Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.803337

52 (2014) 3455–3465
May

Taylor & Francis
Taylor & Francis Group

Overall mass transfer rates during pervaporation: effect of the convective velocity on the separation

Endre Nagy*, Zsolt Prettl, László Hajba, József Dudás

Research Institute of Chemical and Process Engineering, University of Pannonia, Veszprém, Hungary
Tel. +36 624036; Fax: +36 624038; email: nagy@mukki.richem.hu

Received 28 November 2011; Accepted 23 April 2013

ABSTRACT

The polarization layer can strongly affect the separation process by pervaporation. This paper defines the overall mass transfer rates, involving the effect of both the polarization and the membrane layers, in cases of constant diffusion coefficient, variable diffusion coefficient and application of the Flory–Huggins theory. These rate equations enable the user to take into account the exact effect of the polarization layer on the separation. Due to the low value of Peclet number, during pervaporation process the expressions of mass transfer rates, enrichment, and separation factor of binary mixtures can be essentially simplified. It has been stated that the Peclet number does not affect significantly the overall mass transfer rate, while it affects strongly the enrichment or the separation factor. It has been proved that the $k/(k_mH)$ value dominantly affects the separation efficiency during the pervaporation processes.

Keywords: Pervaporation; Overall mass transfer rate; Enrichment; Binary mixture separation

1. Introduction

In order to get exact expressions of the overall mass transfer rates through a pervaporation membrane layer, the simultaneous effect of both the concentration polarization and the membrane layer should be taken into account. A number of papers have analyzed the effect of the concentration polarization and defined the well known equations to its prediction regarding the membrane layer as a black box, and the mass transfer rate is expressed by means of the polarization layer and the outlet mass transfer rate [1–5]. The mass transfer resistance in the boundary layer can strongly alter the concentration in the inlet membrane interface, thus the mass transfer rate through the membrane layer. Almost all of these studies assumes diffusive plus convective flows in the boundary layer, only, defining its Peclet number ($\mathrm{Pe} = \upsilon\delta/D$). Later several papers were published which investigate the mass transport in the membrane layer, only, taking into account e.g. Flory–Huggins [6–8] or Maxwell–Stefan [9–11], etc. The resistance in series model is also applied in the literature. Most of these models are based on the Fick's law, i.e. diffusive flow is taken into account, only, in the boundary layer [12–15] or this diffusion flux is combined with the concentration polarization equation in order to incorporate the contribution of the convective transport in the mass transfer rate [1,3,13,16]. Strictly taken, the resistance in series model with diffusive flow in the boundary layer must not be used in presence of convective flow. Recently, Nagy [17] developed a general model for the mass transport by taking into account the simultaneous effect of both layers on the

---

*Corresponding author.

separation efficiency. This model considers the diffusive plus convective flow in the polarization layer and diffusive flow, only, in the membrane layer. The question to be answered is how the mass transport equation can be simplified by taking into account the low value of the Peclet number during pervaporation. Its value in the polarization layer is generally less than 0.01 [1].

The main aim of this work is to develop general equations of the overall mass transfer rates in closed forms which also contain the simultaneous effect of the membrane's mass transport parameters with variable diffusion coefficient, variable activity coefficient applying the Flory–Huggins approach, and contains both the convective and diffusive flows in the polarization layer. This general equations should also fulfill the $J = \upsilon c_{\mathrm{p}}$ boundary condition applied for pervaporation. This can enable us to predict directly the c_{p} outlet concentration of the liquid permeate, the enrichment, the separation factor, etc. by means of mass transport parameters of the both layers. The methodology applied serves new expressions to estimate the separation efficiency.

2. Theoretical part

Some special cases of the mass transport during pervaporation process will briefly be discussed focusing on the simultaneous effect of the polarization and membrane layers.

2.1. Mass transport with constant diffusion coefficient

Herewith, the overall mass transfer equations will be given using the resistance in series model. The mass transfer rate, enrichment, and polarization modulus should be the same as were obtained by Nagy [17] applying a more complex methodology. The mass transfer rate into the polarization layer, in presence of convective flow as well, can be given as follows [17,18]:

$$J = \beta\left(c_{\mathrm{b}} - e^{-\mathrm{Pe}}c^{*}\right) \tag{1}$$

where

$$\beta = k\mathrm{Pe}\frac{e^{\mathrm{Pe}}}{e^{\mathrm{Pe}} - 1} \tag{2}$$

with

$$k = \frac{D}{\delta}$$

Assuming that the mass transport in the dense, polymer membrane layer is a diffusive process, thus the mass transfer rate is as (at $y = 0$ $\phi = \phi^{*}$ and at $y = \delta$ $\phi = \phi^{*}_{\delta}$):

$$J = \frac{D_{\mathrm{m}}}{\delta_{\mathrm{m}}}(\phi^{*} - \phi^{*}_{\delta}) \equiv k_{\mathrm{m}}\left(\phi^{*} - \phi^{*}_{\delta}\right) \tag{3}$$

The overall mass transfer rate can be obtained by means of Eqs. (1) and (3) as ($\mathrm{H}c^{*} = \phi^{*}$):

$$J = \beta_{\mathrm{ov}}\left(c_{\mathrm{b}} - e^{-\mathrm{Pe}}\phi^{*}_{\delta}/H\right) \tag{4}$$

with

$$\frac{1}{\beta_{\mathrm{ov}}} = \frac{1}{\beta} + \frac{1}{k_{\mathrm{m}}He^{\mathrm{Pe}}} \tag{5}$$

Taking into account that $J = \upsilon c_{\mathrm{p}}$ one can obtain for the condensed permeate concentration as:

$$\upsilon c_{\mathrm{p}} = \beta_{\mathrm{ov}}\left(c_{\mathrm{b}} - e^{-\mathrm{Pe}}\phi^{*}_{\delta}/H\right) \tag{6}$$

After reforming of Eq. (6), one can get the following equation for the dimensionless, permeate concentration, or other saying, enrichment, E ($E = c_{\mathrm{p}}/c_{\mathrm{b}}$), as [17]:

$$E \equiv \frac{c_{\mathrm{p}}}{c_{\mathrm{b}}} = \frac{e^{\mathrm{Pe}} - \phi^{*}_{\delta}/(\mathrm{H}c_{\mathrm{b}})}{e^{\mathrm{Pe}} - 1 + N} \tag{7}$$

with

$$N = \frac{k\mathrm{Pe}}{k_{\mathrm{m}}H}$$

The polarization modulus can be expressed as:

$$I \equiv \frac{c^{*}}{c_{\mathrm{b}}} = \frac{Ne^{\mathrm{Pe}} + (e^{\mathrm{Pe}} - 1)\phi^{*}_{\delta}/(c_{\mathrm{b}}H)}{e^{\mathrm{Pe}} - 1 + N} \tag{8}$$

The value of ϕ^{*}_{δ} means the concentration of the transported component on the permeate side of membrane. It is obvious that there is strict function between the outlet membrane concentration ϕ^{*}_{δ} and the condensed liquid permeate concentration c_{p}. This function can be given for the ith component as (see for details [18]):

$$\phi^{*}_{\delta} = \mathrm{H}c_{i}^{G} = \frac{P_{i}^{\mathrm{sat}}\gamma_{i}M_{i}H}{\varsigma_{i}\rho_{\mathrm{p}}RT}c_{\mathrm{p}i} \tag{9}$$

where P_{i}^{sat} denotes the saturated vapor pressure of i, M_{i} mol weight of the permeated component, ρ_{p}

density of the condensed permeate, γ_i is the activity coefficient, ς_i is the fugacity coefficient, R gas constant, and T is temperature.

Thus, the enrichment can be expressed as:

$$E = \frac{c_\mathrm{p}}{c_\mathrm{b}} = \frac{e^{\mathrm{Pe}}}{e^{\mathrm{Pe}} - 1 + N + \vartheta} \tag{10}$$

with

$$\vartheta = \frac{\gamma_i M_i P_i^{\mathrm{sat}}}{\varsigma_i \rho_\mathrm{p} RT} \tag{11}$$

The enrichment is expressed by Eq. (10) as a function of the mass transfer properties of the polarization and the membrane layers. The E value can directly be calculated with the mass transport data with this equation, while E has been given as a function of the intrinsic enrichment factor in the literature equation [1]. Note that the ϑ value does not depend on the total or partial pressure of the permeated component investigated. Accepting it, it can be stated that the ϕ_δ^* value never can be zero if $c_{\mathrm{p}i} > 0$. Thus, the value of ϑ should be taken into account. Its value depends on the properties of the component investigated. For example, the value of $M_i P_i^{\mathrm{sat}}/(\rho_\mathrm{p} RT)$ for water is equal to 1.295×10^{-4} at 333 K. The fugacity coefficient, ς_i can be regarded to unit at low pressure of the permeate phase.

Look at pervaporation of a binary mixture. The separation achieved by a pervaporation process can be defined by separation factor, ξ_{ij} for components i and j are as follows [1]:

$$\xi_{ij} = \frac{Y_i/Y_j}{X_i/X_j} = \frac{E_i}{E_j} \tag{12}$$

that is, applying Eq. (10), as:

$$\xi_{ij} = \frac{e^{\mathrm{Pe}_j} - 1 + N_j + \vartheta j}{e^{\mathrm{Pe}_i} - 1 + N_i + \vartheta_i} \frac{e^{\mathrm{Pe}_i}}{e^{\mathrm{Pe}_j}} \tag{13}$$

The separation factor can easily be predicted in knowledge of the mass transport parameters of the components to be separated for binary mixtures applying Eq. (13).

2.2. Mass transfer with variable diffusion coefficient

In this section, the mass transfer rate is also defined if the diffusion coefficient in the membrane is not constant. Several approaches can be applied to describe the component transport with variable diffusivity in the membrane [9–11]. To our knowledge no paper was published which takes into account the effect of the polarization layer in the case of variable diffusion coefficient in the membrane. Some special cases will be shown here, to illustrate the methodology applied to the description of the simultaneous effect of the both layers and the mass transfer rate equations obtained.

2.2.1. Exponential concentration dependency

When a membrane is plasticized by more than one species, the diffusion coefficient of a species is facilitated by all the plasticizants. Many membranologists found that the diffusion coefficient of species i in a ternary system of membrane/species i/species j could be generally expressed as [13,21]:

$$D_i = D_{i0} \exp(\alpha_i \phi_i + \kappa_j \phi_j) \tag{14}$$

where D_{i0} represents the diffusion coefficients of species i at infinite solution, ϕ_i and ϕ_j represent the local concentrations of the species of i and j in the membrane, respectively, and α and κ are usually interpreted as the plasticization coefficients of the two species for the membrane (the i and j subscripts can denote any components, in general case). The plasticization coefficient of the less permeable species can be neglected during the dehydration processes, since dehydration membranes generally show overwhelming affinity for water and the concentration of the less permeable species in the membrane is negligibly small [20–22]. The diffusion coefficients of both the species in the membrane are thus dependent on the concentration of water in the membrane phase alone. Thus, the diffusion coefficient of species i can often be written as:

$$D_i = D_{i0} \exp(\alpha_i \phi_i) \tag{15}$$

The mass transfer rate can be given with $\Phi = \phi/(\mathrm{Hc_b})$, $\tilde{\alpha} = \alpha \mathrm{Hc_b}$ (thus $D = D_{\mathrm{m}0} e^{\tilde{\alpha}\Phi}$) as [20,23]:

$$J = D_{\mathrm{m}0} e^{\alpha\phi} \frac{d\phi}{dy} \equiv \frac{D_{\mathrm{m}0}}{\delta_\mathrm{m}} \mathrm{Hc_b} e^{\tilde{\alpha}\Phi} \frac{d\Phi}{dY} \tag{16}$$

The α_i exponents has $\mathrm{m}^3/\mathrm{kmol}$ unit of measure, its dimensionless quantity is the $\tilde{\alpha}$ parameter ($\tilde{\alpha} = \alpha H c_\mathrm{b}$). After solution of Eq. (16) with the common boundary conditions on the bothe sides of the membrane layer, namely at $y = 0$ $\phi = \phi^*$ and at $y = \delta_\mathrm{m}$ $\phi = \phi_\delta^*$, it can be got as [20,23]:

$$J = \frac{D_{\mathrm{m0}}}{\alpha\delta_{\mathrm{m}}}\left(e^{\alpha\phi^*} - e^{\alpha\phi^*_\delta}\right) \equiv \frac{k_{\mathrm{m}}}{\alpha}\left(e^{\tilde{\alpha}\Phi^*} - e^{\tilde{\alpha}\Phi^*_\delta}\right) \tag{17}$$

with

$$k_{\mathrm{m}} = \frac{D_{\mathrm{m0}}}{\delta_{\mathrm{m}}}$$

The overall mass transfer rate can be expressed by means of Eqs. (1) and (2) as well as Eq. (17). Taking into account that these two mass transfer rates are equal to each other, the overall mass transfer rate will be as [23]:

$$\frac{J}{k\mathrm{Pe}}\left(1 - e^{\mathrm{Pe}}\right) + C_{\mathrm{b}}e^{\mathrm{Pe}} = \frac{1}{\alpha H}\ln\left\{\frac{J\alpha}{k_{\mathrm{m}}} + e^{\alpha\phi^*_\delta}\right\} \tag{18a}$$

or in dimensionless form as:

$$\frac{J}{k\mathrm{Pe}c_{\mathrm{b}}}\left(1 - e^{\mathrm{Pe}}\right) + e^{\mathrm{Pe}} = \frac{1}{\tilde{\alpha}}\ln\left\{\frac{J\alpha}{k_{\mathrm{m}}} + e^{\tilde{\alpha}\Phi^*_\delta}\right\} \tag{18b}$$

This newly developed expression of the overall mass transfer rate can be obtained by iteration method by the means of Eq. (18a) or (18b). These equations also involve the effect of the polarization layer which can have more and more role on the separation efficiency when the plasticization effect of the membrane, increasing the value of the membrane diffusion coefficient, increases.

The polarization modulus, *I*, can be expressed as ($I = c^*/c_{\mathrm{b}}$):

$$\frac{\beta\tilde{\alpha}}{k_{\mathrm{m}}H}I + e^{\tilde{\alpha}I} = \frac{\beta\tilde{\alpha}}{k_{\mathrm{m}}H} + e^{\tilde{\alpha}\Phi^*_\delta} \tag{19}$$

The *H* solubility coefficient is regarding as constant for rubbery polymeric membrane. The *I* value can also be determined by trial and error method.

2.2.2. *Flory–Huggins theory for prediction of the mass transfer rate*

The Flory–Huggins equation deals with molecules that are similar chemically, but differ greatly in length. The model is based on the idea that the chain elements arrange themselves randomly on a three-dimensional(3-D) structure. The resulting equation for the activity of the solvent is a simple proportional function of the volume fraction of the solvent. Note that the volume fraction is denoted here by ε to distinguish it from the ϕ concentration ($\varepsilon_i = \phi_i V_i/M_i$ where M_{i} molar weight, kg/kmol; V_i is molar volume of *i*, kmol/m^3, and ε_i is the volume fraction, m^3/m^3) The activity of a component in the membrane can be described according Flory–Huggins thermodynamics [24,25] by:

$$\ln a_i = \ln\varepsilon_i + (1-\varepsilon_i)\left(1 - \frac{V_i}{V_{\mathrm{m}}}\right) + \chi_{i\mathrm{m}}(1-\varepsilon_i)^2 \tag{20}$$

where $\chi_{i\mathrm{m}}$ is an interaction parameter between the component *i* and the membrane which is called as the Flory–Huggins interaction parameter; V_i and V_{m} are molar volumes of solvent and membrane, respectively (kmol/m^3). The χ interaction parameter is a dimensionless quantity characterizing the difference in interaction energy of a solvent molecule immersed in pure polymer compared with one in pure solvent. Its value can be positive or negative. If $\chi > 0$ then the solvent and polymer "dislike" each other, if $\chi = 0$ then the solvent and polymer are similar and if $\chi < 0$ the solvent and polymer attract each other [26].

After differentiating of Eq. (20) it can be got as:

$$\frac{d\ln a_i}{d\varepsilon_i} = \frac{1}{\varepsilon_i} + \left(1 - \frac{V_i}{V_{\mathrm{m}}}\right) - 2\chi_{\mathrm{im}}(1-\varepsilon_i) \tag{21}$$

The mass transfer rate can be given according to Eq. (21) as ($\varepsilon_i = \phi_i\rho/\rho_i$, that is $d\phi_i = \rho_i d\varepsilon_i/\rho$, where ρ is the membrane's density, $\rho = \sum_{j=1}^{n}\rho_i\phi_i$, kg/m^3):

$$\begin{aligned} J_i &= D_i^T\phi_i\frac{d\ln a_i}{d\phi_i}\frac{d\phi_i}{dy} \\ &= D_i^T\phi_i\left\{\frac{\rho_i}{\rho}\frac{1}{\phi_i} + \left(1 - \frac{V_i}{V_{\mathrm{m}}}\right) - 2\chi_{i\mathrm{m}}\left(1 - \frac{\rho}{\rho_i}\phi_i\right)\right\}\frac{d\phi_i}{dy} \end{aligned} \tag{22}$$

where J_i is here the mass transfer rate in kg/m^{2}s;

Integration of Eq. (22) over the membrane layer, the mass transfer rate can be expressed as:

$$\begin{aligned} J_i = \frac{D_i^T}{\delta}\Bigg\{&\frac{\rho_i}{\rho}(\phi_i^* - \phi_{\delta,i}^*) + \left(1 - \frac{V_i}{V_{\mathrm{m}}} - 2\chi_{i\mathrm{m}}\right)\left(\frac{\phi_i^{*2} - \phi_{\delta,i}^{*2}}{2}\right) \\ &+ 2\chi_{i\mathrm{m}}\frac{\rho}{\rho_i}\left(\frac{\phi_i^{*3} - \phi_{\delta,i}^{*3}}{3}\right)\Bigg\} \end{aligned} \tag{23}$$

The value of ϕ_i^* from Eq. (1) [$\phi_i^* = He^{Pe}(C_{\mathrm{b}} - J_i/\beta)$] can be replaced into Eq. (23), thus, one can obtain a third-order algebraic equation for J_i which can be solved analytically or numerically. This J_i value will be then the overall mass transfer rate which involves the effect of the polarization layer as well. Knowing the J value, the value of c_p can be obtained by means of equation of $J = vc_p$.

Obviously, the above defined overall mass transfer rates will be much more complicated expression when the solubility coefficient does not obey the Henry law, e.g. in the case of inorganic or glassy polymer membrane. This case will be discussed in a separate paper.

3. Results and discussion

3.1. *Reforming of the above equations due to the low Peclet number (Pe < 0.01)*

According to Baker et al. [1], Pe is about $1–3 \times 10^{-3}$ during pervaporation of volatile organic components with silicone rubber. Wijmans et al. [5] predict this value to be between about 10^{-3} and 10^{-4} for pervaporation of volatile organic components. Assuming that the value of Pe is less than 0.01 during pervaporation then the e^{Pe} quantity can be approached as $e^{\mathrm{Pe}} \cong 1 + \mathrm{Pe} \approx 1$, accordingly the overall mass transfer rate can be given as:

$$J \cong k_{\mathrm{ov}}\left(c_{\mathrm{b}}[1 + \mathrm{Pe}] - \phi_{\delta}^{*}/H\right) \approx k_{\mathrm{ov}}\left(c_{\mathrm{b}} - \phi_{\delta}^{*}/H\right) \tag{24}$$

or

$$J \cong k_{\mathrm{ov}}(c_{\mathrm{b}}[1 + \mathrm{Pe}] - \vartheta c_{\mathrm{p}}) \cong k_{\mathrm{ov}}(c_{\mathrm{b}} - \vartheta c_{\mathrm{p}}) \tag{25}$$

with

$$\frac{1}{k_{\mathrm{ov}}} = \frac{1}{k} + \frac{1}{k_{\mathrm{m}}H}$$

It is clearly seen from Eq. (25) that the mass transfer rate can be practically given by means of the diffusive model when applying it for both layers, namely for the membrane and polarization layers. The low value of Peclet number does not affect essentially the concentration distribution in the polarization layer at it was shown by Nagy's paper [17]. Thus, enrichment of separation can be approached as:

$$E \cong \frac{1 + \mathrm{Pe}}{\mathrm{Pe} + N + \vartheta} \approx \frac{1}{\mathrm{Pe} + N + \vartheta} \tag{26}$$

Taking into account Eq. (26), the separation factor can be got as:

$$\xi_{\mathrm{ij}} = \frac{1 + \mathrm{Pe}_i}{\mathrm{Pe}_i + N_i + \vartheta_i}\,\frac{\mathrm{Pe}_j + N_j + \vartheta_j}{1 + \mathrm{Pe}_j} \approx \frac{\mathrm{Pe}_j + N_j + \vartheta_j}{\mathrm{Pe}_i + N_i + \vartheta_i} \tag{27}$$

Note that the value of ϑ is often very low, as it was mentioned, for water is equal to 1.295×10^{-4} at 333 K. Otherwise, the value of ϕ_{δ}^{*} is low due to the low permeate side's pressure, thus its value can often be considered to be negligible. Accordingly, after simplification of Eq. (26), one can get as $E = k_{\mathrm{ov}}/\upsilon$ [16], thus, the separation factor will be as:

$$\xi_{ij} = \frac{\mathrm{Pe}_j + N_j}{\mathrm{Pe}_i + N_i} \equiv \frac{k_{\mathrm{ov},j}}{k_{\mathrm{ov},i}} = \frac{D_i}{D_j}\,\frac{1 + \Psi_j}{1 + \Psi_i} \tag{28}$$

with

$$\Psi_i = \frac{k_i}{k_{m,i}H_i};$$

$$\Psi_j = \frac{k_j}{k_{m,j}H_j}$$

Accordingly, the separation factor can easily be predicted by applying the mass transport data of the components. It is clearly seen from Eq. (28) that if one wants to reach high separation factor, one of the Ψ value should have larger than unit. This assumes that the solubility coefficient of a component should be possibly less than unit, while that of the other one should be larger possibly much larger than unit.

An important question to be answered how the convective velocity can affect the value of the diffusive flow in the boundary layer, since the sum of the diffusive and convective flow should be the same in every points of the boundary layer. Let us look first at the change of the ratio of the Fickian diffusive plus convective mass transfer rates $[J = k(c_{\mathrm{b}} - c^{*}) + \upsilon c^{*}]$ to the exact mass transfer rate obtained by Eq. (1) as a function of the low values Peclet number (Fig. 1). This

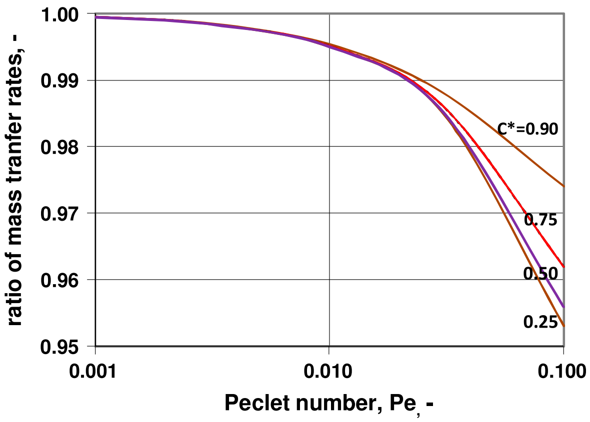

Fig. 1. The ratio of the mass transfer rates obtained by the Fickian diffusive plus convective flows $[J = k(c_{\mathrm{b}} - c^{*}) + \upsilon c^{*}]$ to that obtained by Eq. (1) as a function of the Peclet number at different value of fluid concentration on the feed membrane interface.

figure should illustrate how strongly the convective velocity can change the value of the diffusive flow throughout the boundary layer. The curvature of the concentration distribution increases with the increase of the Pe-number, accordingly the diffusive flow will continuously change in the boundary layer as a function of the space coordinate. In the range of Peclet number investigated, namely $\mathrm{Pe} = 0.001–0.1$, the ratio is close to unit, the difference from unit is not more than 5%. As can be seen in Fig. 1, the deviation from unit is strongly depends on the c^* value as well. These results should mean that the diffusive flux dominates the mass transfer rate in the Pe regime investigated, thus, diffusive model can be used to describe the mass transfer rate from the polarization layer into the membrane layer. The convective flow does not alter essentially the overall mass transfer rate. Consequently the resistance-in-series model with the diffusive mass flows in both layers can be used to determine the overall mass transfer rate for pervaporation process where $\mathrm{Pe} < 0.1$.

But as it is expected, the effect of the Peclet number on the separation efficiency can differ essentially from the effect of the mass transfer rate. Fig. 2 illustrates the effect of the Peclet number on the enrichment factor at different value of Ψ [$\Psi = k/(k_\mathrm{m}H)$]. The solubility, H, may have relatively large value, about 10–100 or more, the D value may be about $1 \times 10^{-8}–10^{-9}\,\mathrm{m}^2/\mathrm{s}$, while that for the membrane is about $1 \times 10^{-11}–10^{-12}\,\mathrm{m}^2/\mathrm{s}$, and the membrane thickness is about 0.3–30 μm [1]. Let us calculate an average value of $k/(k_\mathrm{m}H)$ (with $D = 5 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$, $D_\mathrm{m} = 5 \times 10^{-12}\,\mathrm{m}^2/\mathrm{s}$, $\delta_\mathrm{m} = 3\,\mu\mathrm{m}$, $\delta = 10\,\mu\mathrm{m}$, $H = 100$), one could get that $k/(k_\mathrm{m}H) \cong 3$. The values of E were calculated by means of Eq. (10) for the case of constant diffusion coefficient and it was assumed that ϑ is equal to zero. As can be seen the Peclet number strongly affects the separation by pervaporation. The logarithmic value of E decreases practically linearly with the logarithmic Peclet number. Otherwise, the value of $k/(k_\mathrm{m}H)$ has also strong effect. With its increase the enrichment decreases. These results are in harmony with that obtained by Baker et al. [4] measured the pervaporation of toluene/water binary mixture with silicon membrane of different thickness.

3.2. The role of the polarization layer

As it was mentioned in the first section, most of the literature works analyze the effect of the polarization layer without taking into account the simultaneous effect of the membrane layer or they discussed the complex mass transport through the membrane, taking into account the concentration dependence of diffusion or Flory–Huggins, Maxwell–Stefan approaches, etc. without taking into account the effect of the polarization layer. The polarization modulus illustrates the role of the boundary layer very well. If its value is close to unit then the polarization layer does not have essential influence on the mass transport.

Fig. 3 plots the change of the polarization modulus as a function of the Peclet number at constant diffusion coefficient and at different Ψ values. The polarization modulus was calculated here by Eq. (8) for the case of $\phi^*_\delta = 0$. As it can be seen, the Peclet number slightly influences the value of the polarization modulus, I, at a given Ψ value, only. The effect of the Ψ [$\Psi = k/(k_\mathrm{m}H)$] value on the I value is much stronger. Decreasing Ψ value, i.e. increasing $k_\mathrm{m}H$ value, can essentially increase the effect of the polarization layer.

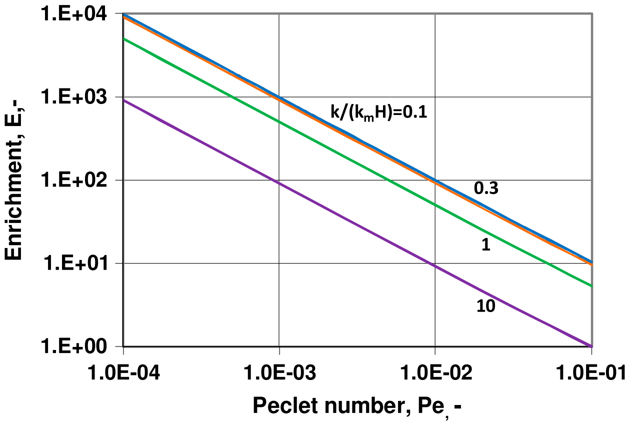

Fig. 2. The effect of the Peclet number on the enrichment by constant diffusion coefficient, at different Ψ ($\Psi = k/(k_mH)$and $\vartheta = 0$.

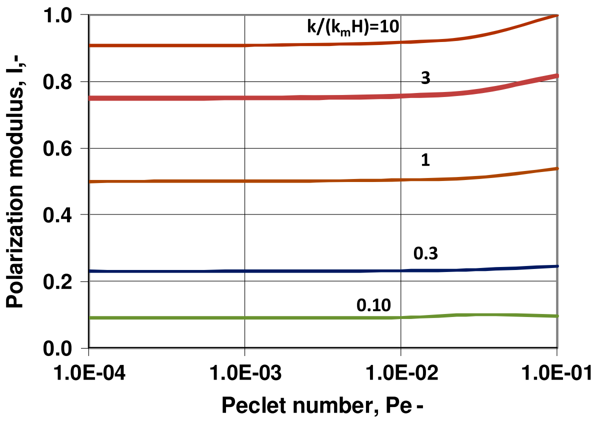

Fig. 3. Polarization modulus as a function of the Peclet number with constant diffusion coefficient in the membrane layer, $\phi^*_\delta = 0$.

That means that the Ψ value dominantly determines the value of the polarization modulus, while the effect of the Peclet number is marginal due to its relatively low values during pervaporation. The equations developed enable the reader to predict whether the polarization layer essentially affects the separation or not. One can predict how the negative effect of the polarization layer can be avoided.

In the case of the concentration dependent diffusion coefficient, the increasing diffusion coefficient can strongly increase the mass transfer rate, and consequently, the effect of the boundary layer on the mass transport. How the plasticization coefficients can affect the value of the polarization modulus is illustrated in Fig. 4, predicted by means of Eq. (19) by trial-error method. The α value can change between about $(1\text{–}100) \times 10^{-6}\,\mathrm{m^3/g}$ [19,27,28], and the H solubility about 10–100, while the value of c_b can change between 10^2 and $10^5\,\mathrm{g/m^3}$. The average value of $\tilde{\alpha}$ will be equal to about 1, with $\alpha = 10 \times 10^{-6}\,\mathrm{m^3/g}$, $H = 100$ and $c_b = 10^3\,\mathrm{g/m^3}$ in the range of the $\alpha H c_b$ exponent investigated, the D value can strongly increase due to its exponential function. With the increase of the concentration in the membrane layer, the value of D can essentially be increased due to expression of $D = D_{m0}\exp(\alpha H c_b \Phi)$. In the range of $\alpha H c_b > 1\text{–}3$, the interface concentration can be strongly decreased as a function of $\alpha H c_b$. The I value will lower down to zero with further increase of the $\alpha H c_b$ value due to the plasticization of the membrane. That means that the mass transfer resistance of the polarization layer will gradually dominate the mass transfer rate. Accordingly, the increase of the diffusion coefficient can be very large and its effect on the concentration distribution in the polarization layer must not generally be neglected.

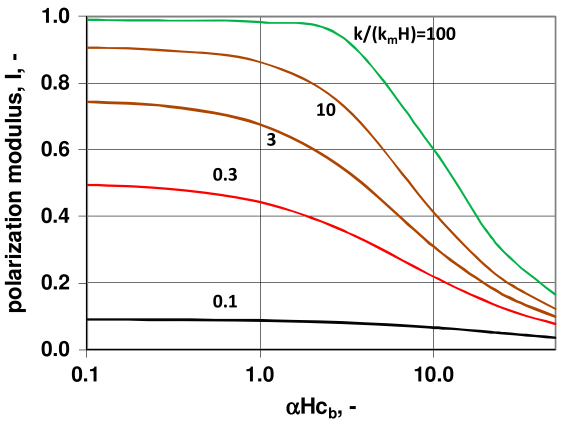

Fig. 4. The effect of the plasticization coefficients, namely $\alpha H c_b$, on the polarization modulus at different $k/(k_m H)$ values.

Looking at Figs. 3 and 4, the importance of the Ψ values can be clearly seen. Its value determines dominantly the mass transfer rate, and thus, the separation efficiency. Producing better and better membranes, thinner ones with better mass transport properties, the $k_m H$ product can be larger and larger. On the other hand, the improvement of the mass transport through the boundary layer can be carried out only limitedly. For elimination of the negative effect of the polarization layer, the Ψ value should be possibly maintained above the unit. At large value of solubility in the membrane and in case of a very thin top membrane layer, this condition is not easy to be fulfilled. Accordingly, it is strictly recommended to be applied a model, in order to get real values of the separation parameters as enrichment, permeate concentration, separation factor, and mass transfer rate, which takes into account the simultaneous effect of both layers for prediction of the separation efficiency during pervaporation.

3.3. Case studies

The effect of the polarization layer on the mass transfer rate should be shown in our examples as case studies. Two examples, taken from the literature [28,29] will be shown here in order to be illustrated on how to apply the expressions presented. Izák et al. [28] measured the permeation rate of organic components, namely toluene, e.g. in toluene/pentan-1-ol binary mixture, through polyethylene membrane at 25°C. The toluene flux measured (◆ are measured data) is plotted in Fig. 5. As it can be seen, the flux strongly

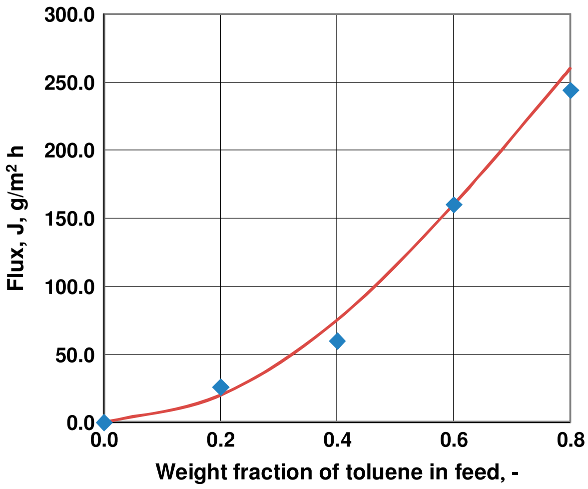

Fig. 5. Partial flux of toluene for the system toluene and pentan-1-ol through polyethylene membrane [28, Fig. 10] (points are measured, line is predicted data) ($D_{m0} = 3.8 \times 10^{-11}\,\mathrm{m^2/s}$; $\delta_m = 70 \times 10^{-6}\,\mathrm{m}$; $\tilde{\alpha} = 6.76$).

increases as a function of the toluene concentration. Assuming exponential function of the toluene diffusion coefficient, the mass transfer rate was modeled by Eq. (17). That means that the external mass transfer resistance is not involved in the calculation. According to the data of Izák et al. [28], the diffusion coefficient is increasing closely exponentially in the concentration range 0–0.8 weight fraction of toluene. Thus, the predicted mass transfer rates with value of $\tilde{\alpha} = 6.76$ (line in Fig. 5) are in very good agreement with the measured data proving that exponential function can really be applied to describe the toluene mass transport through polyethylene membrane. Let us look the role of the external mass transfer resistance in this pervaporation process. Taking for value of the boundary layer's mass transfer coefficient as $k = 5 \times 10^{-5}$ m/s [1,17], and the high flux at $c_b = 0.8$ g/g $\cong 1 \times 10^6$ g/m^3, thus one can obtain that $J = 180 \times 10^3$ g/m^{2}h (assuming c^*=0), while the mass transfer rate measured at this c_b value was 260 g/m^{2}h (the membrane mass transfer coefficient is as $k_m = 3.8 \times 10^{-11}/70 \times 10^{-6} = 5.4 \times 10^{-7}$ m/s, while the H solubility for toluene changed between 0.07 and 0.13 g/g between c_b = 0.2–0.8 g/g {see Fig. 1 in paper [28]}). Thus, it can be concluded that the effect of the external mass transfer resistance is practically negligible in this pervaporation process, due to the relatively high feed concentration.

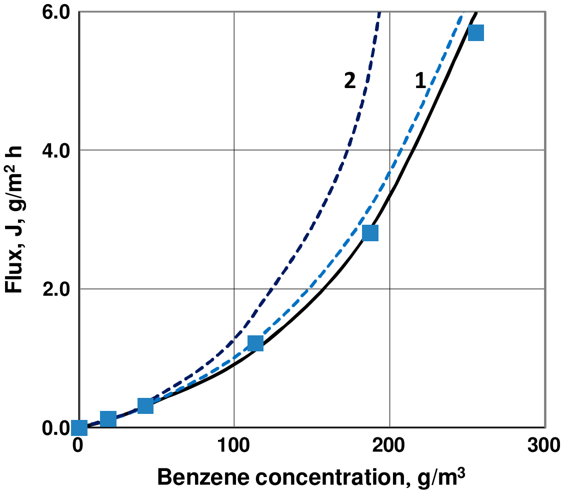

Fig. 6. The measured (points) and calculated benzene flux without external mass transfer resistance assuming $k = 1 \times 10^{-4}$ m/s (continuous line; it means practically negligible external mass transfer resistance, see Fig. 7) and $k = 0.5 \times 10^{-4}$ m/s (dotted line 1) as well as $k = 0.2 \times 10^{-4}$ m/s (dotted line 2) external mass transfer coefficients during measurements as a function of benzene concentration in water/benzene binary mixture using PDMS membrane ($D_{m0} = 1 \times 10^{-11}$ m^2/s; $\delta_m = 700 \times 10^{-6}$ m; $\alpha = 8.1 \times 10^{-5}$ m^3/g; $H = 111$).

Csao et al. [29] measured the mass transport properties (diffusion coefficient, solubility, and permeability coefficient in cm^2/s) of benzene as a function of benzene concentration in water (c_b was changed between 19 g/m^3 and 256 g/m^3) in PDMS membrane. From the permeability data given by the authors the mass transfer rate was calculated by expression of $J_i = P_i \phi^*/\delta_m$ [1] (i = benzene) and this data is assumed as measured mass transfer rates (Fig. 6, points). This expression means that the external mass transfer resistance is negligible, and the outlet membrane concentration is regarded to be zero. The value used for calculation is taken from paper's of Csao et al. [29], namely $D_{m0} = 1 \times 10^{-11}$ m^2/s; $\delta = 700 \times 10^{-6}$ m; H = 111–125, and D_m = (1–4.56) $\times 10^{-11}$ m^2/s due to the concentration dependency. The calculated date are plotted in Fig. 6 (continuous line), the α value obtained is equal to 8.1×10^{-5} m^3/g ($\tilde{\alpha} = \alpha \bar{H} c_b = 8.1 \times 10^{-5}$ m^3/g $\times 111 \times 256$ g/m^3 = 2.3). The experimental and the calculated data are here also in good agreement, proving that the diffusion rate really exponentially changes as a function of the feed concentration. Now look at the external mass transfer rate at $c_b = 300$ g/m^3. With $J_i = k(c_b - c^*)$, one can obtain with $k = 5 \times 10^{-5}$ m/s and $c^* = 0$, that $J = 1.5 \times 10^{-3}$ g/m^2 s = 5.4 g/m^2 h. This value is of the same order of magnitude as the mass transfer rate measured. That means that the negligence of the external mass transfer resistance can cause serious error in the evaluation of the experimental data. The presence of the polarization layer lowers the interface concentrations in the layers, namely values of c^* and ϕ^* and consequently decreases the overall mass transfer rate measured. In order to reach the same flux in the boundary layer and in the membrane, in this case, the relative value (=c^*/c_b) of interface concentration should be decreased and the concentration dependency of the diffusion coefficient should be increased, due to the lower value of ϕ^*. The value of the polarization modulus can exactly be predicted by Eq. (18b), depending on the $k/(k_m H)$. This value, with average parameter values, ($k_m = 5 \times 10^{-11}/7 \times 10^{-4} = 0.7 \times 10^{-7}$ m/s), will be about $5 \times 10^{-5}/(118 \times 0.7 \times 10^{-7}) = 5.9$. As it can be seen in Fig. 4, the polarization modulus can essentially be lowered during the pervaporation at $\tilde{\alpha} = 2.3$ and at $k/(k_m H) = 5.9$. The value of the polarization modulus, I, will fall between 0.6 and 0.7, thus its effect should be taken into account during the evaluation of the results measured.

Let us show how the concentration distribution changes in the boundary and membrane layers at three different values of the external mass transfer

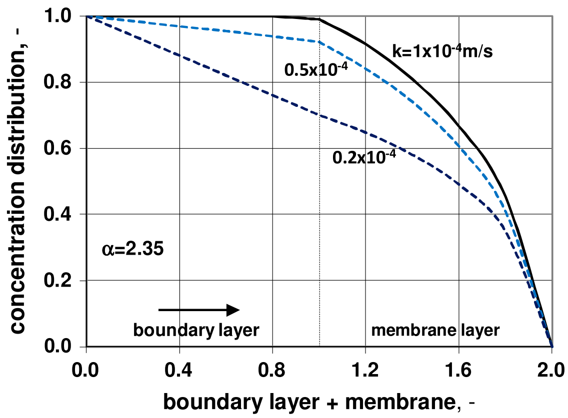

Fig. 7. Concentration distribution of the measured data in the boundary and membrane layers, given by points in Fig. 6, assuming external mass transfer resistances during the measurements.

coefficient, namely $k = 1 \times 10^{-4}$ m/s, 0.5×10^{-4} m/s, and 0.2×10^{-4} m/s, applying the measured mass transfer rates at $c_b = 256$ g/m^3, that is $J = 5.8$ g/m^{2}h (see Fig. 6). The concentration distributions obtained are plotted in Fig. 7. The interface concentration, c^*, was calculated by means of $J = k(c_b\text{-}c^*)$, while the concentration distribution in the membrane layer by the following expression [24, p. 50 with $\Phi^*_\delta = 0$] ($\Phi^* = c^*/c_b$; $\tilde{\alpha} = \alpha H c_b$):

$$\Phi = \frac{1}{\tilde{\alpha}}\ln\left\{e^{\tilde{\alpha}\Phi^*}(1 - Y) + Y\right\} \tag{29}$$

The thickness of the external boundary layer can change between 10 and 20 μm, depending on the mixing intensity of the feed liquid, according to the literature data [1,17]. Accepting that the diffusion coefficient of benzene in water is equal to 1.1×10^{-9} m^2/s, the mass transfer coefficient, k, can change between 1×10^{-4} and 0.5×10^{-4} m/s, in the case of the above mentioned film thickness. It is clearly seen in Fig. 7 that the effect of the external mass transfer coefficient on the mass transfer rate strongly increases with decreasing k value. Its effect is especially strong in the mass transfer range of 0.5×10^{-4} down to 0.2×10^{-4} m/s, since the interface concentration can decrease down to about 0.7. On the other hand, the external mass transfer resistance has no effect on the toluene permeation rate from toluene/pentan-1-ol binary mixture [28], in the above range of the external mass transfer coefficient. This means that the effect of the polarization layer is recommended to be taken into account if the feed concentration of the permeating component is too low as it can often be the case for organic/water mixtures. The mass transfer rate measured obviously depends on the effect on the external mass transfer resistance. In the given case, its presence can essentially lower the measured values. The J values have been recalculated for the cases without concentration gradient in the boundary layer, that is for case of $\Phi^* = 1$, assuming that during the measurements the external mass transfer resistance existed (applying 0.5×10^{-4} and 0.2×10^{-4} m/s k coefficients) and it decreased the measured value of J (Fig. 6, dotted lines: $1 - k = 0.5 \times 10^{-4}$ m/s; $2 - k = 0.2 \times 10^{-4}$ m/s during the experiments). The α value should be increased to get the same, measured mass transfer rate (points in Fig. 6) with decreasing Φ^* values that is with decreased k values. Its value obtained were 8.1×10^{-5}, 8.6×10^{-5}, and 13.2×10^{-5} m^3/g in cases of $k = 1 \times 10^{-4}$, 0.5×10^{-4}, and 0.2×10^{-4} m/s, respectively. The dotted lines were obtained by the above α values assuming $\Phi^* = 1$. The curves of Fig. 6 illustrate how the presence of external mass transfer resistance could decrease the mass transfer rate measured. These results illustrate how important it can be to take into account the external resistance during the evaluation of the measured mass transfer data.

Similarly, low I values was also obtained by Nagy [17] for pervaporation of toluene/water binary mixture by proving the above conclusions.

4. Conclusion

This paper analyzes the simultaneous effect of the polarization and the membrane layer on the mass transport, on the separation factor, and on the enrichment. It can be stated that the convective flow does not affect essentially the mass transfer rate but it can strongly affect the enrichment or separation factor. These parameters can easily be predicted by the simplified equation developed, taking into account the rather low values of the Peclet number during pervaporation process. Methodology is presented in some cases, namely, when the diffusion coefficient is concentration dependent and in case of application of the Flory–Huggins theory, how it can be relativly easily taken into account the simultaneous effect of both layers. According to the results of the case studies, the effect of the polarization layer should be taken into account in the most pervaporation processes, especially when the feed concentration is in ppm order of magnitudes. The expression developed enables the reader to predict easily the simultaneous effect of both mass transport layers, namely the polarization and the membrane layers.

Acknowledgments

The National Development Agency grant TÁMOP-4.2.2/B-10/1-2010-0025) and the project TÁMOP 4.2.1/ B-09/1/ KONV-2010-0003 "Mobility and Environment: Researches in the fields of motor vehicle industry, energetics and environment in the Middle-and West-Transdanubian Regions of Hungary." greatly acknowledged for the financial support.

Nomenclature

c — concentration, g/m^3
c_b — feed phase concentration, g/m^3
c^* — interface liquid concentration, g/m^3
C — dimensionless concentration of the fluid phase, –, ($C = c/c_b$)
D — diffusion coefficient, m^2/s
D_{m0} — diffusion coefficient in the membrane layer when $c \to 0$, m^2/s
E — enrichment factor ($= c_p/c_b$)
H — solubility coefficient, ($\phi^* = Hc^*$), –
J — mass transfer rate, g/m^2 h
k — diffusive mass transfer coefficient; that is for the boundary layer, ($= D/\delta$), m/s
M — molar weight, kg/kmol
$\bar{M}$ — average molar weight, kg/kmol
N — constant defined after Eq. (7), ($= k\mathrm{Pe}/k_m H$),-
P_o — total pressure of permeate phase, Pa
Pe — Peclet number in the boundary layer ($= \upsilon\delta/D$), –
R — gas constant, Pa m^3/kmol K
T — temperature, °K
X — mol fraction, –
y — space co-ordinate perpendicular to the membrane interface, m
Y — dimensionless space coordinate, ($= y/\delta$), –

Greek letters

α — empirical constant (Eq. (15)), m^3/g
$\tilde{\alpha}$ — $= \alpha H c_b$
β — convective plus diffusive mass transfer coefficient for the boundary layer, $[= k\mathrm{Pe}\, e^{\mathrm{Pe}}/(e^{\mathrm{Pe}} - 1)]$ m/s
δ — boundary layer thickness, m
δ_m — membrane thickness, m
γ — activity coefficient, –
ϕ — concentration in the membrane, g/m^3
Φ — dimensionless concentration in the membrane, $[\Phi = \phi/(Hc_b)]$, –
ρ — density, kg/m^3
υ — convective velocity, m/s
ϑ — $= \gamma_i M_i P_i^{sat}/\varsigma_i \rho_p RT$, –
ζ — fugacity coefficient, –

Subscripts

b — inlet
i — ith component to be separated
m — membrane layer
p — permeate

Superscripts

$*$ — at liquid/membrane interface
G — vapor phase
sat — saturated

References

[1] R.W. Baker, Membrane Technology and Applications, Wiley & Sons, Chichester, 2004.

[2] M. She, S.-T. Hwang, Effects of concentration, temperature, and coupling on pervaporation of dilute flavor organics, J. Membr. Sci. 271 (2006) 16–28.

[3] S. Bhattacharya, S.-T. Hwang, Concentration polarization, separation factor, and Peclet number in membrane processes, J. Membr. Sci. 132 (1997) 73–90.

[4] R.W. Baker, J.G. Wijmans, A.L. Athayde, R. Daniels, J.H. Ly, M. Le, The effect of concentration polarization on the separation of volatile organic compounds from water by pervaporation, J. Membr. Sci. 137 (1997) 159–172.

[5] J.G. Wijmans, A.L. Athayde, R. Daniels, J.H. Ly, H.D. Kamanaddin, I. Pinnau, The role of boundary layers in the removal of volatile organic compounds from water by pervaporation, J. Membr. Sci. 109 (1996) 135–146.

[6] Smart., V.M. Starov, R.C. Schucker, D.R. Lloyd, Pervaporative extraction of volatile organic compounds from aqueous systems with use of a tubular transverse flow module. Part II. Experimental results, J. Membr. Sci. 143 (1998) 159–179.

[7] P. Schaetzel, Z. Bendjama, C. Vauclair, Q.T. Nguyen, Ideal and non-ideal diffusion through polymers: Application to pervaporation, J. Membr. Sci. 191 (2001) 95–102.

[8] E. Nagy, Binary, coupled mass transfer with variable diffusivity through cylindrical membrane, J. Membr. Sci. 274 (2006) 159–168.

[9] A. Heintz, W. Stephan, A generalized solution-diffusion model of the pervaporation process through composite membrane, J. Membr. Sci. 89 (1994) 153–169.

[10] P. Izák, L. Bartovská, K. Friess, M. Sipek, P. Uchytil, Description of binary liquid mixtures transport through non-porous membrane by modified Maxwell-Stefan equation, J. Membr. Sci. 214 (2003) 293–309.

[11] E. Nagy, Nonlinear mass transfer through dense membrane, Desalination 163 (2004) 345–354.

[12] O. Trifunovic, G. Trägardh, Mass transport of aliphatic alcohols and esters through hydrophobic pervaporation membranes, Sep. Purif. Technol. 50 (2006) 51–61.

[13] R. Jiraratananon, A. Chanachai, R.Y.M. Huang, Pervaporation dehydration of ethanol–water mixtures with chitosan/ hydroxyethylcellulose (CS/HEC) composite membranes: II. Analysis of mass transport, J. Membr. Sci. 199 (2008) 211–222.

[14] T. Schafer, J. Crespo, Study and optimization of the hydrodynamic upstream conditions during recovery of a complex aroma profile by pervaporation, J. Membr. Sci. 301 (2007) 46–56.

[15] M. She, S.-T. Hwang, Concentration of dilute flavor compounds by pervaporation: Permeate pressure effect and boundary layer resistance modeling, J. Membr. Sci. 236 (2004) 193–202.

[16] A. Noworyta, M. Kubasiewicz-Ponitka, A. Koziol, Mass and heat transport resistance in pervaporation, Desalin. Water Treat. 26 (2011) 226–235.

[17] E. Nagy, Coupled effect of the membrane properties and concentration polarization in pervaporation: Unified mass transport model, Sep. Purif. Technol. 73 (2010) 194–201.

[18] E. Nagy, G. Borbély, The effect of the concentration polarization and the membrane layer mass transport on the membrane separation, J. Appl. Membr. Sci. 6 (2007) 1–8.

[19] M.H.V. Mulder. Pervaporation: Separation of ethanol/water and isomeric xylens, PhD dissertation, Tech. High School, Twente, Netherland, 1984.

[20] P. Schaetzel, R. Bouallouche, H.A. Amar, Q.T. Nguyen, B. Riffault, S. Marais, Mass transfer in pervaporation: The key component approximation for the solution-diffusion model, Desalination 251 (2010) 161–166.

[21] P. Shao, R.Y.M. Huang, Polymeric membrane pervaporation, J. Membr. Sci. 287 (2007) 162–179.

[22] R.Y.M. Huang, V.J.C. Lin, Separation of liquid mixtures using polymer membranes, J. Polym. Sci. 12 (1968) 2615–2631.

[23] E. Nagy, Basic Equation of the Mass Transport Through a Membrane Layer, Elsevier, Amsterdam, 2012.

[24] P. Flory, Principles of Polymer Chemistry, Cornell University press, New York, 1963.

[25] S.J. Lue, F.J. Wang, S.-Y. Hsiaw, Pervaporation of benzene/cyclohexane mixtures using ion-exchange membrane containing copper ions, J. Membr. Sci. 240 (2004) 149–158.

[26] J.A. Wesselingh, R. Krishna, Mass Transfer in Multicomponent Mixture, Delft University Press, Delft, 2000.

[27] P. Schaetzel, C. Vauclair, Q.T. Nguyen, R. Bouzerar, A simplified solution-diffusion theory in pervaporation: The total solvent volume fraction model, J. Membr. Sci. 244 (2004) 117–127.

[28] P. Izak, L. Bartovská, K. Friess, M. Sipek, P. Uchytil, Comparison of various models for transport of binary mixtures through dense polymer membrane, Polymer 44 (2003) 2679–2687.

[29] K.-P. Chao, V.-S. Wang, P. Wang, T.-Y. Wang, Removal of benzene from aqueous solution by adsorption using PDMS membrane devices, Polymer Testing 29 (2010) 939–944.