi_P) - \chi_{j,P}\cdot\frac{\widetilde{V}_i}{\widetilde{V}_j}\cdot\Phi_j\cdot\Phi_P$$

(20)[27]

$$\ln a_j = \ln \Phi_j + \Phi_i\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_i}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_P}\right) + \left(\chi_{i,j}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i + \chi_{j,P}\cdot\Phi_P\right)\cdot(\Phi_i + \Phi_P) - \chi_{i,P}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i\cdot\Phi_P$$

(21)[27]

Flory-Huggins Equation for Cross-linked Membranes:

$$\ln a_i = \ln \Phi_i + \Phi_j\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_{ij}}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_P}\right) + (\chi_{i,j}\cdot\Phi_i + \chi_{i,P}\cdot\Phi_P)\cdot(\Phi_j + \Phi_P)$$
$$- \chi_{j,P}\cdot\frac{\widetilde{V}_i}{\widetilde{V}_{ij}}\cdot\Phi_j\cdot\Phi_P + \frac{\widetilde{V}_i\cdot\rho_P}{M_C}\left(1 - 2\cdot\frac{M_C}{M_P}\right)\cdot\left(\Phi_P^{1/3} - \frac{1}{2}\cdot\Phi_P\right)$$

(22)[27]

$$\ln a_j = \ln \Phi_j + \Phi_i\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_i}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_P}\right) + \left(\chi_{i,j}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i + \chi_{j,P}\cdot\Phi_P\right)\cdot(\Phi_i + \Phi_P)$$
$$- \chi_{i,P}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i\cdot\Phi_P + \frac{\widetilde{V}_j\cdot\rho_P}{M_C}\cdot\left(\frac{1 - 2\cdot M_C}{M_P}\right)\cdot\left(\Phi_P^{1/3} - \frac{1}{2}\cdot\Phi_P\right)$$

(23)[27]

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Flory-Huggins Equation for Semi-crystalline Membranes:

$$\ln a_i = \ln \Phi_i + \Phi_j\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_j}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_P}\right) + (\chi_{i,j}\cdot\Phi_j + \chi_{i,P}\cdot\Phi_P)\cdot(\Phi_j + \Phi_P) - \chi_{j,P}\cdot\frac{\widetilde{V}_i}{\widetilde{V}_j}\cdot\Phi_j\cdot\Phi_P + \left(\frac{\frac{\Delta H_{f,P}}{R}\cdot\left(\frac{1}{T} - \frac{1}{T_m}\right)}{\left(\frac{3}{2}\cdot f\cdot\Phi_P\right)}\right) - 1 \tag{24}$$

$$\ln a_j = \ln \Phi_j + \Phi_i\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_i}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_P}\right) + \left(\chi_{i,j}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i + \chi_{j,P}\cdot\Phi_P\right)\cdot(\Phi_i + \Phi_P) - \chi_{i,P}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i\cdot\Phi_P + \left(\frac{\frac{\Delta H_{f,P}}{R}\cdot\left(\frac{1}{T} - \frac{1}{T_m}\right)}{\left(\frac{3}{2}\cdot f\cdot\Phi_P\right) - 1}\right) \tag{25}$$

Flory-Huggins Equation for Glassy Membranes:

$$\ln a_i = \ln \Phi_i + \Phi_j\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_j}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_i}{\widetilde{V}_P}\right) + (\chi_{i,j}\cdot\Phi_j + \chi_{i,P}\cdot\Phi_P)\cdot(\Phi_j + \Phi_P) - \chi_{j,P}\cdot\frac{\widetilde{V}_i}{\widetilde{V}_j}\cdot\Phi_j\cdot\Phi_P + \frac{\langle a\rangle_0^2\cdot(n/A)\cdot\widetilde{V}_i\cdot\Phi_P^2}{\widetilde{V}_P} \tag{26}$$

$$\ln a_j = \ln \Phi_j + \Phi_i\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_i}\right) + \Phi_P\left(1 - \frac{\widetilde{V}_j}{\widetilde{V}_P}\right) + \left(\chi_{i,j}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i + \chi_{j,P}\cdot\Phi_P\right)\cdot(\Phi_i + \Phi_P) - \chi_{i,P}\cdot\frac{\widetilde{V}_j}{\widetilde{V}_i}\cdot\Phi_i\cdot\Phi_P + \frac{\langle a\rangle_0^2\cdot(n/A)\cdot\widetilde{V}_j\cdot\Phi_P^2}{\widetilde{V}_P} \tag{27}$$

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tions, the factor $(1–2M_C/M_P)$ is a correction for the imperfections of the network effected by chain ends. For a perfect network, this factor reduces to unity as $M \rightarrow \infty$. The last term describing the cross-linking effect has only a second order effect on the system and may be neglected if the swelling of the polymer is low, i.e. rubbery polymers. Nijhuis[27] applied this modified theory to determine sorption behaviour, i.e. the volume fraction of the permeating compounds in the swollen polymer. In this study four different types of polymers with different degrees of cross-linking were analysed for the two binary mixtures toluene-water and trichloroethylene-water as solvent. Comparing the volume fractions in the swollen membrane using experiments and the modified Flory-Huggins theory good agreement between theory and experiments was achieved.

2.3.2 Flory-Huggins-M-H

For cases of semi-crystalline polymers the sorption is influenced by hindered diffusion *(tortuosity effect)*. This effect can be described as physical cross-linking and is similar to chemical cross-linking. The sorption of a pure liquid into a semi-crystalline polymer is described by the Michaels-Hausslein theory[42]:

$$\ln a_i = \ln \Phi_i + \Phi_P + \chi_{i,P} \cdot \Phi_P^2 + \left(\frac{\frac{\Delta H_{f,P}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{m,p}} \right)}{\left(\frac{3}{2} f_P \cdot \Phi_P \right) - 1} \right) \tag{18}$$

Hence, the basic Flory-Huggins theory can be extended to semi-crystalline membranes and binary mixture to obtain Equations *(24)* and *(25)*, Table II. Michaels and Hausslein[42] applied the binary model *(Equation (18))* for systems of PE with different degrees of crystallinity and p-xylene as solvent. In their study good agreement between experiments and theory was observed. Even though it was concluded in this study that the temperature dependency of the polymers is more important that the degree of crystallinity[42].

2.3.3 Flory-Huggins-F-R

For glassy polymers, a term that describes adjacent crystallites as causing restrictions to chain segment mobility, is added to Flory-Huggins theory. The following equation, based on the Flory-Rehner equation[43], can be obtained:

$$\ln a_i = \ln \Phi_i + \Phi_P + \chi_{i,P} \cdot \Phi_P^2 + \frac{\langle a \rangle_0^2 \cdot (n/A) \cdot \widetilde{V}_i \Phi_P^2}{\widetilde{V}_P} \tag{19}$$

In Equation *(19)* $\langle\alpha\rangle_0$ represents the ratio between the mean distance separating the junctions in the unswollen network and the mean end to end distance for the corresponding segment in cases where this segment is unrestricted. However, this model is restricted to networks containing undeformable cross-links[42]. From this, the ternary system, glassy polymer and binary mixture, the activity can be further described using the modified Flory-Huggins Equations *(26)* and *(27)*; these are given in Table II.

Applying the Flory-Huggins theory it is possible to predict the activity of components in the membrane for binary and multi-component systems. Combining this theory with other models such as the Free Volume Theory *(Section 3.2)* allows predictions of the component fluxes through the membrane. Overall, this theory seems to be particularly suitable for membrane development and in combination with other models also for process and module design.

2.4 UNIQUAC Model

The Universal Quasi Chemical *(UNIQUAC)* model was developed by Abrams and Prausnitz[44] to predict fluid phase equilibria in multi-component systems including polymers**.** Later this model was extended to account for strong interactions by hydrogen bonding *(UNIQUAC-HB)* and for free volume effects *(UNIQUAC-FV)* as well as combination of both additional effects *(UNIQUAC-FV+HB)*.

The initial UNIQUAC model, which is used as a foundation for all later extensions, separates the activity of the solvent in the membrane into a combinatorial and residual part[45]:

$$\ln a_i = \ln a_i^C + \ln a_i^R \tag{28}$$

For a binary system solvent-membrane system, the parts of the activity can be determined by:

$$\ln a_i^C = \ln \Phi_i + \frac{Z}{2}\cdot q_i \cdot \ln \frac{\Theta_i}{\Phi_i} + \Phi_P \cdot \left(l_i - \frac{r_i}{r_P}\cdot lp \right) \tag{29}$$

$$\begin{aligned} \ln a_i^R = {} & -q_i \cdot \ln(\Theta_i + \Theta_P \cdot \tau_{Pi}) \\ & + \Theta_P \cdot q_i \cdot \left(\frac{\tau_{Pi}}{\Theta_i + \Theta_P \cdot \tau_{Pi}} - \frac{\tau_{iP}}{\Theta_i \cdot \tau_{iP} + \Theta_P} \right) \end{aligned} \tag{30}$$

with:

$$l_i = \frac{Z}{2}\cdot(r_i - q_i) - (r_i - 1) \qquad Z = 10 \tag{31}$$

$$\Phi_i = \frac{r_i \cdot x_i}{\sum_{j=1}^{n} r_j \cdot x_j}. \tag{32}$$

$$\Theta_i = \frac{q_i \cdot x_i}{\sum_{j=1}^{n} q_j \cdot x_j} \tag{33}$$

All parameters in the UNIQUAC model apart the binary interaction parameters τ_{iP} and τ_{Pi} can be related to pure component data. These two adjustable binary parameters have to be determined from experimental equilibrium data[45]. It should, however, be noted that even for ternary and more component mixture only the binary parameters are required.

This model was successfully applied in the original study by Abrams and Prausnity[44] to predict the vapour sorption of benzene in PIB and water in PEG. More recently Meckl[8] found good agreement between experimental results for the systems of PDMS and PEBA with either trichloroethlyene or aniline, and water. Further successful applications of the model are reported by Enneking[9, 46, 47] for the systems of PU, and PEBA with toluene, cyclohexane, cyclohexene and benzene.

2.4.1 UNIQUAC-HB Model

For systems forming hydrogen bonds the residual part of the original UNIQAC model has been modified, while the combinatorial one remains unchanged:

$$\ln a_i = \ln a_i^{C} + \ln a_i^{R-HB} \tag{34}$$

In the residual part an additional parameter q_i' accounting for the effective surface of the molecule has been included. Hence for binary system the residual part is:

$$\begin{aligned} \ln a_i^{R-HB} = {} & -q_i' \cdot \ln(\Theta_i' + \Theta_P' \cdot \tau_{Pi}) \\ & + \Theta_P' \cdot q_i' \cdot \left(\frac{\tau_{Pi}}{\Theta_i' + \Theta_P' \cdot \tau_{Pi}} - \frac{\tau_{iP}}{\Theta_i' \cdot \tau_{iP} + \Phi_P} \right) \end{aligned} \tag{35}$$

Further, the volume fraction has to be modified using the additional surface parameter q_i':

$$\Theta_i' = \frac{q_i' \cdot x_i}{\sum_{j=1}^{n} q_j' \cdot x_j} \tag{36}$$

Stephan[7, 48] applied this model successfully for multi-component systems of PVA with water, ethanol methanol and i-propanol as well as with dioxane, n-propanol, tetrahydrofuran, and acetone. Further Staudt-Bickel[10] demonstrated the applicability of the model for systems of PEBA and cellulosebutyrate *(CB)* with water, ethanol, and methanol.

2.4.2 UNIQUAC-FV Model

Oishi and Prausnitz[49] suggested to extend the UNIFAC *(Section 2.5)* with an additional term to account for free volume effects. Jonquiéres et al.[50, 51] adopted this model to extend the UNIQUAC model with a free volume term.

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} \tag{37}$$

While the combinatorial and residual part are determined based on the original UNIQUAC model, the free volume extension is based on Flory's equation-of state theory for polymer solutions[52]. This extension contributes to the fact that in polymer-solvent solutions the polymer molecules are denser packed than solvent molecules, and can be determined at low pressures by:

$$\ln a_i^{FV} = 3 \cdot c_6 \cdot \ln\left(\frac{(\langle v \rangle_i^{1/3} - 1)}{(\langle v \rangle_{mix}^{1/3} - 1)}\right) - c_i \cdot \frac{\left(\frac{\langle v \rangle_i}{\langle v \rangle_{mix}} - 1\right)}{\left(1 - \frac{1}{\langle v \rangle_i^{1/3}}\right)} \tag{38}$$

The reduced volume of the solvent can be expressed by:

$$\langle v \rangle_i = (15.17 \cdot b \cdot (r_i / M_i) \cdot \rho_i)^{-1} \tag{39}$$

The reduced volume for the mixture is determined under the assumption that the volume of the liquid mixture is additive by:

$$\langle v \rangle_{mix} = \frac{(w_i / \rho_i + W_P / \rho_P)}{15.17 \cdot b \cdot (r_i \cdot w_i / M_i + r_P \cdot w_P / M_P)} \tag{40}$$

The parameter $3 \cdot c_6$ accounts for the number of external degrees of free per molecule of component *i*. Based on previous works it can be set to 1.1, while for polymer-solvent systems a proportionality factor *b* of 1.28 give best results[49].

2.4.3 UNIQUAC-FV+HB Model

For systems combining rubbery polymers with free volume effects and strong specific interactions by hydrogen bonding, it has been suggested that the previous two approaches should be linked[50, 51]:

$$\ln a_i = \ln a_i^C + \ln a_i^{R-Hb} + \ln a_i^{FV} \tag{41}$$

Hence, this model combines the modification of the residual part of the UNIQUAC-HB model to account for hydrogen bondings with the free volume extension of UNIQUAC-FV model.

A study by Jonquiéres et al.[50, 51] compared the different approaches to the UNIQUAC model for binary systems of polyurethaneimide *(PUI)* and PUI block co-polymers with ethyl-tert-butyl-ether *(ETBE)*, ethanol and ethyl acetate as solvents. It was observed that UNIQUAC-FV gives the best predictions for sorption of ether and ester in PUI. This was related to the importance of free volume effects in the systems. However, for systems involving alcohol, it was found that UNIQUAC-HB gives the best description. Hence in these systems the effects related to strong interaction by hydrogen bonds dominate over the effects of free volume.

The UNIQUAC model can be used to determine the activity of components in the membrane and, therefore, to predict sorption behaviour of binary and multicomponent systems. Several authors[8-10, 46-48] combined the UNIQUAC model with Maxwell-Stefan theory *(Section 4.5)* to predict fluxes through the membrane. Hence the UNIQUAC model can be applied for membrane development but in combination with other models it can be used for process and module design, too.

2.5 UNIFAC Models

The UNIFAC model is a structural group-contribution method developed by Fredenslund et al.[53] to predict phase equilibria for systems when no experimental data is available. The original model was extended to cover polymer-solvent systems more precise by adding a free volume part *(UNIFAC-FV)*. Further modifications were suggested to improve predictions for semi-crystalline, cross-linked, and glassy polymers. Further, a modified UNIFAC model has been suggested for polymer-solvent systems.

Similar to the UNIQUAC model the UNIFAC model consists of a combinatorial and a residual part:

$$\ln a_i = \ln a_i^C + \ln a_i^R \tag{42}$$

The combinatorial part in this model can be calculated according to the UNIQUAC model using Equation *(29)* and calculating the parameter r and q required in Equations *(32)* and *(33)* from the sum of the molar group volume and group area parameters using:

$$r_i = \sum_k \nu_k^{(i)} \cdot R_k \tag{43}$$

$$q_i = \sum_k \nu_k^{(i)} \cdot Q_k \tag{44}$$

Alternatively the Flory-Huggins lattice theory[54] can be applied to estimate the combinatorial part by[55]:

$$\ln a_i^C = \ln \Phi_i + (1 - \Phi_i) \tag{45}$$

The residual part can be calculated using the following approach:

$$\ln a_i^R = \sum_k \nu_k^{(i)} \cdot (\ln \Gamma_{k,UNIFAC} - \ln \Gamma_{k,UNIFAC}^{(i)}) \tag{46}$$

In Equation *(46)* the term $\Gamma_{k,UNIFAC}^{(i)}$ is the group residual activity of group k in reference solution of pure component i and is required to ensure that at $a_\mathrm{i} \to 1$ as $x_\mathrm{i} \to 1$. The required group activity coefficient $\Gamma_{k,UNIFAC}$ can be obtained by:

$$\ln \Gamma_{k,UNIFAC} = Q_k \cdot \left[1 - \ln \cdot \left(\sum_m \theta_m \cdot \Psi_{mk} \right) - \sum_m \frac{\theta_m \cdot \Psi_{km}}{\sum_n \theta_n \cdot \Psi_{nm}} \right] \tag{47}$$

with:

$$\theta_m = \frac{Q_m \cdot x_m}{\sum_n Q_n \cdot x_n} \tag{48}$$

$$\Psi_{mn} = \exp(-a_{mn}/T) \tag{49}$$

It should be noted that the group interaction parameters a_{mn} and a_{nm} are not equal and have to be evaluated from experimental phase equilibrium data.

In a study by Zhong et al.[56] the original UNIFAC model has been applied to fifty-one systems *(for details see Section 2.5.4)*. However, this study revealed, that predictions using UNIFAC varied significantly from experimental data. Hence for solvent-polymer systems commonly the following extensions and modifications should be applied.

2.5.1 UNIFAC-FV Model

In order to apply the UNIFAC model for polymer-solvent it has been extended by Oishi and Prausnitz[49] by adding a free volume part to the combinatorial and residual part:

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} \tag{50}$$

While the combinatorial and the residual part can be calculated according to the original UNIFAC model, the contribution of the free volume effect can be determined similar to the UNIQUAC-FV applying Equations *(38)* to *(40)*.

In the original paper by Oishi and Prausnitz[49] UNIFAC-FV, was applied for 13 binary solvent-polymer systems covering seven polymers and nine polar and unpolar solvents. It was found that the calculated solvent activities had an average error $\leq 11\ \%$ compared to experimental results. A similar result was reported by Goydan et al.[57] analysing the solubility of 35 organic compounds including acids and alcohols in seven different polymers. The predictions by the model were fairly accurate compared to the experimental data. Yamaguchi et al.[58] tested polymethyl acrylate *(PMA)* with five different solvents. The study showed that for two of the solvents, carbon tetrachloride and n-hexane, the UNIFAC-FV values were in-line with the experimental results, while for chloroform, benzene, and toluene the predictions differed from experimental values. It was therefore concluded that the free volume part of the model has to be modified to improve predictions for these three components.

2.5.2 UNIFAC-FV-M-H

The UNIFAC-FV model was extended for semi-crystalline polymers[59, 60] by including the Micheals-Hausslein theory[42]. Hence Equation *(50)* has been extended to:

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} + \ln a_i^{M-H} \tag{51}$$

The combinatorial, residual and free volume part of Equation *(51)* can be determined according to the initial UNIFAC-FV model. Assuming that the force-elongation relations follow the Hookean behaviour for chain polymer segments, the following expression can be used to determine the Micheals-Hausslein part[59-61]:

$$\ln a_i^{M-H} = \frac{\left(\dfrac{M_i \cdot \rho_{z,P}}{\rho_{i\,1}} \dfrac{\Delta H_{f,P}}{R} \cdot \left(\dfrac{1}{T} - \dfrac{1}{T_{m,P}}\right) - (\Phi_i - \chi_{i,P} \cdot \Phi_i^2)\right)}{\left(\dfrac{3}{2 \cdot f_P \cdot \Phi_P} - 1\right)} \tag{52}$$

The Flory-Huggins parameter $\chi_{i,P}$ in Equation *(52)* takes residual and free volume contribution into account and can be calculated using the Flory-Huggins theory by[54]:

$$\chi_{i,P} = \frac{(\ln a_i^R + \ln a_i^{FV})}{\Phi_P^2} \tag{53}$$

The Micheals-Hausslein theory is commonly suggested for semi-crystalline polymers, however, by treating f_P and $T_{m,P}$ as adjustable parameters it can be fit for single component solubility data of glassy polymers.

The applicability of this model to predict sorption behaviour of binary systems has been successfully demonstrated in two studies[59, 61]**.** Details of these studies will be given in the following section. Apart from binary systems, Doong et al.[60] demonstrated that this model can be applied for the system PE with ternary mixture of toluene/p-xylene/mesitylene.

2.5.3 UNIFAC-FV-F-R

Another extension of the UNIFAC-FV model is the introduction of the Flory-Rehner theory to apply the model to swelling of cross-linked membrane polymers and semi-crystalline polymers:

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} + \ln a_i^{F-R} \tag{54}$$

Similar to the UNIFAC-FV-M-H model is the combinatorial, residual and free volume part calculated according to the initial UNIFAC-FV method. The elastic contribution to the activity of the solvent can be determined by[62]:

$$\ln a_i^{F-R} = \left(\frac{\rho_{g,P}\cdot M_i}{\rho_i\cdot M_{CR}}\right)\cdot\Phi_P^{1/3} \tag{55}$$

Comparing the UNIFAC-FV-F-R model with the UNIFAC-FV-M-H model Doong and Ho[59] found for semi-crystalline PE with six components, including polar and unpolar species, at different temperatures, that the temperature dependence is not well presented by the Flory-Rehner theory. Contrary in a similar study for PE and PP with four alkanes at different temperatures, Castro et al.[61] concluded that UNIFAC-FV-M-H is the best model for PE, while the UNIFAC-FV-F-R gives the best fit for PP. The discrepancy between these studies was related to the possible misinterpretation of data[61].

2.5.4 Modified UNIFAC

To improve the predictive accuracy of the UNIFAC model for solvent-polymer solutions in comparison to UNIFAC-FV Zhong et al.[56] suggested the modified version of the original UNIFAC by Fredenslund et al.[53]. Going back to the original model only combinatorial and residual part are considered:

$$\ln a_i = \ln a_i^C + \ln a_i^R \tag{56}$$

The residual part is calculated similar to the original UNIFAC model *(Equations (46) to (49))*, while the combinatorial term has been rewritten based on Kikic et al.[63]:

$$\ln a_i^C = \ln \Phi'_i - \frac{\Phi'_i}{x_i} + 1 - \frac{z}{2}\cdot q_i\cdot\left[\ln\left(\frac{\Phi_i}{\Theta_i}\right) + 1 - \frac{\Phi_i}{\Theta_i}\right] \tag{57}$$

Furthermore, in the combinatorial term the volume fraction Φ_i has been partly replaced by a quantitative approach[64]:

$$\Phi_i' = \frac{x_i \cdot r_i^{e_i}}{\sum_j x_j \cdot r_j^{e_j}} \tag{58}$$

In the modified model by Zhong et al.[56] the exponential terms e_i and e_j were set to be always 2/3, while the surface fraction Θ_i, and volume fraction Φ_i were estimated similar to the UNIQUAC model *(Equations (32) and (33)).* The required volume parameter r_i and the surface parameter q_i were calculated using Equations *(43)* and *(44)*.

This modified model was tested for fifty-one systems combining seventeen polymers and eighteen polar and unpolar solvents including aromatic species. It was observed that this modified model offers better predictions than the original UNIFAC model. In comparison with the UNIFAC-FV model it was revealed that the accuracy of predictions was similar, but the modified UNIFAC required less information, i.e. the molar volume of the polymer and solvent are not required, and is therefore more practical[56].

The UNIFAC model can be used to predict the activity and sorption behaviour of single components or multi-component mixtures in the membrane if no experimental data is available. Similar to the UNIQUAC model it can be combined with other models to predict selectivity and fluxes through membrane, e.g. Doong et al.[60] combined the UNIFAC-FV and free volume theory *(Section 3.2)*. Hence, the applicability range of this model covers the areas of membrane development as well as process and module design.

2.6 Alternative Models to Sorption Behaviour

Apart from the widely used models discussed above, several alternative models have been developed over the years to predict activity coefficients of solvents in polymers. The first two models ASOG-FV and Entropic-FV are directly related to the models based on UNIFAC and UNIQUAC, while the modified NRTL model is related to the Flory-Huggins theory. The ENSIC analyses sorption as a mechanical process.

2.6.1 ASOG-FV

Directly related to the UNIQUAC and UNIFAC model is the ASOG *(Analytical Solution Of Groups)* method developed by Wilson and Deal[65]. This method separates the activity into a size part and a group part:

$$\ln a_i = \ln a_i^S + \ln a_i^G \tag{59}$$

The size-related part can be determined using the Flory-Huggins theory for athermal mixtures of unequal-sized molecules by:

$$\ln a_i^S = 1 - \frac{S_i}{\sum_j s_j \cdot x_j} + \ln\left(\frac{S_i}{\sum_j s_j \cdot x_j}\right) \tag{60}$$

The group related contribution to the activity is given by:

$$\ln a_i^G = \sum_k \nu_{ki}\ \ln \Gamma_{k,ASOG} - \sum_k \nu_{ki} \cdot \Gamma^*_{k,ASOG} \tag{61}$$

The activity coefficients of the group k can be calculated using the Wilson's equation[45]:

$$\ln \Gamma_{k,ASOG} = -\ln \sum_l X_i \cdot A_{ki} + \left(1 - \sum_l \frac{X_i \cdot A_{lk}}{x_m \cdot A_{lm}}\right) \tag{62}$$

$$X_k = \frac{\sum_j x_j \cdot \nu_{kj}}{\sum_j x_j \cdot \sum_k \nu_{kj}} \tag{63}$$

Choi et al.[66] extended the original ASOG model by adding a free volume term:

$$\ln a_i = \ln a_i^S + \ln a_i^G + \ln a_i^{FV} \tag{64}$$

The additional free volume part was calculated similar to the UNIQUAC-FV using Equations *(38)* to *(40)*.

Comparing the ASOG-FV with experimental data for eight systems with PS and unpolar and moderately polar solvents at 393.15 K and 423.15 K the error observed was within the range of 1%[66].

2.6.2 Entropic-FV

The Entropic-FV was developed by Elbro et al.[67] and later modified by Kontogeoris et al.[68]. Similar to the approaches to UNIQUAC and UNIFAC the activity is separated into a combinatorial and residual part:

$$\ln a_i = \ln a_i^{C-FV} + \ln a_i^R \tag{65}$$

However, compared to most of the approaches to UNIFAC, UNIQUAC and ASOG is the effect of free volume is not added, but similar to the modified UNI-

FAC model *(Section 2.5.4)* integrated into the combinatorial part of the activity:

$$\ln a_i^{C-FV} = \ln \Phi_i^{FV} + 1 - \frac{\Phi_i^{FV}}{x_i} \tag{66}$$

The volume fraction of the free volume is determined by:

$$\Phi_i^{FV} = \frac{x_i \cdot \tilde{V}_i^{FV}}{\sum_j x_j \cdot \tilde{V}_j^{FV}} \tag{67}$$

The free volume of each component, inaccessible to other components, was determined according to Bondi[69] by:

$$\tilde{V}_i^{FV} = A_{w,i}\,(\tilde{V}_i^{1/3} - \tilde{V}_{w,i}^{1/3}) \tag{68}$$

Hence, the free volume is a function of the van der Waals surface area $A_{w,i}$. This approach also includes the assumption, that the van der Waals volume $\tilde{V}_{w,i}$, the volume of molecule, which is impenetrable to other molecules under normal condition, is equal to the 'inaccessible' volume. The residual part of the activity can be calculated using to Equations *(46)* to *(49)* given for the UNIFAC model.

Comparing this model with the UNIFAC-FV model for several different polymer-solvent covering athermal to strongly polar and hydrogen bonding solutions, Kontegeorgis et al.[68] concluded that the predictions from the Entropic-FV were more favourable than those from the UNIFAC-FV. Two other models based on equations of state, also considered in this study, were regarded as less favourable and rather complicated. Further, Pappa et al.[70] compared the Entropic-FV with the modified UNIFAC model for several systems of sixteen polymers and thirteen co-polymers with different organic solvents at different temperatures. From their work it was concluded that the Entropic-FV provides the best predictions, while the modified UNIFAC model was considered satisfying due to its simplicity, since it does not require the polymer molar volumes, which have to be obtained from literature or estimated.

2.6.3 Modified NRTL

Wu et al.[71] proposed a modified version of the NRTL *(Non-Random Two-Liquid)* to calculate phase equilibria in polymer solutions. According to their work the activity of a solvent in a polymer can be estimated by:

$$\begin{aligned}\ln a_i = {} & \ln \Phi_i + \left(1 - \frac{r_i^*}{r_P^*}\right) \cdot \Phi_P + a \cdot r_i^* \cdot \left(\frac{1}{\mathrm{r}_i^*} - \frac{1}{r_P^*}\right)^2 \cdot \Phi_P^2 \\ & + q_i^* \cdot x_P^2 \cdot \left[\frac{\tau_{pi}^* \cdot G_{Pi}^2}{(x_i + x_P \cdot G_{Pi})^2} + \frac{\tau_{iP}^* \cdot G_{iP}^2}{(x_P + x_i \cdot G_{iP})^2}\right]\end{aligned} \tag{69}$$

with:

$$G_{ij} = \exp(-a\cdot\tau^{*}_{ij}) \tag{70}$$

$$q^{*}_{i} = r^{*}_{i}\cdot[1 - 2a\cdot(1 - 1/r^{*}_{i})] \tag{71}$$

In cases $\alpha = 0$ this model goes back to the Flory-Huggins theory *(Section 2.3)*. Testing the model for 10 systems using five different polymers, each of them at different average molecular weights, and eight different polar and aromatic solvents at different temperatures, the average error between experimental results and theory was less than 3 %.

2.6.4 ENSIC

The ENSIC *(ENgaged Species Induced Clustering)* model was developed by Favre et al.[72] to describe sorption as a purely mechanical anisotropic process assuming two basic sorption processes for a molecule in a vapour phase, namely:

1. the probability of a molecule condensing on a polymer site is related to the affinity $k_{p,i}$ of the permeating molecule i towards the polymer side, and
2. the probability of a molecule condensing on a previously sorbed molecule is related to the affinity $k_{s,i}$ of the permeating molecule i towards the sorbed molecule.

Combing the two assumptions with a basic lattice concept gives the following expressing for the volume fraction of the permeating component in the polymer:

$$\Phi_i = \left(\frac{k_{P,i}}{k_{S,i} - k_{P,i}}\right)\cdot(\exp((k_{Si} - k_{P,i})\cdot a_i) - 1) \tag{72}$$

This model was successfully applied to describe the sorption of various solvents in wide range of polymers[73]. Comparing this model with different approaches to the Flory-Huggins theory[39] and to the UNIQUAC model[50] for the sorption of ETBE, ethanol and ethyl acetate into PUI, it was concluded that this model gives the best predictions.

Overall, all additional models to sorption behaviour can be used directly in membrane development. Alternatively combined with other models they can also be applied for process and module design.

2.7 Molecular Simulations for Sorption

Molecular simulations are the most recent approach to predict solubilities and sorption behaviour in pervaporation. Tamai et al.[74] determined the solubilities of ethanol and water in PDMS and PE as part of an overall molecular simulation of the membrane *(including diffusion)* to predict permeation rates. To examine the sorption, they calculated the excess chemical potential, the difference in chemical potential between the liquid and the membrane phase, of the analysed systems. Their results showed higher solubility of ethanol compared to water. This was related to Lennard-Jones interaction based on the molecular distance between ethanol and the hydrophobic membrane materials. The hydrophobic PDMS had a larger free volume than other systems, which enables it to dissolve larger molecules. Comparing their calculated permeation rates with their predictions good agreement was observed. Even though the diffusion coefficient for water was higher, ethanol had the higher permeation rate. This was related to the higher solubility of ethanol in PDMS. Hence it was concluded that the solubility determines the ethanol selectivity of the PDMS.

Fritz and Hofmann[75] also studied the transport of water and ethanol through PDMS membranes using molecular simulations. In order to analyse the sorption behaviour they analysed the interfacial region on the feed side. Focusing on hydrogen bond forces, it was observed that the separation of the water-ethanol feed mixture is achieved by accumulation of ethanol molecules on the PDMS surface. Further it was revealed that the swelling behaviour of the membrane is related to the ethanol concentration in the feed. Swelling of the membrane increased with the ethanol concentration in the feed. From this work it was concluded that molecular simulation of the interfacial region can be used to analyse and predict the sorption behaviour and therefore to predict separation properties of the whole membrane. Later this study[76] was extended to cover systems of water-ethanol and ethanol with PDMS, POMS *(polyoctylmethylsiloxane)* and PMPhS *(polymethylphenylsiloxane)* membranes. Similar to the initial results with water-ethanol with PDMS system, it was observed that interfacial behaviour and membrane swelling are very much determined by the feed concentration of the solvent. A similar molecular simulation was used by Schepers et al.[77] to study the sorption behaviour of a binary organic feed mixture containing 80 wt.% n-heptane and 20 wt.% benzene towards PMPhS and five selected poly *(methacrylates)* containing 6-membered rings and having cyclic structures. From the study it was observed that PMPhS has a solubility related enrichment factor of 2 for benzene, while all studied methacrylates sorbed, in-line with expectations, preferentially the major feed component n-heptane.

Overall molecular simulations will become important tools to predict and analyse sorption behaviour of novel membrane materials. Further new membrane polymers can be tested before the synthesis of the polymers is achieved. However, so far this approach is restricted by the computer capacity required for the highly complex simulations. Therefore applications are so far restricted to membrane development.

2.8 Observations on Models of Membrane Sorption

Most of the models to predict and analyse membrane sorption are of semi-empirical nature, and, therefore, try to predict the sorption behaviour based on a minimum set of sorption experiments. Among the different semi-empirical models the solubility parameter theory seems to be a less favourable approach to membrane sorption. It might be used only for initial predictions when the sorption behaviour of components differs significantly. The other semi-empirical models based on Flory-Huggins, UNIQUAC, NRTL, Entropic-FV and ASOG seem to provide fairly good predictions. However, the precision of the models depends very much on the systems to be analysed. The same is true for the polymer-sorption specific model ENSIC. Selection of a model will therefore be based mainly on the availability of the required interaction parameters or affinities for the system to be analysed. In cases no experimental data are available the models based on UNIFAC seem to be very suitable. In particular the modified UNIFAC model seems to be interesting, because it needs only a minimum set of component values. Overall the selection of an appropriate model for a given system has often to be based on a rule of thumb using past experience with related systems, since so far no comprehensive study has been carried out covering all different models for a wide range of systems. The future with regard to the modelling of the membrane sorption behaviour will be molecular computer simulations. This approach is so far restricted by the computer capacity for the complex and detailed calculations, but will provide further understanding of the sorption behaviour of polymers even before the polymer synthesis is achieved. Overall, all models for membrane sorption are suitable for membrane development and in combination with other models like the Stefan-Maxwell theory *(Section 4.5)*, the semi-empirical sorption models can be used for process and module design.

3. MODELS OF MEMBRANE DIFFUSION

The models to predict trans-membrane diffusion of binary and multi-component mixtures for pervaporation based on data of the pure components are still in their infancies. The problems of predicting the flux and selectivity of membranes can mainly be related to coupling effects and membrane swelling. The swelling depends on the concentrations of the permeating components in the polymer structure and the related changes within the polymer structure. Michaels and Brixler[78] stated that if a polymer is solvated by a permeating component with a concentration in excess of 1 % of the polymer by volume, the diffusion process might be altered ‘catastrophically’ due swelling. While in reverse osmosis and nanofiltration the swelling based on the migration of the penetrate into the polymer structure is homogenous over the membrane thickness, in pervaporation the permeate side is nearly dry[79]. This leads to a strong non-linear concentration profile and, therefore, to local variations of diffusion coefficients. In order to describe the diffusion of a permeating molecule through a dense polymer, several theories has been developed and applied to describe diffusion in pervaporation. Binning et al.[80] believed that within the polymer there is vapour-liquid interface and that diffusion of the permeate from liquid phase to vapour phase is the rate-controlling step in pervaporation. Hence, it was assumed that the selectivity of the permeation process is dominated by the interface between the vapour and the liquid phase. Micheals et al.[81] described the diffusion process as a molecular sieving, or screening effect. In this model the polymer is described as a 'sieve' consisting of intercrystalline glassy regions, the 'holes', and extensively interconnected crystalline elements, the 'mesh'. Sweeny and Rose[82] proposed that chemical effects, i.e. hydrogen bonding between the solvent and the polymer, play an important role in the diffusion mechanism compared to dimensions, shapes and spacings of the polymer molecules. Long[83] stated that the individual diffusion and concentration gradients of the single components are the key factors influencing diffusion. Peppas and Reinhardt[84] suggested that the diffusion coefficient of the solute in highly swollen polymers and membranes can be described as a function of the solute size, the degree of swelling and the structural characteristic of the polymer, such as the mesh size between the cross-links of the polymer network. Yoshikawa et al.[85-87] related diffusion to hydrogen-bonding interactions between the permeating component and the polymer. In this theory separation of liquids mixtures through a membrane is achieved by the different strength of hydrogen-bonding between the polymer and the different components.

The key to membrane diffusion is the diffusion coefficient. In the following different models to predict and describe diffusion coefficients will be presented.

3.1 Empirical Models for Concentration-Dependent Diffusion Coefficients

To describe the concentration dependency of the diffusion coefficient several empirical models have been developed. In all models the diffusion coefficient at infinite dilution of the permeating component D_i^0 is used as a reference value.

For single component diffusion often the following exponential relationship is used[79, 88]:

$$\dot{D}_i = D_i^0 \cdot \exp(\varepsilon_i \cdot \Phi_i) \tag{73}$$

In this model ε_i is an empirical constant. Böddeker[79] called this constant *'softener'* since it accounts for the relationship between sorption of a component *i* and the related swelling of the membrane, which leads to an increased mobility in the membrane. This model was suggested by Néel[89] to describe the concentration dependency for diffusion through a rubbery polymer.

With an increasing number of permeating components the complexity of the model increases because it has to cover component-component as well as component-membrane interactions. Hence for a ternary systems this exponential model can be extended to[83, 88]:

$$\dot{D}_i = D_i^0 \cdot \exp(\varepsilon_i \cdot \Phi_i + \varepsilon_j \cdot \Phi_j) \tag{74}$$

$$\dot{D}_j = D_j^0 - \exp(\varepsilon_j \cdot \Phi_i + \varepsilon_i \cdot \Phi_j) \tag{75}$$

In the literature several successful applications of the model for a wide range of binary and ternary systems can be found[15, 88, 90-96].

Alternatively, linear models to describe diffusion can be found in the literature. For single component diffusion the following expression has been proposed[97]:

$$\dot{D}_i = D_i^0 \cdot (1 + E_i \cdot \Phi_i) \tag{76}$$

The linear models are particularly suitable for glassy membranes[89] and for some systems they might even be further simplified to[97]:

$$\dot{D}_i = D_i^0 \cdot \Phi_i \tag{77}$$

For ternary systems the following two linear correlations were proposed and applied[98, 99]:

$$\dot{D}_i = D_i^0 \cdot (\Phi_i + E_{ji} \cdot \Phi_j) \tag{78}$$

$$\dot{D}_j = D_j^0 \cdot (\Phi_j + E_{ij} \cdot \Phi_i) \tag{79}$$

The parameters E_{ij} and E_{ji} can be described as interrelated 'softener' constants. It has been demonstrated that in case of permeation of chemically similar components these parameters become 1. Hence there is a linear relationship between the diffusion coefficient and the total sorption into the membrane.

This model was later adapted by Albrecht and Rautenbach[97, 100] to describe the flux through the membrane in pervaporation. In contrast to Greenlaw et al.[98], they defined the two parameters E_{ij} and E_{ji} as coupling parameters. In the case of 'ideal' pervaporation without coupling these parameters are set to 1.

An alternative model to describe experimental results of non-ideal mixtures taking component-component as well as component-polymer interactions into account was suggested by Meuleman[96]:

$$\dot{D}_i = D_i^0 + \omega_i \cdot (\Phi_i + \theta_j \cdot \Phi_j)^{\vartheta i} \tag{80}$$

$$\dot{D}_j = D_j^0 + \omega_j \cdot (\Phi_j + \theta_i \cdot \Phi_i)^{\vartheta}{}_j \tag{81}$$

Even though the different authors try to give different empirical constants in the models a 'meaning', the nature of the models is purely empirical. The main aim of these models is to give a good representation of the experimental values. However, when the complexity of the systems increases, the complexity of the empirical model as well as the number of empirical parameters required to describe the system reasonably good, increases too. These models are therefore more suitable for process and module design than for membrane development.

3.2 Free Volume Theory

The free volume theory was developed by Fujita[101] to describe the mass transfer through polymeric membranes based on molecule movements from one place to another. The mass transport mechanism is therefore reduced to physical phenomena. The foundation of this theory is Fick's first law, which is commonly restricted to ideal systems, i.e. binary systems. The idea behind the theory is that an outside molecule can only move in a polymer if an appropriate space or free volume exists. The rearrangement of these spaces is caused by erratic fluctuation in the local density of the polymer[102]. The fundamental assumption of the model is that the mobility of both polymer segments and solvent molecules is based on the available free volume in the membrane structure. This free volume is defined as the volume within the cage of a molecule minus the volume of the molecule itself. Alternatively the free volume can be described as microvoids or temporary hollow spaces in the polymer structure. These free volume capacities appear in the membrane structure as a result of temporary density deviations of the polymer. If the free volume is large enough to take up of a solvent molecule, it can be occupied. The diffusion of molecules through the membrane is caused by redistribution of the fractional free volume in the polymer-solvent-system. Based on the assumption that sorption and desorption of a molecule are much faster than its diffusion through the membrane, the actual mass transport is completed when the equilibrium at the phase boundaries is adjusted. In the model it is further assumed that only one-way-diffusion occurs and no convection exists.

The model was originally developed for non-porous glassy polymeric membranes in contact with one solvent, but later it has been extended to binary solvent mixtures and, subsequently, modified for semi-crystalline and rubbery as well as cross-linked polymers.

One of the basic assumptions of the free volume mode is that the temperature dependency of the diffusion coefficient above the glass transition temperature can be described by the follow equation proposed by Doolittle[103, 104]:

$$D_i^T(\Phi_i,\Phi_{C,P},T) = R\cdot T\cdot A_{di}\cdot\exp\left(-\frac{B_{di}}{f_{iP}^{FV}(\Phi_i,\Phi_{C,P},T)}\right) \tag{82}$$

In this equation A_i represents the shape and size of the diffusing components and B_i is a measure of the size of sorption places in the membrane polymer. The free volume f_{iP}^{FV} is a function of Φ_i the volume fraction of solvent i in the membrane, $\Phi_{C,P}$ the volume fraction of crystalline parts in the polymer, and temperature T.

The free volume f_{iP}^{FV} can be defined as the volume in the membrane, which is available for molecules and atoms. In cases the temperature is less than the glass-transition temperature the free volume of many polymers is about 2.5% of the total volume and increases linearly above the glass transition temperature[105].

To determine the free volume f_{iP}^{FV} in a glassy polymeric membrane $(\Phi_{C,P} = 0)$ for a given solvent volume in the membrane, the following expression by Fujita[101] can be used:

$$f_{iP}(\Phi_i, 0, T) = f_{iP}(0, 0, T) + \beta_i(T) \cdot \Phi_i \tag{83}$$

In this equation β_i is a concentration dependent coefficient, which accounts for the free volume difference between solvent and membrane polymer. For semi-crystalline membrane polymers Kreituss and Frisch[106] suggested to calculate the free volume by:

$$f_{iP}^{FV}(\Phi_i, \Phi_{C,P}, T) = (1 - \Phi_{C,P}) \cdot (f_{iP}^{FV}(0, 0, T) + \beta_i(T) \cdot \Phi_i) \tag{84}$$

Introducing Equations *(83)* and *(84)* into Equation *(82)* the following two expressions for thermodynamic diffusion coefficients can be developed:

(1) glassy membranes ($\Phi_C = 0$):

$$D_i^T(\Phi_i, 0, T) = R \cdot T \cdot A_{di} \cdot \exp\left(-\frac{B_{di}}{f_{iP}^{FV}(0, 0, T) + \beta_i(T) \cdot \Phi_i}\right) \tag{85}$$

(2) semi-crystalline membranes:

$$D_i^T(\Phi_i, \Phi_{C,P}, T) = R \cdot T \cdot A_{di} \cdot \exp\left(-\frac{B_{di}}{(1 - \Phi_{C,P}) \cdot (f_{iP}^{FV}(0, 0, T) + \beta_i(T) \cdot \Phi_i)}\right) \tag{86}$$

An alternative approach to the free volume theory was developed by Fels and Huang[107] by introducing the following relationship between thermodynamic and the Fickian diffuison coefficient:

$$D_i^T(\Phi_i, \Phi_{C,P}, T) = \frac{\dot{D}_i}{\mathbf{1} - \Phi_i} \cdot \frac{d \ln \Phi_i}{d \ln a_i} \tag{87}$$

For a binary system component-membrane the term $d \ln a_i / d \ln \Phi_i$ can be determined by:

$$\frac{d \ln \Phi_i}{d \ln a_i} \cong [(1 - \Phi_i) \cdot (1 - 2 \cdot \chi_{i,P} \cdot \Phi_i)]^{-1} \tag{88}$$

In Equation *(88)* the interaction parameter $\chi_{i,P}$ is related to Flory-Huggins theory[54] and can be determined according to Equations *(14)* to *(17)* in Section 2.3, while the activity a_i of the component in the polymer can be determined by selecting an appropriate model from Sections 2.3 to 2.6. Furthermore, in order to determine the free volume parameters, a numerical solution of the diffusion equation was fitted to experimental desorption data. Using this theory for the system benzene-PE with an interaction parameter $\chi_{i,P}$ of 0.5, Fels and Huang[107] found good agreement between calculated and experimental values.

Rhim and Huang[108, 109] extended the previous models from binary to ternary systems. To determine the thermodynamic diffusion coefficient Equations *(87)* and *(88)* can be used similar to the previous model by Fels and Huang[107]. To determine the component-membrane term $d \ln a_i / d \ln \Phi_i$ for the ternary system Equation *(88)* has to be extended to:

$$\begin{aligned}\frac{\ln a_i}{\ln \Phi_i} = \Phi_i \cdot \Bigg(\frac{1}{\Phi_i} - 1 + \frac{\widetilde{V}_i}{\widetilde{V}_P} - \chi_{x,j} \cdot \Phi_i \\ + X_{j,P} \cdot \Phi_j \cdot \frac{\widetilde{V}_i}{\widetilde{V}_j} - \chi_{i,P} \cdot (2 - 2 \cdot \Phi_i - \Phi_j) \Bigg)\end{aligned} \tag{89}$$

$$\begin{aligned}\frac{\ln a_j}{\ln \Phi_j} = \Phi_j \cdot \Bigg(\frac{1}{\Phi_j} - 1 + \frac{\widetilde{V}_j}{\widetilde{V}_P} - \chi_{i,j} \cdot \Phi_i \cdot \frac{\widetilde{V}_j}{\widetilde{V}_i} \\ + \chi_{i,P} \cdot \Phi_i \cdot \frac{\widetilde{V}_j}{\widetilde{V}_i} - \chi_{j,P} \cdot (2 \cdot \Phi_j + \Phi_i - 2) \Bigg)\end{aligned} \tag{90}$$

The required interaction parameters $\chi_{i,P}$, $\chi_{j,P,}$ and $\chi_{i,j}$ and the activity of the component in the membrane can be estimated similar to the binary model.

Comparing the predicted permeabilities of n-Hexane and Benzene in PE at different temperatures and concentrations it was demonstrated that the results obtained with the model are closer to the experimental values than those predicted by the Fels and Huang model[108, 109]. In another study by Huang et al.[110] the applicability of this model was further demonstrated for a binary mixture of methanol - pentane using a cross-linked blended membrane of nylon 6 and poly*(arcylic acid) (PAA)*. A reasonable agreement between experimental results and calculated values was observed. It should be noted that for the calculations it was assumed the effect of cross-linking did not effect the Flory-Huggins thermodynamics.

Generalising and improving previous models for glassy and semi-crystalline membranes, Yeom and Huang[111] defined a new generalised parameter B_i that covers semi-crystalline and glassy membrane polymers:

$$B_i^{FV} = \frac{B_{di}}{(1 - \Phi_{C,P})} \tag{91}$$

The parameter B_i^{FV} was determined by fitting a numerical solution of the diffusion equation based on the free volume theory to steady state pervaporation data.

Using this model it was possible to predict the permeation of benzene, toluene, n-hexane and n-heptane through a PE membrane at different temperatures with a high accuracy in comparison with experimental data[111].

Yeom and Huang[112] later extended this model from binary to ternary systems. Extending Equation *(82)* this improved model also considered the coupling of fluxes in the membrane, which could not be explained by the previous models:

$$D_i^T(\Phi_i,\Phi_{C,P},T) = R\cdot T\cdot A_{di} \cdot\exp\left(\frac{-f_{iP}^{FV}(0,0,T)}{B_i^{FV}} + \frac{\beta_i\,(T)}{B_i^{FV}}\cdot\Phi_i + \frac{\beta_j\,(T)\cdot B_j^{FV}}{B_i^{FV}}\cdot\Phi_i\right)^{-1} \quad (92)$$

The required activity a_i in the membrane and the interactions parameter $\chi_{i,j}$ were estimated in a similar manner as before. This model was successfully applied to predict permeation of ethanol-water mixtures through cross-linked PVA membranes[112]. The free-volume theory was further successfully applied to analyse the pervaporation of a water-ethanol mixture through PAN and four different co-polymers in a study by Kim et al.[113]. Some limitations of this model were shown in a study analysing the pervaporative separation of the highly non-ideal mixture of methanol-carbon tetrachloride through LDPE membranes. From this study it was concluded that not all interactions between membrane and components are covered by the model[114].

Overall, the free volume model is particularly suitable for membrane development. In the case of glassy, semi-crystalline, and rubbery as well as cross-linked membrane polymers it can be used as a fundamental theory to understand diffusion through polymers.

3.3 Dual Sorption Model

Similar to the free volume model, the dual sorption model by Vieth and Sladek[115], later extended by Vieth et al.[116], describes diffusion based on free spaces, so-called microvoids, in the polymer structure. These microvoids or hollow spaces in the polymer structure are assumed to be uniformly distributed. In case a microvoid with an appropriate size is next to a solvent molecule, this microvoid can dissolve the molecule. The energy of this molecule has therefore to be high enough to enable it to move into the hole. Diffusion occurs if the free space of the moved molecule will be taken by another molecule. This mechanism is known as 'Dual Sorption Model'. Initially it has been developed for glassy polymers to describe negative deviation from Henry's Law concerning the absorption of gases into polymers. This model distinguishes two parallel mechanisms of sorption in a micro-heterogeneous medium by dividing the solvents into *(1)* diffusing molecules $C_{D,i}$, and *(2)* molecules that are immobilised in microvoids or holes $C_{H,i}$:

$$C_i = C_{D,i} + C_{H,i} \tag{93}$$

The overall process is described by a non-linear sorption isotherm, which can be divided into a linear part accounting for normal dissolution which can be described by a Henry's Law isotherm *(Equation (1))* and a non-linear Langmuir-type part representing the immobilised molecules in the polymer *(Equation (2))*. It should be noted that the immobilised molecules do not affect the Henry-distribution-equilibrium. In order to take this factor into account a hole affinity constant b_i has been defined as the ratio of rate constants of sorption and desorption of permeating components in the holes. Based on this Equation *(93)* can be rearranged to:

$$C_i = {}_{D,i} + C_{H,i} = k_{D,i} \cdot p_i + \frac{C'_{H,i} \cdot b_i \cdot p_i}{1 + b_i \cdot p_i} \tag{94}$$

The local equilibrium between the two sorption modes, i.e. the mobile molecules and the immobilised molecules, can be expressed by:

$$C_{H,i} = \frac{(C'_{H,i} \cdot b_i / k_{D,i}) \cdot C_{D,i}}{1 + (b_i / k_{D,i}) \cdot C_{D,i}} \tag{95}$$

Based on the dual sorption model the permeability of a component is given by[117]:

$$P_i^P = k_{D,i} \cdot D_{D,i} + \frac{C'_{H,i} \cdot b_i \cdot D_{H,i}}{1 + b_i \cdot p_i} = k_{D,i} \cdot D_{D,i} \cdot \left(1 + \frac{F_i \cdot K_i}{1 + b_i \cdot p_i}\right) \tag{96}$$

with

$$F_i = \frac{D_{H,i}}{D_{D,i}}, \quad \textit{and} \tag{97}$$

$$K_i = \frac{C'_{H,i} \cdot b_i}{k_{D,i}} \tag{98}$$

Okuno et al.[117] used this model successfully to predict the single component permeation of water and ethanol vapours through a PVA membrane.

The basic model of dual sorption has been later extended by Vieth et al.[116, 118] to account for the swelling of glassy membranes in case of water sorption. This swelling leads to a positive deviation from Henry's Law and can be accounted for using a concentration-dependent activity coefficient. In case of a swollen membrane it is assumed that the total concentration C_i depends of the concentration of the diffusing component $C_{D,i}$, and the components side-bounded in the polymer $C_{S,i}$:

$$C_i = C_{D,i} + C_{S,i} \tag{99}$$

This model has been successfully applied to determine water permeation in different polymers[118].

The dual sorption model has been further extended to predict permeabilities of multi-component systems. Koros[119] suggested the following two extensions of the dual sorption theory for the concentrations of the components *i* and *j* in a binary mixture as a function of their partial pressures:

$$C_i = k_{D,i} \cdot p_i + \frac{C'_{H,i} \cdot b_i}{(1 + b_i \cdot p_i + b_j \cdot p_j)} \tag{100}$$

$$C_j = k_{D,i} \cdot p_i + \frac{C'_{H,j} \cdot b_j}{(1 + b_j \cdot p_j + b_i \cdot p_i)} \tag{101}$$

The permeability of a component *i* in a mixed vapour through a glassy polymer can be expressed by[120]:

$$P_i^P = k_{D,i} \cdot D_{D,i} \cdot \left(1 + \frac{F_i \cdot K_i}{1 + b_i \cdot p_i + b_j \cdot p_j}\right) \tag{102}$$

The required parameters F_i and K_i can be determined using Equations *(97)* and *(98)*. Rewriting Equation *(102)* in terms of mole fraction for component *i* gives[120]:

$$P_i^P = k_{D,i} \cdot D_{D,i} \cdot \left(1 + \frac{F_i \cdot K_i}{1 + b_j \cdot p + x_i \cdot p \cdot (b_i - b_j)}\right) \tag{103}$$

This model for binary mixtures was applied by Okuno et al.[117] to predict permeabilities of a water-ethanol vapour through a PVC membrane. Comparing experimental and theoretical values it was observed that the experimental permeability of ethanol was significantly lower than predicted from the model while for water a higher permeability than predicted was measured.

Similar to the free volume model the dual sorption model should therefore be applied in the field of membrane development. So far the dual sorption model has been mainly applied for gas separation membranes but it has some potentials in the development of pervaporation membranes, since it seems to be applicable to vapour permeation at low pressures. Although it has been stated that the dual sorption mode might be insignificant for practical pervaporation due to the high concentration of permeating components in the membrane[121], it might nevertheless be used as a foundation to understand the complex diffusion process of high concentrations of liquids and vapours through glassy polymers.

3.4 Molecular Simulations for Diffusion

In order to analyse the diffusion in pervaporation also molecular computer simulations can be applied to investigate the behaviour of the permeating components in a polymer matrix.

Similar to their studies on sorption behaviour *(Section 2.7)* Tamai et al.[122] used molecular simulations to investigate the diffusion of water and ethanol through PDMS and PE. From the study it was shown that ethanol has smaller diffusion coefficients in PDMS and PE than water. Further, it was observed that water and ethanol aggregates in the PDMS. These aggregations reduced the diffusion coefficient to one-fiftieth of the value without aggregations, since the diffusion coefficient of aggregated molecules is virtually zero. Comparing their results with experimental values it was revealed that diffusion coefficients simulated for non-aggregated molecules are close to experimental values. The general difference between experimental results and simulation was related to the fact that the simulation does not account for relaxation effects *(swelling)* of the polymer chains due to presence of ethanol molecules.

Fritz and Hofmann[75] also used a molecular simulation focusing on the bulk region of the membrane to analyse diffusion of water-ethanol through PDMS membranes. In their simulation the elementary mechanism is a sequence of jumps between pre-existing cavities in the polymer matrix, which allow low concentrations of small permeating components to migrate through a membrane. For higher concentrations of permeating components, e.g. in solvent-swollen membranes, the diffusion mechanism gradually changes to liquid-like diffusion around polymer chains. In the simulation the small penetrating molecules stay in assigned small regions of space for relatively long periods of time. During these quasi-stationary periods, the permeating molecules are reflected from the thermally vibrating polymer matrix every few pico seconds. Thus, the permeating components explore the occupied holes in the free volume. These quasi-stationary periods are interrupted by quick jumps from one hole to another. It became apparent that during the same simulation time for the system water-ethanol, the water molecules realised more jumps, while ethanol molecules staid longer in their occupied cavities in the polymer structure. Hence water moves faster through the polymer structure than ethanol. Combined with their results on membrane sorption *(Section 2.7)* it was concluded that sorption behaviour dominates the analysed system. In a later study[123] the investigation also included POMS membranes with water and ethanol. It was revealed that in the more densely packed POMS larger polymer segment movements are required than in PDMS to allow a permeating component to jump. This resulted in a lower diffusion coefficient compared to PDMS. This study also covered the simulation of some glassy polymers. However, the results presented were restricted to diffusion of gases.

Overall dynamic computer simulation seems to become an important tool in the development of new improved membranes. Furthermore, simulations can cover a wide range of different membranes, including membranes of which the synthesis is not established.

3.5 Observations on Models of Membrane Diffusion

Most of the models to analyse and predict membrane diffusion are of empirical nature. These models are very suitable to describe individual systems but lack fundamental understanding of the diffusion process. Hence, the models are useful for a practical process and module design but not for membrane development. The free volume model and the dual sorption model have a more sound background. Particularly the free volume model seems to be very interesting to analyse diffusion in pervaporation since it covers a wide range of polymer types, while the dual sorption model is restricted to glassy membranes. Similar to modelling of the sorption behaviour, the future of analysing and predicting membrane diffusion is molecular simulations.

4. MODELS OF THE TRANS-MEMBRANE MASS TRANSFER

The following models have been developed to predict and analyse the overall trans-membrane mass transfer in pervaporation. These models either combine features of the above models or introduce new semi-empirical or empirical parameters to cover sorption, diffusion, and desorption.

The measure of the trans-membrane mass transfer is the flux across the membrane. The flux is a measure of the productivity of the membrane system and determinates the size of the system and is, therefore, associated with the capital cost. It can be used for an economic assessment of the system[124]. Hence, predicting and analysing the flux as a result of trans-membrane mass transfer is one of the most important tasks to design new processes and modules and to develop new membranes.

4.1 Empirical Model to Trans-Membrane Mass Transfer

The empirical model proposed by Franke[125] is directly based on pervaporation experiments. The aim of this approach is to achieve a good mathematical description of the mass transport by interpolation of the measurements. Hence, the total system can be seen as a so-called "*black box*" in which no physico-chemical relations are considered. To apply this model successfully Franke[125] made a few assumptions, which simplifies the process crucially:

- The permeate concentration is independent of the temperature.
- The effect of temperature on the permeability can be described by an Arrhenius-type equation.
- On the permeate side free permeate flow is assumed.
- The permeate pressure is assumed to be constant during the experiments.

Based on theses assumptions, the flux through the membrane, J_i, can be described as a function of the following parameters:

$$J_i = f(x_{Fi}, T_F, p_p) \tag{104}$$

Assuming that the temperature dependency of the membrane can be described by an Arrhenius-type of equation, Equation *(104)* can be rewritten as:

$$J_i = f(x_{Fi}, T_F, p_p) \cdot \exp\left[-\frac{E_i}{R} \cdot \left(\frac{1}{T^0} - \frac{1}{T_F}\right)\right] \tag{105}$$

The required activation energy E_i in Equation *(105)* can be estimated by two measurements under the same conditions *(i.e. permeate pressure, feed concentration and hydrodynamic conditions are kept constant but the temperature changed)*.

It was found that this model offers a good foundation for interpolation of pervaporation data and reduces the number of parameters to estimate and therefore the number of required experiments. Franke[125] claims that 5 measurements at a constant permeate pressure often provide a reasonable description of the mass transport through the membrane for a given set of parameters. This model was successfully integrated into PVDesign, a simulation package developed by the Department of Chemical Engineering at the University of Aachen *(Germany)* and later used as a foundation of their ASPEN Plus^{TM} user block. This user block was successfully applied to design and optimise pervaporation units, e.g. in combination with distillation for the production of MTBE *(Methyl Tert-Butyl Ether)*[126]. Hence, this model seems to be suitable for process design. However, the applicability of the model is commonly restricted to the process conditions covered by experiments. Within the area of membrane development it might be used for some initial comparisons but does not provide the required depth for membrane improvements.

4.2 Solution-Diffusion Model

The solution-diffusion model was originally developed by Graham[127] to describe the permeation of gases through rubber septa. Binning et al.[80] introduced the model to pervaporation. The solution-diffusion model describes the mass transport through a dense membrane in three steps:

1. sorption of the permeating compounds into the polymer,
2. diffusion through the polymer along the gradient of the chemical potential, and
3. desorption at the permeate side.

The typical profiles through the membranes are given in a schematic overview in Figure 3. It should, however, be noted that the concentration profile

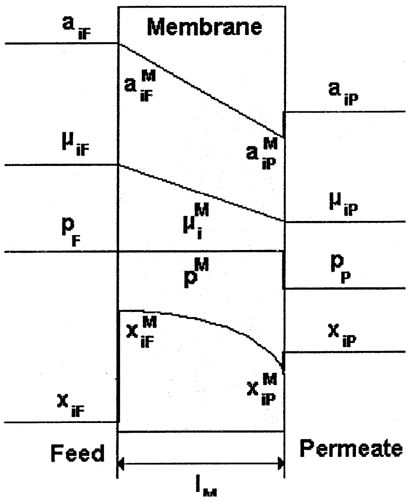

Figure 3. Gradients through the selective layer of a pervaporation membrane.

in the membrane depends on the swelling the membrane[128]. Furthermore, Figure 3 includes the assumption that the pressure in the membrane is constant, and equilibrium exists at the membrane interfaces.

In the literature two different starting points can be found to derive a mathematical description of the flux J_i based on the solution-diffusion model:

1. Starting point for the first approach is the Nernst's Equation:

$$D_i^T = R\cdot T\cdot b_{M,i} \tag{106}$$

For pervaporation the following general formulation for the flux J_i can be developed by extending the diffusion equation:

$$J_i\,(z) = -C_i\,(z)\cdot\frac{D_i^T\,(z)}{R\cdot T}\cdot\frac{da_i\,(z)}{dz} \tag{107}$$

2. Starting point of the second approach is Fick's First Law (neglecting the convective flow term):

$$J_i\,(z) = -\,\dot{D}_i\,(z)\cdot\frac{dC_i\,(z)}{dz} \tag{108}$$

Depending on the starting point of the deviation either a Fickian diffusion coefficient or thermodynamic diffusion coefficient have been used. The relationship between these two diffusion coefficients has been given by Fels and Huang[107] in Equation *(87)*.

For pervaporation, finally both approaches lead to the following general equation for the flux J_i :

$$J_i = \frac{\dot{D}_{M,i}\cdot C_{M,i}}{a_{M,i}}\cdot\frac{1}{l_M}\cdot(a_{F,i} - a_{P,i}] \qquad (109)$$

Since independent determination of $\dot{D}_{M,i}$, $C_{M,i}$ and $a_{M,i}$ involves uncertainties and requires great experimental effort a phenomenological permeability P_i is introduced, which can be determined for each system by simple pervaporation experiments:

$$P_i = \frac{\dot{D}_{M,i}\cdot C_{M,i}}{a_{M,i}} \qquad (110)$$

Introducing the permeability, Equation *(109)* can be rearranged to:

$$J_i = \frac{P_i}{l_M}(a_{F,i} - a_{P,i}) \qquad (111)$$

The temperature dependency of the permeability is often described using an Arrhenius-type of equation similar to Equation *(105)*:

$$P_i(T_F) = P_i(T^0)\cdot\exp\left[-\frac{E_i}{R}\cdot\left(\frac{1}{T^0} - \frac{1}{T^F}\right)\right] \qquad (112)$$

A more detailed development of how to derive the equation *(109)* from the fundamental equations *(107)* and *(108)* can be found elsewhere in the literature, e.g. Stürken[129], Bennett[130], Hausmanns[131]. Additionally, Wijmans and Baker[132] published a review on the solution-diffusion model for different membrane processes

The solution-diffusion model has been successfully used for the testing and comparison of membranes, when the coupling of fluxes can be neglected *(i.e. for very low concentrations of the preferentially permeating components in the feed).* Cóte and Lipski[133] integrated the solution diffusion model into the resistance-in-series model for pervaporation covering the mass transfer through the feed side concentration boundary layer and the membrane. This basic resistance-in-series model and subsequent extensions and modifications have been used by several authors[27, 129-131, 134-137] to model and simulate different membrane-solvent systems.

Since the model includes the influence of all important process parameters the solution-diffusion model seems to be particularly suitable for the development and optimisation of the process using all different types of polymeric membranes. However, for membrane development and optimisation the use of the model is limited, since all fundamental values are summarised in the permeability.

4.3 Semi-Empirical Models Related to the Solution-Diffusion Model

Over the years several modifications of the solution-diffusion model have been published. These models try to overcome some restrictions of the basic solution-diffusion, i.e. coupling of fluxes. In the following these models will be introduced.

4.3.1 Semi-Empirical Model After Meyer-Blumenroth

The semi-empirical model by Meyer-Blumenroth[125, 138, 139] extends the initial solution-diffusion model by including the effect of coupling for up to three feed components. Furthermore, the driving force in this model is the pressure-based fugacity instead of concentration-based activity in the initial solution-diffusion model. However, it should be noted that both driving forces can be related to the chemical potential. The model itself is based on a one-dimensional flux though a membrane using Fick's Law:

$$J_i = -C_i \cdot \frac{D_i^T}{f_i^0} \cdot \frac{1}{\gamma_i} \cdot \frac{df_i}{dz} \tag{113}$$

In order to integrate Equation *(113)* across the membrane thickness it has been suggested to introduce the following relationships between the local activity coefficients and the local fugacities:

$$\gamma_i = \exp\left(B_{ii} \cdot \left[1 - \left[\frac{f_i}{f_i^0} + B_{ij} \cdot \frac{f_j}{f_j^0}\right]\right]\right) \tag{114}$$

$$\gamma_j = \exp\left(B_{jj} \cdot \left[1 - \left[\frac{f_j}{f_j^0} + B_{ji} \cdot \frac{f_i}{f_i^0}\right]\right]\right) \tag{115}$$

These relationships are based on a model by Brun et al.[91] and include the effect of coupling by the means of coupling coefficients B_{ij} and B_{ji}. Assuming equilibrium at the interfaces of the membrane, the fugacities of the feed and permeate side can be used as boundary conditions for the integration of Equation *(113)*. Hence no additional sorption experiments are required to determine the sorption equilibrium. Introducing an average activity coefficient across the membrane further simplifies the integration:

$$\gamma_{M,i} = \sqrt{\gamma_i\,(f_{F,i}, f_{F,j}) \cdot \gamma_i\,(f_{P,i}, f_{P,j})} \tag{116}$$

Finally, integration of Equation *(113)* gives the following expression for the flux of the component i across the membrane:

$$J_i = \frac{\overline{D}_i^T}{\overline{\gamma}_{M,i}}\cdot\left[\frac{f_{F,i} - f_{P,i}}{f_i^0}\right] = \frac{\overline{D}_i^T}{\overline{\gamma}_{M,i}}\cdot(a_{F,i} - a_{P,i}) \tag{117}$$

with:

$$\overline{D}_i^T = \frac{C_{M,i}\cdot D_i^0}{l_M} \tag{118}$$

Comparing Equations *(117)* and *(118)* with Equations *(110)* and *(111)* the similarity between the semi-empirical model by Meyer-Blumenroth[125, 138, 139] and the solution-diffusion model are demonstrated. Further, the temperature dependency of the thermodynamic diffusion coefficient is represented by an Arrhenius-type of equation:

$$\overline{D}_i^T(T_F) = \overline{D}_i^T(T^0)\cdot\exp\left[-\frac{E_i}{R}\cdot\left(\frac{1}{T^0} - \frac{1}{T_F}\right)\right] \tag{119}$$

This model was originally developed by Meyer-Blumenroth[138] to describe vapour permeation and then later adopted by Franke[125] for pervaporation. The model was also further extended to account for the influence of the support structure of composite membranes. When applying this model for a PVA/polyacrylonitrile *(PAN)* membrane for different binary aqueous organic mixtures; a good agreement between the model and experimental results was observed[125].

The model was later modified to be applicable for ternary feed mixtures[125]. Therefore the relationship between the local activity coefficient and the local fugacity was extended to account for the coupling with regard to the third component:

$$\gamma_i = \exp\left(B_{ii}\cdot\left[1 - \left[\frac{f_i}{f_i^0} + B_{ij}\cdot\frac{f_j}{f_j^0} + B_{ik}\cdot\frac{f_k}{f_k^0}\right]\right]\right) \tag{120}$$

$$\gamma_j = \exp\left(B_{jj}\cdot\left[1 - \left[\frac{f_j}{f_j^0} + B_{ji}\cdot\frac{f_i}{f_i^0} + B_{jk}\cdot\frac{f_k}{f_k^0}\right]\right]\right) \tag{121}$$

$$\gamma_k = \exp\left(B_{kk}\cdot\left[1 - \left[\frac{f_k}{f_k^0} + B_{ki}\cdot\frac{f_i}{f_i^0} + B_{kj}\cdot\frac{f_j}{f_j^0}\right]\right]\right) \tag{122}$$

Further, the determination of the average activity coefficient has to include the extra component:

$$\gamma_{M,i} = \sqrt{\gamma_i\,(f_{F,i}, f_{F,j}, f_{F,k})\cdot\gamma_i\,(f_{P,i}, f_{P,j}, f_{P,k})} \tag{123}$$

For the ternary feed mixture, the flux can be calculated similar to the binary mixture using Equation *(117)*, while the influence of temperature on the flux can be predicted accordingly with Equation *(119)*. Extending the model to account for the support structure of composite membranes it was applied to analyse three systems with PAN/PAV membranes and ternary feed mixtures. Applying this model it was revealed that for two feed mixtures *(water-ethanol-butanol and water-isopropanol-methanol)* the model gave good agreement between experimental results and theory. For a third system with water-ethanol-methanol a clear deviation between experimental values and theory was obtained. This was, however, related to inhomogenities of the membrane material[125].

This semi-empirical model with purely empirical coupling coefficients has no physical meaning. This certainly improves predictions if coupling effects influence the mass transfer. However, in cases coupling is not effecting the mass transfer, these additional coupling parameter increases the complexity of the model and does not improve the results compared to the solution-diffusion model. As a result, the typical applications of this model should be similar to the solution-diffusion model in the process and module design.

4.3.2 Q_i-Model

Another alternative model to predict fluxes including coupling related to the solution-diffusion has been developed by Klatt[1]. The flux is described as a function of the permeability and the difference in chemical potential between the feed and the permeate side, the driving force of pervaporation:

$$J_i = Q_i \cdot \Delta\mu_i = Q_i \cdot R \cdot T_F \cdot \ln\left(\frac{x_{F,i} \cdot \gamma_{F,i} \cdot p_i^0}{\gamma_{P,i} \cdot p_p}\right) \tag{124}$$

Applying this model the driving force $\Delta\mu_i$ can be determined from the local process conditions at membrane and assuming Qi constant, fluxes can be predicted under changed conditions. With reference to the semi-empirical nature of the model, the permeability is a function of the geometric average of mixing term of the chemical potential using five empirical model parameters:

$$Q_i = A_1 \cdot \bar{\kappa}^{A_3} \tag{125}$$

$$Q_j = A_2 \cdot \bar{\kappa}^{A_4} \tag{126}$$

with:

$$\bar{\kappa} = \kappa_i + A_5 \cdot \kappa_j \tag{127}$$

and

$$\kappa_i = \sqrt{\ln(x_{F,i} \cdot \gamma_{F,i}) \cdot \ln\left(\frac{y_{P,i} \cdot p_p}{p_i^0}\right)} \tag{128}$$

The temperature dependency of the permeability is expressed using an Arrhenius-type equation similar to Equation *(112)*:

$$Q_i(T_F) = Q_i(T^0)\cdot\exp\left[-\frac{E_i}{R}\cdot\left(\frac{1}{T^0}-\frac{1}{T_F}\right)\right] \tag{129}$$

This model has been successfully applied for several different membranes using binary water-organic and organic-water mixtures. Nevertheless, in case of systems with strong non-ideal behaviours, e.g. polybutadiene membranes with phenol and water, the model was not applicable[1]. So far the model has been restricted to binary mixtures. Compared to the semi-empirical model by Meyer-Blumenroth[138] *(Section 4.3.1)* the number of parameters to be determined to describe a ternary system including coupling has been reduced from nine to seven. This modified model of the solution-diffusion model offers an improved prediction in case of coupling but requires therefore an extra coupling factor A_5 that has to be determined empirically. Nevertheless the coupling parameters have no physical meaning and therefore typical applications are similar to those for the solution-diffusion model in the area of process and module design.

4.3.3 Process-Specific Permeability Functions

The model of process-specific permeability functions by Vier[140] uses a further approach to include coupling in the solution-diffusion model by dividing the permeability into permeability functions. Starting point is an integral transport equation based on the solution-diffusion model to describe the flux of the components as a function of permeability P_i and driving force DF_i :

$$J_i = P_i(x_{F,i},T_F,p_p)\cdot DF_i(x_{F,i},T_F,p_p) \tag{130}$$

The driving force is the difference in the chemical potential between the feed and the permeate side and can be reduced to the activity difference across the membrane. In cases when the effect of coupling of the fluxes can be neglected, the flux can be determined by:

$$\begin{aligned} J_i &= J_i^0\cdot P_i(x_{F,i})\cdot P_i(T_F)\cdot P_i(a_{P,i})\cdot DF_i \\ &= J_i^0\cdot P_i(x_{F,i})\cdot P_i\cdot(T_F)\cdot P_i(a_{P,i})\cdot(a_{F,i}-a_{P,i}) \end{aligned} \tag{131}$$

The determination of the permeability function for the activity $P_i(a_{iP})$, the feed concentration $P_i(x_{iF})$, and the feed temperature $P_i(T_F)$ is purely empirical. However, in cases of strong coupling of the fluxes additionally a coupling factor k_i has been introduced as part of the driving force term:

$$\begin{aligned} J_i &= J_i^0\cdot P_i(x_{F,i})\cdot P_i(T_F)\cdot P_i(a_{P,i})\cdot Df_i \\ &= J_i^0\cdot P_i(x_{F,i})\cdot P_i(T_F)\cdot(P_i)(a_{P,i})\cdot(a_{F,i}-a_{P,i}+k_i\cdot(a_{F,j}-a_{P,j})) \end{aligned} \tag{132}$$

For the activity based permeability function the following expression has been suggested to describe hydrophilic pervaporation with binary mixtures:

$$P_i(a_{P,i} = K_{1,i}\cdot\exp(c_i\cdot(a_{P,i} - a_{P,i}^2)) \tag{133}$$

The determination of constants c_i is based on sets of experiments of different permeate pressures keeping the other process conditions constant.

For target-organophilic and hydrophobic pervaporation using binary mixtures an alternative model for the activity-based permeability function has been given:

$$P_i(a_{P,i}) = K_{2,i}\cdot(c_i\cdot(a_{P,i} - a_{P,i}^2))^{d_i} \tag{134}$$

In this case the exponential term d_i has to be determined experimentally, too. The feed concentration-based permeability function is based on the Freundlich's sorption theory and is determined by:

$$P_i(x_{F,i}) = K_{3,i}\cdot x_{F,i}^{n_i} \tag{135}$$

Finally, the temperature-based permeability function can be expressed similar to the solution-diffusion model *(Equation (112))* based on an Arrhenius-type of equation:

$$P_i(T_F) = K_{4,i}\cdot\exp\left(\frac{E_i}{R}\cdot\left(\frac{1}{T_0} - \frac{1}{T_F}\right)\right) \tag{136}$$

In the models c_i, d_i, n_i and E_i are component specific parameters. All parameters have to be determined by independent pervaporation experiments. The different *K*-factors in Equations (133) to (136) depend on the permeability functions and are only required for the prediction of the different parameters of the permeability functions. In the overall expression for the flux *(Equations (131) and (132))* they are replaced by a reference flux J_i^0, which has been determined after all parameters of permeability functions have been found.

This model has been successfully applied to a number of organic-water and organic-organic systems[140]. Similar to the models of Klatt[1] and of Meyer-Blumenroth[138] this modification of the solution-diffusion model offers an improved prediction of fluxes in case of coupling and non-ideal systems. However, the model is so restricted to binary mixtures and even this model using permeability functions does not give a depth required for membrane development, since the different parameters are purely empirical. Hence, applications will be in the area of process and module design.

Overall the different modifications of the solution-diffusion model offer improved predictions in case of no ideal systems and coupling. However, additional parameters have to be introduced, which increases the complexity of the model. Apart from the semi-empirical model by Meyer-Blumenroth[138] *(Section 4.3.1)* all models are restricted to binary systems and it is foreseeable that the number of parameters will further increase with the number of components.

4.4 Thermodynamics of Irreversible Process (TIP)

The thermodynamics of irreversible process *(TIP)* have been introduced to describe coupled diffusion and, consequently, coupled fluxes through membranes. Most models to describe mass transfer across the membrane are developed for binary feed mixtures or neglect coupling. Other models related to the solution-diffusion model including coupling have a significantly increasing complexity when the number of components in the feed stream increases *(Section 4.3)*. The TIP theory combines a minimum of complexity with the opportunity to analyse multi-component mixtures and to account for coupling. Kedem[141, 142] introduced this theory to pervaporation for pervaporation. The basic phenomenological equations to describe the fluxes of multi-component systems are given by:

$$\begin{aligned} J_i &= L_{ii}\cdot\frac{d\mu_i}{dz} + L_{ij}\cdot\frac{d\mu_j}{dz} + \cdots + L_{in}\cdot\frac{d\mu_n}{dz} \\ J_j &= L_{ji}\cdot\frac{d\mu_i}{dz} + L_{jj}\cdot\frac{d\mu_j}{dz} + \cdots + L_{jn}\cdot\frac{d\mu_n}{dz} \\ &\vdots \qquad\quad \vdots \qquad\qquad \vdots \qquad\qquad\qquad \vdots \\ J_n &= L_{ni}\cdot\frac{d\mu_{ii}}{dz} + L_{nj}\cdot\frac{d\mu_j}{dz} + \cdots + L_{nn}\cdot\frac{d\mu_n}{dz} \end{aligned} \tag{137}$$

For a ternary system the two fluxes can be described by the following equations:

$$J_i = -L_{ii} grad \gamma_i - L_{ij} grad \gamma_j \tag{138}$$

$$J_j = -L_{ji} grad \gamma_i - L_{jj} grad \gamma_j \tag{139}$$

L_{ii} and L_{jj} are phenomenological coefficients of the pure flux of the components *i* and *j*, while L_{ij} and L_{ji} describe the coupled flux of the components. The number of phenomenological coefficients increases with the number of penetrates but according to Onsager's relationship:

$$L_{ij} = L_{ji} \tag{140}$$

Using this relationship the number of coefficients required decreases from n^2 to $0.5n^2+n$. Furthermore, according to the thermodynamic principle of entropy production in irreversible systems, the following inequalities must be fulfilled:

$$L_{ii} > 0, L_{jj} > 0, \quad \text{and} \tag{141}$$

$$L_{ii}\cdot L_{jj} \geq L_j^2 \tag{142}$$

In a study by Simon et al.[143] the TIP was successfully applied to determine the degree of coupling in case of binary mixtures and its effect on the separation factor. Molina et al.[144] used the TIP model for pervaporation data of ethanolic solutions through a PDMS membrane using different pressures on the permeate side. Applying the model a close fit between experimental data and theoretical values was obtained.

In a related model by Radovanovic et al.[145] analysed the permeation of water and ethanol through silicone membranes. The study assumes that the ethanol is partly transported as ethanol-water cluster C_{ij}. For this case the following transport equations have been determined:

$$J_i = -\dot{D}_{M,i} \cdot \frac{dC_{M,i}}{dz} - \dot{D}_{M,ij} \cdot \frac{dC_{M,ij}}{dz} \tag{143}$$

$$J_i = -\frac{\dot{D}_{M,j} \cdot dC_{M,j}}{dz} - \dot{D}_{M,ji} \cdot \frac{dC_{M,ji}}{dz} \tag{144}$$

In the study this model was successfully applied to explain the mass transfer of ethanol-water through a silicone membrane. It was observed that the model was consistent with experimental results over the whole activity range of water. However, for ethanol it was limited to activities up to 0.6. To overcome this limitation for ethanol Soltanieh and Zaare-Asl[146] extended the model by adding an additional factor to account for pure ethanol cluster:

$$J_i = \dot{D}_{M,i} \cdot \frac{dC_{M,i}}{dz} - \dot{D}_{M,ij} \cdot \frac{dC_{M,ij}}{dz} - \dot{D}_{M,i}^{pure} \cdot \frac{dC_{M,i}^{pure}}{dz} \tag{145}$$

The last term in Equation *(145)* refers to the pure ethanol clusters in the membrane polymer, while the concentration of the clusters in the membrane can be defined using an equilibrium constant:

$$C_{M,i}^{pure} = K_{equi} \cdot C_i^g \tag{146}$$

Applying this model it was possible to extend the model by Radovanovic et al.[145] to predict ethanol fluxes over the whole activity range.

Models based on TIP seem to be an interesting way to test and compare membranes for multi-component systems by taking the effect of coupling into account. Further, the model also seems to be appropriate for process development and optimisation in case of multi-component systems. Nevertheless, similar to the pore flow model *(Section 4.6)* and solution-diffusion model *(Sections 4.2 and 4.3)*, the TIP does not provide the fundamental understanding required for membrane development, hence its main applications will be in the area of process and module design. Nevertheless, the models by Radovanovic et al.[145] and Soltanieh and Zaare-Asl[146] provide some additional understanding of coupling in case of membrane systems with water and ethanol.

4.5 Maxwell-Stefan Theory

The Maxwell-theory was introduced to pervaporation by Stephan[7]. In this model the solution-diffusion model and the influence of coupled diffusion according to the Maxwell-Stefan theory are combined. Based on the thermodynamics of irreversible processes every component in the system is influenced by a driving force, the gradient of the chemical potential, and a friction force, based on interactions between the different components in the system. As a result of this friction force each component in the system has a constant velocity. The sum of friction forces on the component is proportional to the relative velocities and is balanced by the driving force:

$$\frac{1}{RT}\cdot\frac{d\mu_i}{dz} = \sum_{j=1}^{n} \Phi_j \frac{\nu_j - \nu_i}{\hat{D}_{ji}} \qquad \textit{Driving Force} = \textit{Friction Force} \tag{147}$$

The sum of friction forces on the right side of the Maxwell-Stefan Equation *(147)* is proportional to the average relative velocity v_j - v_i. The contribution of the component to the friction force is proportional to the volume fractions of the components in the system. It should be noted that in the original Maxwell-Stefan equation mole fractions were used instead of volume fractions but for systems with polymers a modified expression based on volume fractions is suggested[7].

For the development of the flux equations for a ternary system the Hintroff's frame of reference has been selected. This approach takes one of the components in the system as reference system. Hence this component is fixed, while the other components are moving. In the solvent/polymer system, the permeating components are assumed to move in a fixed polymer reference system, see Figure 4. This includes the assumption that the membrane is not swelling while diffusion occurs.

Hence for a two liquid components permeating through a membrane the following two correlations can be developed by introducing the chemical potential of liquids into the Stefan-Maxwell theory:

$$\textit{Component } i\text{:} \quad \frac{d\ln\Phi_i}{dz} = \Phi_j \frac{\nu_j - \nu_i}{\tilde{D}_{ij}} - \Phi_M \frac{\nu_i}{\tilde{D}_{Mi}} \tag{148}$$

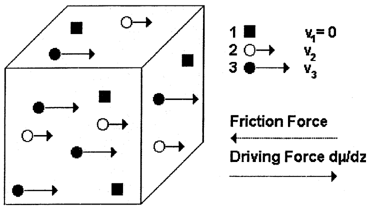

Figure 4. System of three components diffusing with different speeds based on the Maxwell-Stefan model *(adapted from [8])*.

$$\textit{Component } j\text{:}\quad \frac{d\ln\Phi_j}{dz} = \Phi_i\frac{\nu_i-\nu_j}{\tilde{D}_{ji}} - \Phi_M\frac{\nu_j}{\tilde{D}_{Mj}} \tag{149}$$

The diffusion coefficients in Equations *(148)* and *(149)* are the effective diffusion coefficients, which depend on the concentrations of all components in the system and which are defined as:

$$\tilde{D}_{ij} = \hat{D}_{ij}\frac{d\ln a_i}{d\ln\Phi_i} \tag{150}$$

Rearranging and solving Equations *(148)* and *(149)* give the following two expressions for the flux through the membrane[7]:

$$\begin{aligned} J_i = &-\frac{\tilde{D}_{Mi}}{\Phi_M}\cdot\left(\frac{\Phi_i\tilde{D}_{Mj}+\Phi_M\tilde{D}_{ij}}{\Phi_M\tilde{D}_{ij}+\Phi_i\tilde{D}_{Mj}+\Phi_j\tilde{D}_{Mi}}\right)\frac{dC_i}{dz}\\ &+\frac{\tilde{D}_{Mi}}{\Phi_M}\cdot\left(\frac{\Phi_i\tilde{D}_{Mj}}{\Phi_M\tilde{D}_{ij}+\Phi_i\tilde{D}_{Mj}+\Phi_j\tilde{D}_{Mi}}\right)\frac{dC_j}{dz}\end{aligned} \tag{151}$$

$$\begin{aligned} J_j = &\frac{\tilde{D}_{Mj}}{\Phi_M}\cdot\left(\frac{\Phi_j\tilde{D}_{Mi}+\Phi_M\tilde{D}_{ij}}{\Phi_M\tilde{D}_{ij}+\Phi_j\tilde{D}_{Mi}+\Phi_i\tilde{D}_{Mj}}\right)\frac{dC_j}{dz}\\ &+\frac{\tilde{D}_{Mj}}{\Phi_M}\cdot\left(\frac{\Phi_j\tilde{D}_{Mi}}{\Phi_M\tilde{D}_{ij}+\Phi_j\tilde{D}_{Mi}+\Phi_i\tilde{D}_{Mj}}\right)\frac{dC_j}{dz}\end{aligned} \tag{152}$$

Applying the equations it is possible to describe the coupling of fluxes and to determine the selectivity of the membrane as a function of the partial fluxes. In case no coupling occurs, $\tilde{D}_{ij} \to \infty$ Equations *(151)* and *(152)* can be reduced simply to the first Fick's Law:

$$J_i = -D_{Mi}\frac{dC_i}{dz} \tag{153}$$

$$J_j = -D_{Mj}\frac{dC_j}{dz} \tag{154}$$

with:

$$D_{Mi} = \tilde{D}_{Mi}/\Phi_M,\ \textit{and}\ D_{Mj} = \tilde{D}_{Mj}/\Phi_M \tag{155}$$

However, to obtain the final solutions, the two Equations *(151)* and *(152)* have to be solved numerically. The required boundary concentrations of a component *i* in the membrane *($\Phi_{F,i}$ or Φ_{Pi})* can be determined appropriately by equilibrium models, see Section 2. Even though the UNIQUAC model was proposed in the original papers[48, 146], it should be noted that all models discussed in Sections 2.3 to 2.6

can be applied in combination with the Stephan-Maxwell theory to determine activity and volume fractions. Overall, the model has potentials to be applied for both process and module design as well as membrane development.

Stephan[7, 48], Meckl[8], Staudt-Bickel[10], and Enneking[9, 46, 47] applied this model successfully for several ternary and quartary systems and found a good agreement between experimental data and theoretical predictions. Furthermore, the model has been extended and applied to include the support layer of composite membranes and the concentration boundary layer[7, 148].

The key advantage of this model is that it is possible to determine and predict fluxes and selectivities for non-ideal multi-component mixtures based on single component-membrane experiments. Hence, the number of experiments required can be minimised for multi-component systems. Furthermore, different combinations of multi-component systems can be analysed using a uniform database. The different parameters such as diffusion coefficients and sorption equilibrium are easily accessible in the model and have a physical meaning for membrane development, while the simplicity of the model for multi-component systems makes it an useful tool for membrane development.

4.6 Pore Flow Model

The pore flow model was introduced to pervaporation by Okada and Matsuura[149, 150]. The basic assumption of the model is that the selective layer of the membrane can be seen as a bundle of straight cylindrical pores distributed across the surface layer of the membrane. It is further assumed that the length of the pores l_M is equal to the thickness of the selective layer membrane and that the pores are in an isothermal condition. From the pore inlet at the feed side, a distance of the pore l_{liquid} is filled with liquid and the remaining distance l_{vapour} is filled with vapour, see Figure 5. Evaporation of the permeating compounds takes place at the liquid-vapour boundary. The driving force of the process is the pressure difference between the liquid feed p^{liquid}, and the vapour permeate p^{vapour}. At the boundary between the liquid and the vapour, the pressure is the saturated vapour pressure p^{sat} of the feed component. According to the theory of the model[151] the length of the pore filled with liquid l_{liquid} represents the proportion of the membrane where the permeating components are flowing by liquid transport. Consequently, for the vapour filled part of the pore l_{vapour} it is assumed that the permeating components are transported by means of vapour transport. It is further stated that there should be a discontinuous change of composition and density due the rapid phase change at the liquid-vapour boundary in the pore.

Based on the assumptions above, the following model for single component permeation was developed. The mass transport in the liquid part of the membrane

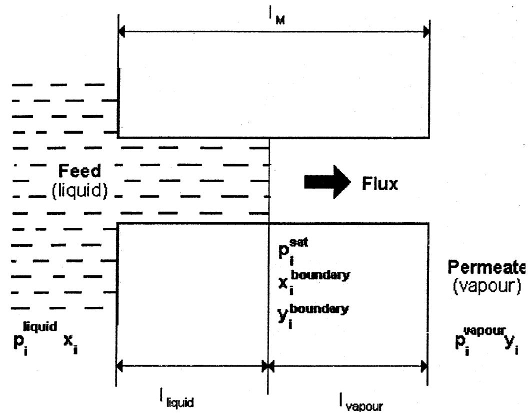

Figure 5. Pore flow model *($p^{vapour} > p^{sat}$) (after [150]).*

can be determined by:

$$J_{liquid} = \frac{A^{Pore}}{l_{liquid}} \cdot (p^{liquid} - p^{sat}) \tag{156}$$

In the vapour part it can be expressed using:

$$J_{vapour} = \frac{B^{Pore}}{l_{vapour}} \cdot (p^{sat} - p^{vapour}) \tag{157}$$

Therefore, at steady state the fluxes in the membrane are constant:

$$J = J_{liquid} = J_{vapour} \tag{158}$$

Hence the overall flux of a component can be determined by:

$$J = \frac{A^{Pore}}{l_M} (p^{liquid} - p^{sat}) + \frac{B^{Pore}}{l_M} \cdot ((p^{sat})^2 - (p^{vapour})^2) \tag{159}$$

Initially the constant A has been defined according to Darcy's Equation for liquid transport through cylindrical pores by[150, 151]:

$$A^{Pore} = \frac{\pi \cdot r^4{}_{Pore} \cdot \rho_i \cdot N_t}{8 \cdot \eta_i \cdot M_i} \tag{160}$$

The second constant B accounting for the vapour transport was accordingly defined by simplification of Henry's Law and monolayer adsorption[150, 151]:

$$B^{Pore} = \frac{\pi \cdot (2 \cdot r_{Pore} \cdot l_{Ad} - l_{Ad}^2)^2 \cdot l_{Ad} \cdot N_t}{8 \cdot r_{Pore}} \cdot \frac{R \cdot T}{\mu_i} (k'_{D,i})^2 \tag{161}$$

However, in the subsequent papers[149-153], these constants were treated as purely empirical parameters accounting for the pressure effects on the liquid transport and vapour transport in the pores.

This single-component model was used to describe fluxes of pure organic components *(2-propanol, methanol, ethanol, heptane)* and water through Cellulose and PDMS membranes at various feed and permeate pressures[149-151, 153, 154].

This model was then extended to binary mixtures assuming that l_{liquid} can be neglected, when the pore diameter is sufficiently small and the swelling of the membrane low[153]. Hence for a binary systems Equation *(159)* can be rewritten to:

$$J_i = \frac{B_i^{Pore}}{l_M}((p_i^{sat})^2 - (p_i^{vapour})^2) \tag{162}$$

$$J_j = \frac{B_j^{Pore}}{l_M}((p_j^{sat})^2 - (p_j^{vapour})^2) \tag{163}$$

Hence, for binary systems, the driving force of pervaporation becomes the pressure difference between saturated pressure and the partial pressure of each component at the permeate side. Applying this model for binary feed mixtures *(ethyl alcohol-heptane, ethanol-n-heptane, water-ethanol)* and five different types of membranes in hydrophobic and hydrophilic pervaporation, it was possible to predict both the flux and permeate concentrations with a good agreement between theoretical and experimental results[149-153]. It was, however, noticed that the constants determined for single component pervaporation are not transferable to two-component pervaporation. Hence, the effect of flux coupling has to be accounted for by additional experiments. This model was later also adapted by Tyagi et al.[155-157] to predict a concentration boundary layer and the concentration profile inside the membrane for the system acetic acid and water with PA membranes.

This semi-empirical model offers similar features to the solution-diffusion, i.e a permeability term including the membrane thickness and one driving force term. The main difference between the two models is the driving forces. The solution-diffusion model uses the activity or concentration difference between the feed and the permeate side, while the pore flow model for single component permeation is based on the pressure difference between feed pressure and permeate pressure as driving force. The pore flow model for binary feed mixtures uses, however, the pressure difference between saturated pressure and partial pressure on the permeate side as driving force. The key feature of both pore flow models is the liquid-vapour boundary inside the membrane. While the solution-diffusion model assumes that evaporation takes place on the permeate side of the membrane, the pore flow model is based on evaporation of permeating components at the boundary inside the membrane. The limitations of the pore flow model are similar to that of the solution-diffusion model. As soon as coupling effects have to be considered, the complexity of the model increases. Furthermore, since the constants A and B seem to loose their physical meaning and become empirical parameters for pervaporation, the applications of the model are mainly related to process and module design, even though the opportunity to model the concentration profile inside the membrane might have some implications for membrane development.

4.7 Pseudophase-Change Solution-Diffusion Model

The pseudophase-change solution-diffusion model by Shieh and Huang[158, 159] integrates the pseudophase-change inside membrane, a key feature of the pore flow model, and the coupling phenomena into the solution-diffusion model. The model was first established for single component pervaporation[158] and has then been extended to binary feed mixtures.

The development of the model was based on the following assumptions[158, 159]:

1. The permeation of the components in both the liquid and vapour phase can be described by the solution-diffusion mechanism.
2. Thermodynamic equilibrium can be assumed at the feed and permeate side interfaces of the membrane.
3. A phase change of the permeating components from liquid to vapour occurs inside the membrane.
4. The pressure at the feed and permeate side interface is equal to the adjacent applied pressure.
5. The pervaporation process can be assumed to be isothermal.

The one-component model is based on the mass balance of the stationary system and one-direction mass transfer using the chemical potential across the membrane as driving force:

$$J = \frac{C_{M,i} \cdot b_{M,i}}{(1 - w_{M,i}) \cdot M_i} \cdot \frac{d\mu_i}{dz} \tag{164}$$

To cover the concentration and mobility of component i in the model, two constants $K_{C,i}$ and $K_{M,i}$ are introduced:

$$K_{C,i} = \frac{S_{M,i}}{a_i} = S_{M,i} \cdot \frac{p^{sat}}{p} \tag{165}$$

$$K_{M,i} = \frac{b_{M,i}}{S_{M,i}} \tag{166}$$

Assuming the concentration and mobility of component i are pressure independent and the activity in the liquid zone of the membrane is constant, the following relation for the one-component liquid transport through membrane from Position

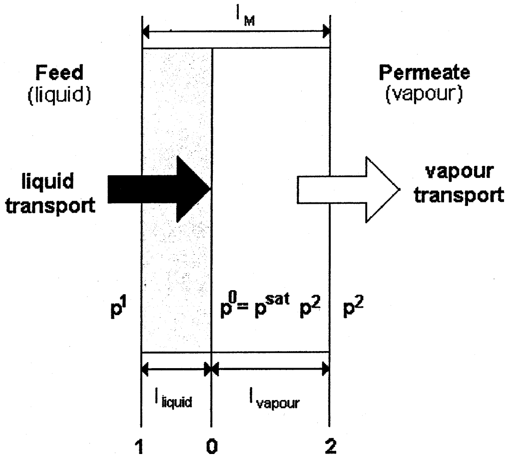

Figure 6. Pseudophase-change solution-diffusion model *(after [158, 159]).*

1 to Position 0, see Figure 6, can be developed by integrating Equation *(164)* and introducing Equations *(165)* and *(166)*:

$$J_{liquid} = \frac{K_{M,i} \cdot K_{C,i} \cdot \tilde{V}_i \cdot \rho_M}{l_{liquid} \cdot M_i} \cdot (p^{liquid} - p^{sat}) \tag{167}$$

In a similar manner the mass flux function for the vapour phase of membrane can be determined:

$$J_{vapour} = \frac{K_{M,i} \cdot K_{C,i}^2 \cdot \tilde{V}_i \cdot \rho_M \cdot R \cdot T}{l_{vapour} \cdot M_i} \cdot ((p^{sat})^2 - (p^{liquid})^2) \tag{168}$$

Combining Equations *(167)* and *(168)* in a similar manner as in Equations *(156)* and *(157)* in the pore flow model *(Section 4.6)*, the following equation for the overall mass transfer can be obtained:

$$J = \frac{A^{PPCSD}}{l_M} (p^{liquid} - p^{sat}) + \frac{B^{PPCSD}}{l_M} ((p^{sat})^2 - (p^{vapour})^2) \tag{169}$$

with:

$$A^{PPCSD} = \frac{K_{M,i} \cdot K_{C,i} \cdot \tilde{V}_i \cdot \rho_M}{M_i} \tag{170}$$

$$B^{PPCSD} = \frac{K_{M,i} \cdot K_{C,i}^2 \cdot \tilde{V}_i \cdot \rho_M \cdot R \cdot T}{M_i} \tag{171}$$

Comparing Equation *(169)* with Equation *(159)* of the pore flow model *(Section 4.6)*, the relationship between the two models becomes apparent. Using this model to study the permeation of hexane through a PE membrane using different feed and permeate pressure it was possible to determine the pressure and concentration profiles within the membrane. According to the models it was revealed that the pressure in the liquid zone of the membrane decreases linearly and that it decreases gradually in the vapour zone. The concentration profile of the component in the membrane decreases gradually across the whole membrane. It was further noted that the flux of the liquid permeation is always less than in vapour permeation unless very high feed pressures are applied[158].

This model was then extended for binary feed mixtures including the effect of coupling. Therefore Equation *(164)* was modified to account for the influence of the two component fluxes on each other by:

$$J_i = \frac{1 - w_{M,j}}{1 - w_{M,i} - w_{M,j}} \cdot \frac{C_{M,i} \cdot b_{M,i}}{M_i} \cdot \left(\frac{d\mu_i}{dz} \right) - \frac{1 - w_{M,i}}{1 - w_{M,i} - w_{M,j}} \cdot \frac{C_{M,j} \cdot b_{M,j}}{M_j} \cdot \left(\frac{d\mu_j}{dz} \right) \tag{172}$$

$$J_j = \frac{1 - w_{M,i}}{1 - w_{M,i} - w_{M,j}} \cdot \frac{C_{M,j} \cdot b_{M,j}}{M_j} \cdot \left(\frac{d\mu_i}{dz} \right) - \frac{1 - w_{M,i}}{1 - w_{M,i} - w_{M,j}} \cdot \frac{C_{M,i} \cdot b_{M,i}}{M_i} \cdot \left(\frac{d\mu_i}{dz} \right) \tag{ 173}$$

with:

$$w_{M,i} = \frac{S_{M,i}}{1 + S_{M,i} + S_{M,j}}, \qquad w_{M,j} = \frac{S_{M,j}}{1 + S_{M,i} + S_{M,j}}, \quad \text{and} \tag{174}$$

$$C_{M,i} = \frac{S_{M,i} \cdot \rho_M}{1 + S_{M,i} + S_{M,j}}, \qquad C_{M,j} = \frac{S_{M,j} \cdot \rho_M}{1 + S_{M,i} + S_{M,j}} \tag{175}$$

Similar to the one-component liquid mass transport, the following relationship can be developed based on Equation *(171)*:

$$J_{liquid,i} = \left(\frac{1 - w_{M,i}}{1 - w_{M,i} - w_{M,j}} \cdot C_{M,i} \cdot b_{M,i} \cdot \tilde{V}_i + \frac{w_{M,j}}{1 - w_{M,i} - w_{M,j}} \cdot C_{M,j} \cdot b_{M,j} \cdot \tilde{V}_j \right) \cdot \frac{(p^{liquid} - p^{sat})}{l_{liquid} + M_i} \tag{176}$$

For the vapour mass transport the chemical potential of the individual components has to be taken into account which leads to the following expression:

$$J_{vapour,i} = -\frac{R\cdot T}{M_i}\int_{(a_{0,i},a_{0,j})}^{(a_{2,i},a_{2,j})}\left(\frac{1-w_{M,j}}{1-w_{M,i}-w_{M,j}}\cdot\frac{C_{M,i}\cdot b_{M,i}}{a_i}\right)da_i + \left(\frac{w_{M,i}}{1-w_{M,i}-w_{M,j}}\cdot\frac{C_{M,j}\cdot b_{M,j}}{a_j}\right)da_j \tag{177}$$

Combining Equations *(175)* and *(176)*, the flux equation for component *i* can be derived:

$$\begin{aligned} J_i = \frac{1}{l_M\cdot M_i}\cdot\Bigg[\Bigg(&\frac{1-w_{M,i}}{1-w_{M,i}-w_{M,j}}\cdot C_{M,i}\cdot b_{M,i}\cdot\tilde{V}_i \\ &+\frac{w_{M,j}}{1-w_{M,i}-w_{M,j}}\times C_{M,j}\cdot b_{M,j}\cdot\tilde{V}_j\Bigg)\cdot(p^{liquid}-p^{sat})\Bigg]^{liquid} \\ &+\Bigg[R\cdot T\cdot\int_{(a_{0,i},a_{0,j})}^{(a_{2,i},a_{2,j})}\times\left(\frac{1-w_{M,j}}{1-w_{M,i}-w_{M,j}}\cdot\frac{C_{M,i}\cdot b_{M,i}}{a_i}\right)da_i \\ &+\left(\frac{w_{M,i}}{1-w_{M,i}-w_{M,j}}\cdot\frac{C_{M,j}\cdot b_{M,j}}{a_j}\right)da_j\Bigg]^{vapour} \end{aligned} \tag{178}$$

In a similar manner, the appropriate correlation for component *j* can be developed:

$$\begin{aligned} J_j = \frac{1}{l_M\cdot M_j}\cdot\Bigg[\Bigg(&\frac{1-w_{M,i}}{1-w_{M,i}-w_{M,j}}\cdot C_{M,j}\cdot b_{M,j}\cdot\tilde{V}_j \\ &+\frac{w_{M,j}}{1-w_{M,i}-w_{M,j}}\cdot C_{M,i}\cdot b_{M,i}\cdot\tilde{V}_i\Bigg)\cdot(p^{liquid}-p^{sat})\Bigg]^{liquid} \\ &+\Bigg[R\cdot T\int_{(a_{0,i},a_{0,j})}^{(a_{2,i},a_{2,j})}\left(\frac{1-w_{M,i}}{1-w_{M,i}-w_{M,j}}\cdot\frac{C_{M,i}\cdot b_{M,i}}{a_j}\right)\,da_i \\ &+\left(\frac{w_{M,i}}{1-w_{M,i}-w_{M,j}}\cdot\frac{C_{M,i}\cdot b_{M,i}}{a_i}\right)da_i\Bigg]^{vapour} \end{aligned} \tag{179}$$

This model was used to study the system hexane-heptane through a PE membrane. Analysing the effects of feed pressure, permeate pressure and feed concentration good agreement between model and experimental data was observed. It was further possible to analyse the effect of plasticizing and coupling on the membrane performance.

The pseudophase-change solution-diffusion model provides some new understanding of the mass transfer through the membrane. Further it integrates phase-change inside the membrane and the coupling phenomena into the solution-diffusion model. Similar to the approach based on the Maxwell-Stephan theory the different parameters in the model have a physical meaning and can be related to the solubility and mobility of the component inside the membrane. However, so far it is restricted to binary systems and including the coupling effect increases the complexity of the model. Therefore, the applications of this model will be in the membrane development to gain further understanding of the mass transport in the membrane system.

4.8 Observations on Approaches to Model the Trans-Membrane Mass Transfer

The modelling of the mass transfer through the membrane is mainly based on semi-empirical models. In these semi-empirical models all permeation-related effects, such as sorption, diffusion and coupling, are summarised in empirical parameters. Therefore, the models are generally applicable for process and module design. Comparing the different models, it can generally be observed that the number of parameters in the models increases with the number of components. Furthermore, in most cases when coupling is included the number of parameters to be determined for n components is at least $0.5n^2+n$. Hence, most of the models are restricted to binary systems, particularly when they include the effect of coupling. In the Maxwell-Stefan theory and in the pseudophase-change solution-diffusion model, all parameters applied have physical meaning and are easily accessible. Hence, the models are particularly interesting for membrane development. The models also seem to provide a good foundation to develop new models for process and module design for multi-component systems.

5. CONCLUSIONS

Models for the different steps in the mass transfer and for the overall trans-membrane mass transfer in pervaporation were reviewed. It was observed that most of the models in the literature focus on sorption and the trans-membrane mass transfer, while the number of models for diffusion is limited. The complexity of these models increases from empirical models with a low complexity to theoretical models with a high complexity. Overall, the nature of models is mainly semi-empirical, while for diffusion most of the models are empirical. This trend towards empirical models to predict diffusion is also reflected in the models for the trans-membrane mass transfer. In these mainly semi-empirical models the driving force is well established, while the permeability term is generally of an empirical nature. For all models the complexity also increases with the number of components, in particular when coupled sorption and coupled diffusion are considered. For the empirical and semi-empirical models in particular the number of parameters to be determined by experiments increases significantly for these systems. Theoretical models require less parameters, but these parameters are fundamental, e.g. diffusion coefficients, and require therefore different experimental set-ups, which increases the experimental complexity.

The selection of an appropriate model is determined by the application of the model. For process and module design the semi-empirical models of the trans-membrane mass transfer should generally provide the desired depth to design and optimise processes. For systems without coupling the common solution-diffusion model and the pore flow model are very simple and suitable models. For more complex systems with coupling the complexity of these models increases significantly. In these cases the Maxwell-Stefan theory or the pseudophase-change solution-diffusion model are required. Further this review offers the opportunity to consider new combinations of models to predict and analyse the overall process, e.g. combining modified UNIFAC with the free volume theory. It should be noted that these models for the trans-membrane mass are only a foundation to model the mass transfer in process and module design, since other effects such as concentration polarisation, support layer, permeate pressure drop, flow pattern, and heat transfer have also to be considered and therefore included in the model of the overall mass transfer in pervaporation.

In membrane development it is important to distinguish between models for membrane sorption and membrane diffusion. For membrane sorption the semi-empirical models based on Flory-Huggins, UNIQUAC, NRTL, Entropic-FV, ASOG and ENSIC provide fairly good predictions, and selection of model will be determined by the availability of the required interaction parameters or affinities for the system to be analysed. In case no data are available the modified UNIFAC is the obvious choice. To model membrane diffusion the free volume theory should be selected, since it has been successfully applied for a wide range of polymers.

In the future molecular simulations will become increasingly important for membrane development since they can provide information on the sorption and diffusion behaviour of membrane polymers before the polymer synthesis is achieved.

Overall, further success of pervaporation will depend on improved membranes as well as process and module designs based on optimised models.

6. ACKNOWLEDGMENTS

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7. LIST OF SYMBOLS

A	Avogadro number [-]
A_{di}	free volume parameter of component *i* for the glassy region in polymer [-]
$A_{kl.}$, A_{lm}, A_{lm}	ASOG group interaction parameters [-]
A_1, A_2, A_3, A_4, A_5	empirical parameters of Q_i-model *(Section 4.3.2)* [-]
$a_{F,i}$	activity of component *i* in feed [-]
a_i, a_j	activity of component *i*, and component *j* [-]
a_i^C	activity of component *i* from combinatorial contribution [-]
a_i^{C-FV}	activity of component *i* from combinatorial contribution including free volume contribution [-]
a_i^{F-R}	activity contribution for component *i* from Flory-Rehner theory [-]
a_i^{FV}	activity of component *i* from free volume contribution [-]
a_i^G	activity of component *i* from group-related contribution [-]
a_i^{M-H}	activity contribution for component *i* from Micheals-Hausslein theory [-]
a_i^R	activity of component *i* from residual contribution [-]
a_i^{R-HB}	activity of component *i* from residual contribution *(UNIQAC-HB)* [-]
a_i^S	activity of component *i* from size-related contribution [-]
$a_{M,i}$	activity of component *i* in membrane *M* [-]
$a_{P,i}$	activity of component *i* in permeate [-]
$a_{0,i}$, $a_{0,j}$	activity of component *i,* and component *j* at position 0 in Figure 5 [-]
$a_{2,i}$, $a_{2,j}$	activity of component *i,* and component *j* at position 0 in Figure 5 [-]
B_{di}	free volume parameter of component *i* for the glassy region in polymer [-]
B_i	second virial coefficient of component *i* [cm^3]
B_{ii}, B_{ij}, B_{jj}, B_{ji}, B_{ik}, B_{jk}, B_{kk}, B_{ki}, B_{kj}	coupling coefficients between the components *i*, *j*, and *k* in semi-empirical model after Meyer-Blumenroth *(Section 4.3.1)* [-]
B_i^{FV}, B_j^{FV}	generalised free volume parameter of component *i,* and component *j* [-]
b	proportionality factor in Equations *(39)* and *(40)* [-]

b_i, b_j	adsorption or hole affinity constant of component i, and component j [bar^{-1}]
$b_{M,i}$, $b_{M,j}$	mobility of component i, and component j in membrane M [m^2·mol·J^{-1}·s^{-1}]
C_i	concentration of component i [kmol·m^{-3}, kg·m^{-3}]
$C_{D,i}$	concentration of diffusing component i in membrane [kmol·m^{-3}, kg·m^{-3}]
$C_{H,i}$	concentration of component i in microvoids [kmol·m^{-3}, kg·m^{-3}]
$C'_{H,i}$	hole saturation constant of component i in membrane [kmol·m^{-3}, kg·m^{-3}]
$C_{M,i,\ CM,j}$	concentration of component i and component j in membrane M [kmol·m^{-3}, kg·m^{-3}]
$C_{M,ij}$	concentration of components i and j in mixed clusters inside membrane M [kmol·m^{-3}, kg·m^{-3}]
$C_{M,i}^{pure}$	concentration of components i one component clusters inside membrane M [kmol·m^{-3}, kg·m^{-3}]
c_i	empirical parameter of component i in Equation *(133)* [-]
c_1, c_2, c_3	adjustable parameters in Equation *(16)* [-]
c_4, c_5	adjustable parameters in Equation *(17)* [-]
$3\cdot c_6$	number of external degrees of freedom per solvent molecule in Equation *(38)* [-]
$D_{D,i}$	diffusion coefficient of component i in the Langmuir mode [m^2·s^{-1}]
$D_{H,i}$	diffusion coefficient of component i in the Henry's Law mode [m^2·s^{-1}]
$\dot{D}_i$, $\dot{D}_j$	Fickian diffusion coefficient of component i, and component j [m^2·s^{-1}]
$\dot{D}_{M,i,}$ $\dot{D}_{M,i}$	Fickian diffusion coefficient of component i, and component j in membrane M [m^2·s^{-1}]
$\dot{D}_{M,ij,}$ $\dot{D}_{M,ji}$	Fickian diffusion coefficient of component i, and component j through mixed component clusters in membrane M [m^2·s^{-1}]
$\dot{D}_{M,i}^{pure}$	Fickian diffusion coefficient of component i through one component clusters inside membrane M [m^2·s^{-1}]
$\hat{D}_{ij}$, $\hat{D}_{ji}$	Maxwell-Stefan interaction parameter [m^2·s^{-1}]
$\tilde{D}_{j,}$ $\tilde{D}_j$, $\tilde{D}_{iM}$, $\tilde{D}_{jM}$	effective concentration-depending diffusion coefficient of component i in component j, component j in component i, component i in Membrane M, and component j in Membrane M [m^2·s^{-1}]
D_i^0, D_j^0	reference diffuison coefficient at zero concentration of component i, and component j [m^2·s^{-1}]

D_i^T	thermodynamic diffusion coefficient of component i [$m^2 \cdot s^{-1}$]
$\overline{D}_i^T$	modified thermodynamic diffusion coefficient of component i *(Equation (117))* [$m^2 \cdot s^{-1}$]
DF_i	driving force term of component i [-]
d_i	empirical parameter of component i in Equation *(133)* [-]
E_i	activation energy of component i [$J \cdot mol^{-1}$]
$\Delta E_{vap,i}$	energy of vaporisation of component i [$J \cdot mol^{-1}$]
$\Delta E_{df,i}$	energy required to overcome dispersion forces with reference to component i [$J \cdot mol^{-1}$]
$\Delta E_{di,i}$	energy required to overcome dispersion polar interactions with reference to component i [$J \cdot mol^{-1}$]
$\Delta E_{hb,i}$	energy required to overcome hydrogen bonds with reference to component i [$J \cdot mol^{-1}$]
e_i, e_j	exponents of component i, and component j in Equation *(56)*, $0 < e_i, e_j < 1$ [-]
F_i	as defined in Equation *(96)* [-]
$f_{F,i}, f_{F,j}, f_{F,k}$	fugacity of component i, component j, and component k in feed [bar]
f_i, f_j, f_k	fugacity of component i, component j, and component k [bar]
f_i^0, f_j^0, f_k^0	reference fugacity of component i, component j, and component k [bar]
f_{iP}^{FV}	free volume [-]
f_P	mass fraction of polymer P, which is elastically effective [-]
$f_{P,i}, f_{P,j}, f_{P,k}$	fugacity of component i, component j, and component k in permeate [bar]
g	curve fitting parameter in Equation (146) [-]
G_{ij}, G_{ji}	binary parameters in NRTL, see Equations *(68)* and *(69)* [-]
ΔG^{mix}	free energy of mixing [$J \cdot mol^{-1}$]
ΔG^E	excess free energy of mixing [$J \cdot mol^{-1}$]
$\Delta H_{f,P}$	heat of fusion of the polymer P [$J \cdot mol^{-1}$]
J_i	flux of component i [$kmol \cdot m^{-2} \cdot s^{-1}$]
J_i^0	reference flux of component i [$kmol \cdot m^{-2} \cdot s^{-1}$]
J_{liquid}	flux for liquid phase [$kmol \cdot m^{-2} \cdot s^{-1}$]
J_{vapour}	flux for vapour phase [$kmol \cdot m^{-2} \cdot s^{-1}$]
$K_{1,i}$, $K_{2,i}$, $K_{3,i}$, $K_{4,i}$	empirical development factors for the process-specific permeability functions of component i [-]
$K_{C,i}$	sorption coefficient of component i as defined in Equation *(165)* [-]
K_{equi}	equilibrium constant for polymerisation reaction [-]
K_i	as defined in Equation *(97)* [-]
$K_{M,i}$	mobility coefficient of component i as defined in Equation *(166)* [kg/kg]

k	represent dispersion force *(df)*, dispersion polar interactions *(di)* and hydrogen bonds *(hb)* respectively in Equation *(9)* [-]
k_i	coupling factor in Equation *(131)* [-]
$k_{D,i}$	Henry's law constant referring to component *i* [bar^{-1}]
$k^*_{D,i}$	(unit weight of polymer per volume of adsorbed gas molecule *i*)$\times$ $k_{D,i}$ [mol·m^{-3}·bar^{-1}]
$k_{P,i}$	affinity $k_{P,i}$ of the permeating molecule *i* towards the polymer side [-]
$k_{S,i}$	affinity of the permeating molecule *i* towards the like molecules [-]
L_{ii}, L_{ij}, L_{in} L_{ji}, L_{jj}, L_{jn} L_{ni}, L_{nj}, L_{nn}	phenomenological coupling parameters in TIP model *(Section4.4)* between component *i*, component *j* and component *n* [-]
l_{Ad}	thickness of the adsorption monolayer [m]
l_i, l_P	UNIQUAC parameter for component *i,* and polymer *P*, defined in Equation *(31)* [-]
l_{liquid}	length of the liquid-filled proportion of the pore in the pore flow model *(Section 4.6)* [m]
l_M	thickness of membrane *M* [m]
l_{vapour}	length of the vapour-filled proportion of the pore in the pore flow model *(Section 4.6)* [m]
M_C	molar weight per cross-linked unit [kg·kmol^{-1}]
M_{CR}	molar weight of chain between two crystallites [kg·kmol^{-1}]
M_i, M_j	molar weight of component *i,* and component *j* [kg·kmol^{-1}]
M_P	molar weight of polymer P before cross-linking [kg·kmol^{-1}]
N_t	total number of pores per effective membrane area [-]
n	number of effective segments in the sample [-]
n_i	empirical parameter of component *i* in Equation *(134)* [-]
P_i	permeability of component *i* with reference to an activity driving force [kmol·m^{-1}·s^{-1}]
P_i^P	permeability of component *i* with reference to a pressure driving force [m^3(STP)·m·s^{-1}·m^{-2}·atm^{-1}]
p	pressure [bar, Pa]
p_i	partial pressure of component *i* [bar, Pa]
p^{liquid}	total pressure of liquid phase [bar, Pa]
p^{sat}	saturated pressure [bar, Pa]
p_i^{sat}, p_j^{sat}	saturated pressure of component *i,* and component *j* [bar, Pa]
p^{vapour}	total pressure of vapour phase [bar, Pa]
P_i^{vapour}, p_j^{vapour}	partial pressure of component *i,* and component *j* in vapour phase [bar, Pa]
p_P	permeate pressure [bar, Pa]
Q_i, Q_j	permeability of component *i* and component *j* in Q_i-model *(Section 4.3.2)* [kg m^{-2}·s^{-1}]

Q_k	surface area parameter per mole of group type k [-]
q_i	relative surface parameter of component i *(UNIQUAC)* [-]
q'_i	modified relative surface parameter of component i *(UNIQUAC)* [-]
q_i^*	effective segment number of component i [-]
R	gas constant [J·mol^{-1}·K^{-1}]
R_k	volume parameter per mole of group k [-]
r_i, r_j r_P	relative volume parameter of component i, component j, and polymer P *(UNIQUAC)* [-]
r_i^*, r_P^*	number of segments of component i, and polymer P *(NRTL)* [-]
r_{Pore}	pore radius [m]
$S_{M,i}$, $S_{M,j}$	solubility of component i, and component j in membrane M [-]
s_i, s_j	number of size groups in molecule i, and molecule j [-]
T	temperature [K]
T_F	feed temperature [K]
T^0	reference temperature [K]
$T_{m,P}$	melting temperature of polymer P [K]
$\tilde{V}_i$, $\tilde{V}_j$, $\tilde{V}_P$	molar volume of component i, component j, and polymer P [m^3·mol^{-1}]
$\tilde{V}_i^{FV}$, $\tilde{V}_j^{FV}$,	molar volume of component i, and component j associated with free volume FV [m^3·mol^{-1}]
$\tilde{V}_{w,i}$	molar van der Waals volume of component i [m^3·mol^{-1}]
v_i, v_j	velocity of component i, and component j [m^2·s]
$v_k^{(i)}$	number of functional groups of type k in the component i [-]
v_{ki}, v_{kj}	number of interaction groups k in molecule i and molecule j [-]
$\langle v\rangle_i$, $\langle v\rangle_{mix}$	reduced volume for component i, and for the polymer/solvent mixture [m^3·kmol^{-1}]
W_1, W_2, W_3	weight factors for three dimensional solubility parameters [-]
w_i, w_P	weight fraction of component i, and polymer P [-]
$w_{M,i}$, $w_{M,j}$	weight fraction of component i, and component j in membrane M [-]
x_i, x_j, x_P	mole fraction of component i, component j, and polymer P [-]
$x_i^{boundary}$	liquid mole fraction of component i at the liquid-vapour boundary in the pore flow model *(Section 4.6)* [-]
$x_{F,i}$	liquid mole fraction of component i in feed [-]
$y_{P,i}$	vapour mole fraction of component i in permeate [-]
$y_i^{boundary}$	vapour mole fraction of component i at the liquid-vapour boundary in the pore flow model *(Section 4.6)* [-]

Z	co-ordination number UNIQUAC *(commonly $z=10$)* [-]
z	z-co-ordinate [m]

Greek Symbols

A^{Pore}	constant defined in Equation *(160)* for a pure component system in the pore flow model [-]
A^{PPCSD}	constant defined in Equation *(169)* for a pure component system in the pseudophase-change solution diffusion model [-]
α	non-random factor in NRTL model [-]
$\langle\alpha\rangle_0$	ratio between the mean distance separating the junctions in the unswollen network [-]
B^{Pore}	constant defined in Equation *(161)* for a pure component system in the pore flow model [-]
B^{PPCSD}	constant defined in Equation *(170)* for a pure component system in the pseudophase-change solution diffusion model [-]
B_i^{Pore}, B^{Pore}	values of B for component i and component j [-]
β_i, β_j	proportional constant of component i, and component j in free volume theory [-]
X_k, X_l	group mole fraction for group k and group l *(ASOG)* [-]
χ_i	constant in Equation *(15)* [-]
$\chi_{i,j}, \chi_{i,P}, \chi_{j,P}$	Flory-Huggins binary interaction parameter between component i - component j, component i - polymer P, and component j - polymer P [-]
$\Delta_{i,j}$ $\Delta_{P,i}$, $\Delta_{P,j}$	distance between component i and component j, between polymer P and component i, and between polymer P and component j in δ-space $[J^{1/2}\cdot m^{-3/2}]$
$\Delta_{P,ij}^{mix}$	combined parameter for the two components i and j with reference to polymer P $[J^{1/2}\cdot m^{-3/2}]$
$\Delta_{P,i}^{W}$	distance between polymer P and component i in δ-space using weight factors $[J^{1/2}\cdot m^{-3/2}]$
δ_i, δ_P	solubility parameter of component i, and polymer P $[J^{1/2}\cdot m^{-3/2}]$
$\delta_{df,i}$,$\delta_{df,P}$	solubility parameter due to dispersion forces with reference to component i, and polymer P $[J^{1/2}\cdot m^{-3/2}]$
$\delta_{di,i}$, $\delta_{di,P}$	solubility parameter due to dispersion polar interactions with reference to component i, and polymer P $[J^{1/2}\cdot m^{-3/2}]$
$\delta_{hb,i}$, $\delta_{hb,P}$	solubility parameter due to hydrogen bonds with reference to component i, and polymer P $[J^{1/2}\cdot m^{-3/2}]$
$\delta_{k,ij}^{max}$	combined solubility parameter for the two components i and j with k referring to different forces $[J^{1/2}\cdot m^{-3/2}]$
ε_i, ε_j	empirical constant or ‘softener’ for component i and component j in Equations *(72) – (74)* [-]

E_i	empirical constant for component *i* in Equation *(75)* [-]
E_{ij}, E_{ji}	empirical constants or interrelated ‘softener’ for components *i* and *j* in Equations *(77)* and *(78)* [-]
$\Phi_{C,P}$	crystallinity of polymer *P* [-]
Φ_i, Φ_j, Φ_P, Φ_M	volume fraction of component *i*, component *j,* polymer *P,* and membrane *M* [-]
$\Phi_{M,i}$, $\Phi_{M,j}$	volume fraction of component *i*, component *j* in membrane *M* [-]
Φ_i^{FV}	volume fraction of component *i* associated with free volume *FV* [-]
Φ_i'	volume fraction term of component *i* in modified UNIFAC model [-]
$\Gamma_{k,UNIFAC}$	residual activity of group *k* in mixture, see UNIFAC model Equation *(46)* [-]
$\Gamma_{k,ASOG}$	activity coefficient of group k in the standard state, see ASOG-FV Equation *(61)* [-]
$\Gamma_{UNIFAC}^{(i)}$	residual activity of group *k* in a reference solution of pure component *i (UNIFAC)* [-]
$\Gamma_{k,ASOG}^{*}$	activity coefficient of group k in standard state *(ASOG)* [-]
κ_i, κ_j	geometrical average of the mixing term of the chemical potential in the membrane with regard to component *i,* and component *j* [-]
$\bar{\kappa}$	weighted overall mixing term of the chemical potential *(Equation (126))* [-]
γ_i, γ_j	activity coefficient of component *i*, and component *j* [-]
$\bar{\gamma}_{M,i}$	average activity coefficient of component *i* in membrane *M* [-]
η_i	liquid viscosity of component *i* [Pa·s]
μ_i, μ_j, μ_n	chemical potential of component i, component *j* and component *n* [J·mol^{-1}]
$\Delta\mu_i$	difference in the chemical potential of component *i* between feed and permeate side [J·mol^{-1}]
$\bar{\omega}_i$, $\bar{\omega}_j$	empirical constant for component *i,* and component *j* in Equations *(79)* and *(80)* [-]
θ_i,θ_j	empirical constant for component *i,* and component *j* in Equations *(79)* and *(80)* [-]
ϑ_i, ϑ_j	empirical constant for component *i,* and component *j* in Equations *(79)* and *(80)* [-]
Θ_i, Θ_P	surface fraction of component *i*, and polymer *P* [-]
Θ_i', Θ_P'	modified surface fraction of component *i*, and polymer *P* [-]
$\rho_{g,P}$	density of glassy phase of polymer *P* [kg·m^{-3}]
ρ_i,	density of component *i* [kg·m^{-3}]
ρ_M	density of membrane *M* [kg·m^{-3}]

ρ_P	density of polymer *P* [kg·m^{-3}]
τ_{Pi}, τ_{iP}	binary interaction parameters *(UNIQUAC)* between component *i*, and polymer *P* [-]
τ^*_{Pi}, τ^*_{ip}, τ^*_{ij}	binary interaction parameters *(NRTL)*between component *i*, and polymer *P*, between component *i* and component *j* [-]

Polymers

LDPE	low density polyethylene
PA	polyamide
PAN	polyacrylonitrile
PBI	polybenzimidazole
PE	polyethylene
PDMS	polydimetylsiloxane
PIP	polyisoprene
PMA	polymethyl acrylate
PMPhS	polymethylphenylsiloxane
POMS	polyoctylmethylsiloxane
PP	polypropylene
PUI	polyurethaneimide
PVA	polyvinyl alcohol
PVC	polyvinyl chloride

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