Modeling of Liquid/Liquid Separation by Pervaporation: Toluene from Water

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The resistances-in-series model, the modified solution-diffusion model, the Flory–Rehner theory, and the film theory were used to calculate the diffusion coefficients of two components of a liquid-feed mixture that are separated by pervaporation. The toluene and water fluxes through EPDM membranes of various thicknesses were modeled for different mass-transfer coefficients in the feed boundary layer (k_L). It is shown that the toluene flux depends strongly on the k_L and the membrane resistance affects significantly the toluene flux only for very high values of k_L ($> 10^{-4}$ m/s). The water flux increases linearly with the reciprocal value of the membrane thickness and is not affected by the boundary-layer resistance. The small increase in the water flux, due to the toluene concentration increase in the feed, can adequately be described by this model.

Introduction

Pervaporation is a process in which a liquid feed mixture is separated by a dense homogeneous membrane. At the feed or upstream side a liquid is in contact with the membrane at atmospheric pressure, while at the permeate or downstream side a low partial pressure is maintained by a vacuum pump or a sweeping gas. The permeate is removed as a vapor. The driving force for the process is the chemical-potential difference or partial-pressure difference across the membrane.

Ji et al. (1993) modeled multicomponent pervaporation with the resistance-in-series model, in which the film theory was incorporated for the transport through the liquid boundary layer, and the solution-diffusion model with constant permeability coefficients. Their experiments with PDMS membranes showed that the VOC flux increased linearly with VOC concentration in the feed. The water flux decreased linearly with increasing membrane thickness. Furthermore, the water flux increased about 10% when the toluene concentration in the feed was increased from 20 to 500 ppm. From these results Ji et al. concluded that the process can be described satisfactorily by a solution-diffusion model with constant permeability coefficients neglecting the small increase in water flux. In addition, they incorporated the effect of the permeate pressure (drop) in their modeling.

Michaels (1995) used equations for the different transport steps in the resistances-in-series model that were even more simplified. He suggested a dimensionless parameter that could serve as a predictor of the performance of a given pervaporation membrane and membrane module with a limited amount of experimental information. Michaels suggested that his proposed correlations together with the observations of Ji et al. (1994) would be a reliable basis for the selection of membranes, membrane modules, and process parameters. Before Michaels, many researchers introduced closely related dimensionless parameters to show the polarization effect of the pervaporative removal of barely soluble VOCs from water (Gooding et al., 1992; Raghunath et al., 1992; Wijmans and Baker, 1993; Feng and Huang, 1994).

The work described in this article is based on the earlier studies of Mulder and Smolders (1984), who described the transport through a dense membrane, and the film theory to account for the mass-transfer limitations in the boundary layer.

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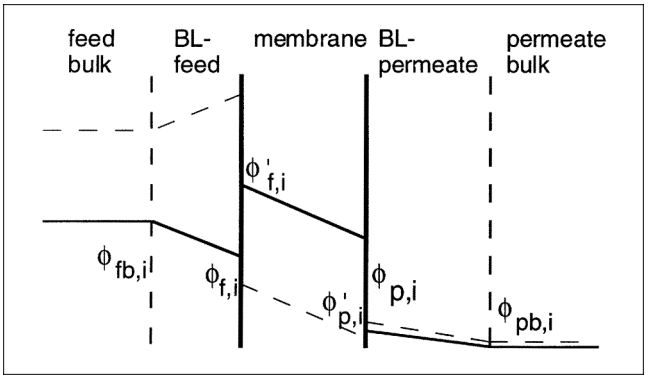

Figure 1. Concentration profiles at both sides of a membrane during pervaporation (according to the film theory): BL = boundary layer.

Mass Transfer

The transport mechanism in pervaporation through a homogeneous dense membrane can be described by five consecutive steps:

1. Transfer of a component from the bulk of the feed to the membrane surface.
2. Partition of a component between the liquid feed and the membrane.
3. Transport of the component across the membrane.
4. Desorption of the component as vapor on the permeate side of the membrane.
5. Transfer of the component from the membrane surface to the permeate bulk.

This general transport mechanism can be applied for each component present in the liquid mixture. The treatment of the mass transport in the membranes is based on the film theory, Fick's law, the thermodynamics of irreversible processes and the Maxwell–Stefan equations. The Maxwell–Stefan equations will not be discussed in this work; this discussion can be found in Heintz and Stephan (1994) and Wesselingh and Krishna (1990).

Film theory and resistances-in-series model

The concentration profiles in volume fractions (ϕ) for a binary mixture according to the film theory and the resistances-in-series model at steady state are given in Figure 1. The dashed line shows the concentration profile of the slower permeating component, and the full line shows the concentration profile of the component that is permeating preferentially.

The mass-transfer across the boundary layer at the feed side of the membrane can be described using Eq. 1:

$$J_i = k_{L,i}\left(\phi_{fb,i} - \phi_{f,i}\right), \tag{1}$$

where $k_{L,i}$ is a mass-transfer coefficient that can be obtained from a Sherwood relation. The mass transfer across the membrane is given by Eq. 2

$$J_i = k_{m,i}\left(\phi'_{f,i} - \phi'_{p,i}\right), \tag{2}$$

in which $k_{m,i}$ is the mass-transfer coefficient in the membrane. Usually the mass-transfer resistance of the permeate boundary layer is assumed to be negligible. The flux across the boundary layer at the permeate side of the membrane can be described by

$$J_i = k_{p,i}\left(\phi_{p,i} - \phi_{pb,i}\right) \tag{3}$$

here $k_{p,i}$ is the mass-transfer coefficient in the downstream-side boundary layer. The following partition coefficients can be introduced for the upstream side ($s_{f,i}$) and the downstream side ($s_{p,i}$), respectively. This equation includes resistances in the membrane support material and boundary layer at the permeate side as well.

$$s_{f,i} = \frac{\phi'_{f,i}}{\phi_{f,i}} \qquad \text{and} \qquad s_{p,i} = \frac{\phi'_{p,i}}{\phi_{p,i}}. \tag{4}$$

At steady state the flux through each layer is the same and combination of Eqs. 1, 2, 3, and 4 leads to an expression that describes the overall mass transfer:

$$J_i = \frac{\phi_{fb,i} - \dfrac{s_{p,i}}{s_{f,i}}\phi_{pb,i}}{\dfrac{1}{k_{L,i}} + \dfrac{1}{s_{f,i}k_{m,i}} + \dfrac{s_{p,i}}{s_{f,i}k_{p,i}}}. \tag{5}$$

Generally, the mass-transfer resistance and the concentration at the permeate side are neglected, which leads to

$$J_i = \frac{\phi_{fb,i}}{\dfrac{1}{k_{L,i}} + \dfrac{1}{s_{f,i}k_{m,i}}}. \tag{6}$$

Equation 6 can be further modified by introducing an overall mass-transfer coefficient (k_{ov})

$$J_i = \frac{\phi_{fb,i}}{\dfrac{1}{k_{L,i}} + \dfrac{1}{s_{f,i}k_{m,i}}} = k_{ov}\phi_{fb,i}$$

in which

$$\frac{1}{k_{ov}} = \frac{1}{k_{L,i}} + \frac{1}{s_{f,i}k_{m,i}}. \tag{7}$$

The overall mass-transfer coefficient can be obtained from flux measurements at various feed concentrations.

Fick's law with concentration-dependent diffusion coefficients

According to Fick's law the flux J of component i through a homogeneous membrane is proportional to its concentration gradient:

$$J_i = D_i\frac{d\phi'_i}{dx}, \tag{8}$$

where D_i is the diffusion coefficient, ϕ_i' is the concentration in the membrane of component i, and x is the directional coordinate. The diffusion coefficient of low molecular components in polymers is concentration-dependent. In pervaporation processes there are large concentration differences across the membrane. One of the most commonly used relations to describe this dependence is an exponential relation (Mulder, 1991):

$$D_i = D_{0,i} e^{\tau_i \phi_i'}, \tag{9}$$

here τ is the plasticizing coefficient describing the interaction between permeating species and membrane, and $D_{0,i}$ is the Fickian diffusion coefficient at infinite dilution of the permeant. Using Eq. 9 in Fick's Eq. 8 with the following boundary conditions: $x = 0$, $\phi_i' = \phi_{0,i}'$ and $x = l$, $\phi_i' = 0$ leads to

$$J_i = \frac{D_{0,i}}{l\tau_i}\left(e^{\tau_i \phi_{0,i}'} - 1\right). \tag{10}$$

Modeling multicomponent pervaporation is more complex, because not only component–membrane but also component–component interactions have to be considered. A component in a mixture usually has a higher diffusivity in the membrane than it has as a single component. Greenlaw et al. (1977) used a linear relationship between the concentrations of components in the membrane and their diffusion coefficients. For ideal liquid mixtures (like heptane–hexane) this may hold, but for nonideal mixtures in which mutual interactions and polymer–component interactions have to be taken into account, other relationships would give a better description of the experimental results:

$$D_i = D_{i,0} + f \cdot \left(\phi_i' + g\phi_j'\right)^h. \tag{11}$$

The constants f and h on components i and the constant g on component j.

Exponentially modified diffusion coefficients are also used (Long, 1965; Mulder and Smolders, 1984):

$$D_i = D_{0,i} e^{l\phi_i' + m\phi_j'}, \tag{13}$$

where the constants l and m depend on components i and component j, respectively.

Solution-Diffusion Model

Pervaporation processes are usually described with a solution-diffusion model. If no external forces (like pressure difference) are present and if there is no coupling of flows, then the flux of component i is proportional to its chemical potential gradient ($d\mu_i/dx$) (Lonsdale et al., 1965; Merten, 1966; Lee, 1975):

$$J_i = -\frac{D_i^T}{RT} \cdot \phi_i \frac{d\mu_i}{dx}, \tag{14}$$

where D_i^T is the thermodynamic diffusion coefficient and may depend on the concentration and therefore on the place in the membrane (Mulder and Smolders, 1984). The chemical potential can be described as

$$\mu_i = \mu_i^0 + RT \ln a_i. \tag{15}$$

Substituting μ_i in Eq. 14 gives

$$J_i = -D_i^T \phi_i \frac{\ln a_i}{dx}. \tag{16}$$

Equation 8 can be written as

$$J_i = -D_i \frac{d\phi_i}{d\ln a_i} \frac{d\ln a_i}{dx}. \tag{17}$$

Combining Eqs. 16 and 17 leads to a relation between D_i and D_i^T:

$$D_i^T \phi_i = D_i \frac{d\phi_i}{d\ln a_i} \Leftrightarrow D_i = D_i^T \frac{d\ln a_i}{d\ln \phi_i}. \tag{18}$$

Lee (1975) used a solution-diffusion model with a concentration independent diffusion coefficient and without considering a possible coupling of fluxes. In the case of liquid mixtures that hardly show any mutual interaction nor any interaction with the polymer, this assumption is valid, but with other nonideal mixtures this approach is often too simple.

Modeling assumptions

To describe the mass transfer through the membrane the assumptions and boundary conditions must be defined as follows.

1. Steady-state conditions are assumed. The permeation rate is independent of time and no accumulation of components takes place in the membrane. The membrane undergoes no structural changes. The chemical potential of component i is a function of the volume fraction of all components present.

2. Mass transfer in the membrane and in the feed are taken into account. Mass-transfer resistance in the permeate is neglected.

3. The concentrations of the components at the boundary of the membrane can be calculated from thermodynamic principles. At the membrane interface the thermodynamic potentials of the membrane and its adjacent phase are assumed to be equal (Lee, 1975):

$$\mu_{f,i} = \mu_{f,i}' \quad \text{and} \quad \mu_{p,i} = \mu_{p,i}'. \tag{19}$$

The chemical potentials at the boundary of the membrane are

$$\mu_{f,i} = \mu_0 + \mathrm{RT}\ \ln a_{f,i}, \tag{20}$$

$$\mu_{f,i}' = \mu_0 + \mathrm{RT}\ \ln a_{f,i}', \tag{21}$$

$$\mu_{p,i} = \mu_0 + \mathrm{RT}\ \ln a_{p,i}, \tag{22}$$

$$\mu_{p,i}' = \mu_0 + \mathrm{RT}\ \ln a_{p,i}'. \tag{23}$$

Combining Eqs. 19, 20, and 21 and Eqs. 19, 22, and 23 leads

to

$$a'_{f,i} = a_{f,i}, \tag{24}$$

$$a'_{p,i} = a_{p,i}. \tag{25}$$

The activities on the outside of the membrane can be described by using activity coefficients (γ): $a_i = \gamma_i \phi_i$.

4. The chemical potential inside the membrane is described by the Flory–Rehner theory (Flory, 1953). Therefore, in the following a short description of this theory is given.

Solubility aspects, Flory – Huggins theory

Nijhuis (1990) showed that the Flory–Rehner theory describes the sorption of penetrants (toluene, trichloro–ethylene, and water) well in a cross-linked film (various elastomers such as ethylene–propylene terpolymer, polydimethylsiloxane). Equations 26 and 27 give the expressions for the activities (a) in ternary systems, in which the index 1 denotes an organic component, 2 water and 3 the polymer:

$$\ln a_1 = \ln \phi_1 + (1-\phi_1) - \phi_2 \frac{V_1}{V_2} - \phi_3 \frac{V_1}{V_3} + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23}\frac{V_1}{V_2}\phi_2\phi_3 + \frac{V_1 \rho_3}{M_c}\left(1 - \frac{2M_c}{M}\right)\left(\phi_3^{1/3} - \frac{1}{2}\phi_3\right), \tag{26}$$

$$\ln a_2 = \ln \phi_2 + (1-\phi_2) - \phi_1 \frac{V_2}{V_1} - \phi_3 \frac{V_2}{V_3} + \left(\chi_{12}\phi_1 \frac{V_2}{V_1} + \chi_{23}\phi_3\right)(\phi_1 + \phi_3) - \chi_{13}\frac{V_2}{V_1}\phi_1\phi_3 + \frac{V_2 \rho_3}{M_c}\left(1 - \frac{2M_c}{M}\right)\left(\phi_3^{1/3} - \frac{1}{2}\phi_3\right), \tag{27}$$

where V is the molar volume, χ_{ij} is a binary interaction parameter between components i and j, ρ is the density, M is the molecular weight, and M_c is the molecular weight between two cross-links. The first four terms on the righthand side describe the entropy of mixing, the fifth and the sixth term the enthalpy of mixing, and the last term describes the elasticity phenomenon that opposes swelling. This elastic term is necessary, since by swelling the chain between the cross-link points will be elongated and this causes a force exerted by the network. In the original Flory–Huggins theory the interaction parameters are constant. In practice, these parameters are taken to be concentration-dependent.

Computation with the Solution-Diffusion Model

Flux equations for components 1 and 2 can be written with Eq. 14 as

$$J_1 = -\phi_1 D_1 \frac{d \ln a_1}{dx} = -\phi_1 D_1 \left(b_{11}\frac{d\phi_1}{dx} + b_{12}\frac{d\phi_2}{dx}\right), \tag{28}$$

$$J_2 = -\phi_2 D_2 \frac{d \ln a_2}{dx} = -\phi_2 D_2 \left(b_{21}\frac{d\phi_1}{dx} + b_{22}\frac{d\phi_2}{dx}\right), \tag{29}$$

in which

$$b_{11} = \frac{\partial \ln a_1}{\partial \phi_1}, \qquad b_{12} = \frac{\partial \ln a_1}{\partial \phi_2}, \qquad b_{21} = \frac{\partial \ln a_2}{\partial \phi_1},$$

$$\text{and} \qquad b_{22} = \frac{\partial \ln a_2}{\partial \phi_2}.$$

Expressions for b can be obtained by differentiation of the Flory–Huggins equations (Eqs. 26 and 27) and are given by Mulder and Smolders (1984). If the membrane is subdivided in m layers with thickness Δx, the volume fractions ϕ_i can be calculated on each place n on the membrane. The discrete analog of Eqs. 28 and 29 are

$$J_1 \Delta x = -\phi_1(n-1) D_1 \big[b_{11}(n-1)\big(\phi_1(n) - \phi_1(n-1)\big) + b_{12}(n-1)\big(\phi_2(n) - \phi_2(n-1)\big)\big], \tag{30}$$

$$J_2 \Delta x = -\phi_1\phi_2(n-1) D_2 \big[b_{21}(n-1)\big(\phi_1(n) - \phi_1(n-1)\big) + b_{22}(n-1)\big(\phi_2(n) - \phi_2(n-1)\big)\big]. \tag{31}$$

With Eqs. 30 and 31 all $\phi_i(n)$ can now be calculated for $n = 1$ to m. It is not necessary to first differentiate Eqs. 30 and 31 to ϕ_1 and ϕ_2 as was done previously (Ji et al., 1994b), but the discrete analogon can be presented as

$$J_1 = -\phi_1 D_1 \frac{d \ln a_1}{dx} \approx -\phi_1 D_1 \frac{\Delta(\ln a_1)}{\Delta x}, \tag{32}$$

$$J_2 = -\phi_2 D_2 \frac{d \ln a_2}{dx} \approx -\phi_2 D_2 \frac{\Delta(\ln a_2)}{\Delta x}. \tag{33}$$

The values of $\ln a_1$ and $\ln a_2$ at place n of the membrane can now be calculated with the values of $\ln a_1$ and $\ln a_2$ on place $(n-1)$: [in which $\Delta \ln a_i = \ln a_i(n) - \ln a_i(n-1)$].

$$\ln a_1(n) = \ln a_1(n-1) - \frac{J_1}{\phi_1(n-1) D_1}, \tag{34}$$

$$\ln a_2(n) = \ln a_2(n-1) - \frac{J_2}{\phi_2(n-1) D_2}. \tag{35}$$

The values of $\phi_1(n)$ and $\phi_2(n)$ must be calculated from the values of $\ln a_1(n)$ and $\ln a_2(n)$ with the Flory–Huggins equations in an iterative way. Two advantages might be given for calculating the volume fractions in this way over the calculations via differentiation to ϕ_1 and ϕ_2 performed by Mulder (1984):

1. b_{ij} is not differentiated anymore. The differentiated terms b_{ij} were calculated at place $(n-1)$, therefore, accuracy was reduced.

2. Parameters like χ are assumed to be constant. However, if they are considered to be dependent on the volume fractions or other parameters in the model, it will be much easier to incorporate them in a computer program.

The fluxes through EPDM membranes for the removal of toluene from water were obtained from Nijhuis (1990) at different membrane thicknesses. Some results are in Table 1.

Table 1. Toluene and Water Fluxes

Membrane Thickness [μm]	J_1 (Water) [-10^{-10} m/s]	J_2 (Toluene) [-10^{-9} m/s]	J_2/J_1
40	2.5	2.78	11.1
72	1.6	1.98	12.4
120	0.83	1.76	21.2
200	0.50	1.15	23

Source: Nijhuis (1990).

Because the toluene flux and concentration ($\phi_{fb,2}$) are known, the concentration at the membrane interface ($\phi_{f,2}$) can be calculated with Eq. 1:

$$J_i = k_{L,i}(\phi_{fb,i} - \phi_{f,i}), \tag{1}$$

where $\phi_{fb,2} = 2.9\times10^{-4}$ m^3/m^3, which is 250 ppm. A $k_{L,i}$-value of 1.3×10^{-5} (m/s), which was determined by Nijhuis, was used in the calculations. The concentration at the interface ($\phi_{f,i}$) is used to calculate the activity. Therefore, an activity coefficient from the literature was used. Some values from the literature are listed in Table 2.

From these values it is not very clear which activity coefficient should be used in the calculations. An averaged value of 1,500 (based on volume fractions) was used. The activity of water was assumed to be 1. With Eqs. 34 and 35 the activities were calculated through the membrane using a Runge–Kutta procedure. On each step n the volume fractions ϕ_1 and ϕ_2 were iterated with Secant's method (Press et al., 1990). On the permeate side the activities are assumed to be equal to their partial pressures, since at very low reduced pressures ($p_r = p/p_c$) the activity coefficients are 1. The critical pressures (p_c) are 217.7 and 40.5 atm for water and toluene, respectively (Vargaftik, 1975), and the total pressure on the permeate side is assumed to be 0.001 atm, so the activity coefficient is 1. Therefore, the activities of the components are

$$a_{p,i} = p_p y_{p,i} = p_p \frac{J_i}{J_1 + J_2}. \tag{36}$$

The (vapor) volume fractions (y) are assumed to be proportional to their fluxes. The pressure at the membrane interface at the vapor side is assumed to be p_p, so the activities at the membrane surface are equal to those in the vapor phase:

$$a'_{p,i} = a_{p,i}. \tag{25}$$

The activities at the surface of the membrane ($a'_{p,i}$) are calculated with the Flory–Huggins equations (Eqs. 26 and 27),

Table 2. Toluene Activity Coefficient in Water (0–500 ppm)

T (C)	γ^*	γ^{**}	Reference
12.5	7,100	1,390	Karger et al. (1971)
20.0	4,500	880	Thomas et al. (1982)
22.0	9,700	1,890	Economou et al. (1991)
23.0	10,400	2,040	Nielsen et al. (1994)

*Mole fractions.
**Volume fractions.

and the following values are used in the equations:

$$V_1 = 1.07\times10^{-4} \quad \chi_{12} = 12.2 \quad \rho_1 = 0.87$$
$$V_2 = 1.8\times10^{-5} \quad \chi_{13} = 0.3 \quad \rho_2 = 1.00$$
$$V_3 = 0.116 \quad \chi_{23} = 6.3 \quad \rho_3 = 0.86$$
$$\gamma_1 = 1{,}500$$
$$\phi_{fb,1} = 2.9\times10^{-4}$$
$$a_{f,2} = 0.99975$$
$$k_{L,1} = 1.3\times10^{-5}.$$

The values of V, χ, ρ, $\phi_{fb,1}$, and $k_{L,1}$ are obtained from Nijhuis (1990). The only parameters that are not known are the diffusion coefficients. These coefficients were assumed to be constant (which means, not a function of volume fractions) in the first runs and fitted on the experimental results. Therefore, a computer program was written that calculated volume-fraction profiles. Calculations were carried out from the permeate side to the feed side. The Flory–Huggins equations can be used to calculate $\phi_1(1)$ and $\phi_2(1)$, and $\phi_3(1)$ can be calculated from $\phi_1 + \phi_2 + \phi_3 = 1$. The initial activities were given by Eq. 36.

The activity of toluene in the liquid can be calculated with $a_i = \gamma_i \phi_i$. This activity must be equal to the activity at the membranes surface (Eqs. 24 and 25). Sets of diffusion coefficients were solved by the simplex method until a minimum between the sum of the actual activity values and the calculated values was obtained. The set of water and toluene diffusion coefficients was used to calculate volume-fraction profiles at membrane thicknesses of 40, 72, 120, and 200 mm. A diffusion coefficient for toluene (D_1) of 3.2×10^{-12} m^2/s was found and for water (D_2) of 1.4×10^{-11} m^2/s. The mean difference between the calculated and real toluene and water activities on the permeate side was about 10%.

Some concentration-dependent diffusion coefficients were also calculated. First, we tried to find a minimum with linear descriptions:

$$D_1 = D_{0,1}(1 + \kappa_{11}\phi_1 + \lambda_{12}\phi_2), \tag{37}$$
$$D_2 = D_{0,2}(1 + \kappa_{21}\phi_1 + \lambda_{22}\phi_2). \tag{38}$$

where κ and λ are fitting constants. It was not possible to give a better description of Nijhuis' experiments with these diffusion coefficients. The relative mean difference between the calculated and real toluene and water activities were the same as with constant diffusion coefficients. The same can be said about the exponential relationships Eqs. 39 and 40:

$$D_1 = D_{0,1}\exp(l_{11}\phi_1 + m_{12}\phi_2), \tag{39}$$
$$D_2 = D_{0,2}\exp(l_{21}\phi_1 + m_{22}\phi_2). \tag{40}$$

where l and m are the fitting constants.

With the diffusion coefficients (for toluene $D_1 = 3.2\times10^{-12}$ m^2/s and for water $D_2 = 1.4\times10^{-11}$ m^2/s) it is possible to calculate the fluxes at different membrane thicknesses. This must be done in an iterative way. With a simplex method the

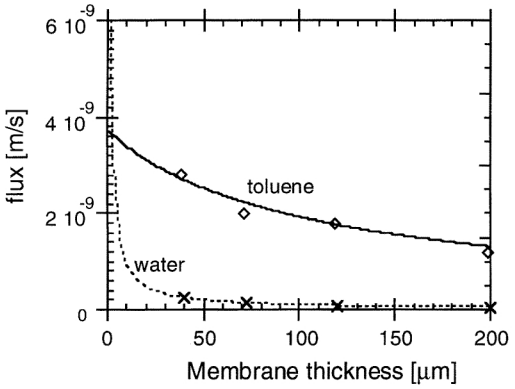

Figure 2. Experimental flux (◇ for toluene and × for water) and simulated flux (line and dashed line) as a function of the membrane thickness (feed toluene concentration = 250 ppm and $k_L = 1.3\times10^{-5}$ m/s).

two fluxes J_1 and J_2 were solved numerically until the right activities on the feed side were obtained ($a_{f,1} = \gamma\phi_{f,1}$, $a_{f,2} = 0.99975$). These results are discussed in the next section.

Results and Discussion

In this section the numerical results are given for the removal of toluene from water through EPDM, with pervaporation as a function of the membrane thickness. Also the mass-transfer coefficient in the feed concentration has been varied. Standard conditions are a mass-transfer coefficient of 1.3×10^{-5} m/s and a toluene concentration of 250 ppm in the feed. First are reported in m/s. These values can be multiplied by approximately 36×10^8 for toluene and 7.0×10^8 for water to get g/m$^2\cdot$h as a unit.

Figure 2 shows the experimental toluene and water fluxes and the simulated curves as a function of the membrane thickness. The most important conclusion that can be drawn from these results is that a further decrease in membrane thickness is not very effective, since the water flux will increase strongly and the toluene flux only a little.

Figure 3 is basically the same as Figure 2 and shows the toluene and water fluxes as a function of the reciprocal thickness. Furthermore, the fluxes have been calculated for higher and lower mass-transfer coefficients. Various values were taken that might be characteristic of a simple plate-and-frame module $k_L = 1.3\times10^{-6}$ m/s, for a very well-stirred flat membrane module or inside-flow capillary module $k_L = 1.3\times10^{-5}$ m/s and for well-spaced spiral-wound and transverse flow modules $k_L = 1.3\times10^{-4}$ m/s.

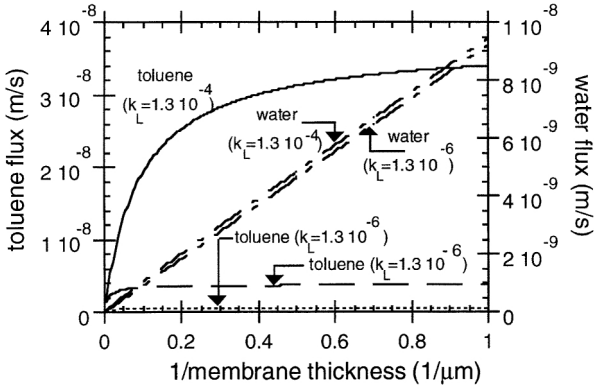

Figure 3. Fluxes vs. the reciprocal membrane thickness for various values of k_L.

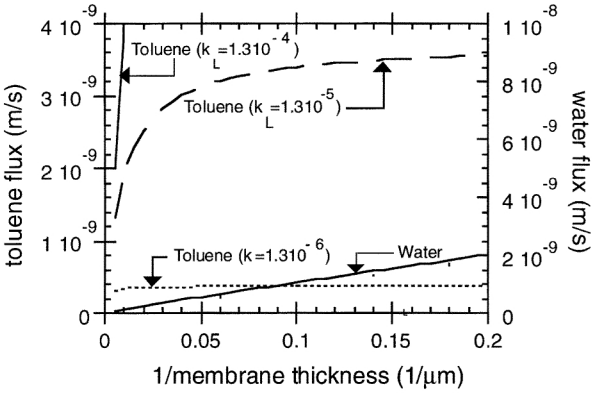

Figure 4. Magnification of Figure 3.

Figure 3 shows how the toluene flux depends strongly on the mass transfer in the feed. The toluene flux for a 20-μm-thick ($= 0.05\ \mu m^{-1}$) membrane changes approximately linearly with the mass-transfer coefficient. On the other hand, the water flux increases linearly with the reciprocal value of the membrane thickness, as may be expected. This latter parameter hardly depends on k_L. With a higher value of k_L, the toluene concentration in the membrane film increases; consequently, the swelling increases a little and the water flux might increase slightly. The influence of the toluene concentration on the water flux is clearly demonstrated by Figures 5 and 6. In Figure 5 a 10-μm-thick membrane, and in Figure 6 a 200-μm-thick membrane, have been simulated. For the thinner membrane the water flux increases roughly 5%, while for the thicker membrane an increase of roughly 50% can be observed when the toluene concentration increases from 0 to 500 ppm. This can be ascribed to the effect of swelling, which

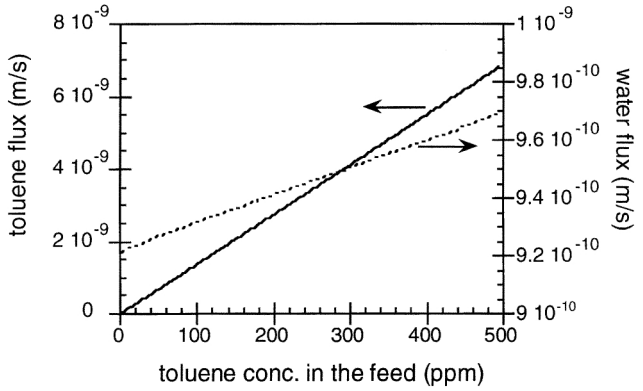

Figure 5. Water flux and toluene flux vs. the toluene feed concentration for a 10-μm-thick membrane ($k_L = 1.3\times10^{-5}$ m/s).

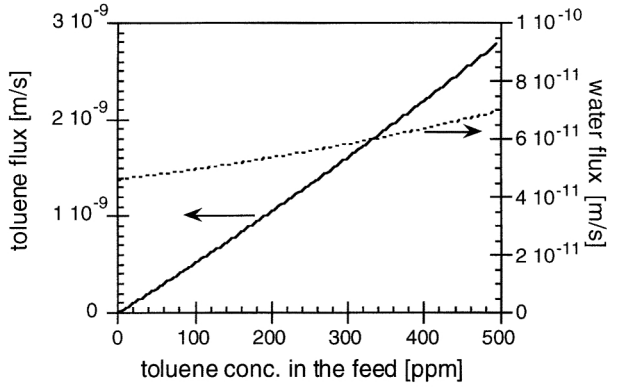

Figure 6. Water flux and toluene flux vs. the feed toluene concentration for a 200-μm-thick membrane ($k_L = 1.3\times10^{-5}$ m/s).

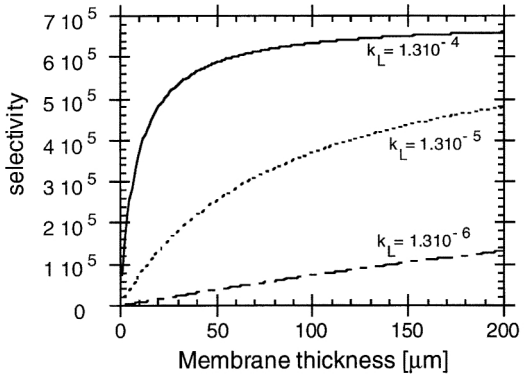

Figure 8. Overall selectivity vs. the membrane thickness and k_L in m/s.

results in an increase in diffusion coefficient and which is more pronounced for thicker membranes. In the case of the thicker membrane, the toluene concentration at the membrane interface at constant bulk concentration will be higher due to the fact that the influence of concentration polarization is less. Consequently, the upstream side will be more swollen, which results in higher permeabilities.

Ji et al. (1990) show in their results a water flux increase of about 10% when the concentration of toluene in the feed is increased from 120 ppm to 500 ppm for a 27-μm polyether–block-polyamide membrane. Experimentally, a water flux increase of 100% is found when the toluene concentration increases from 0 ppm to 300 ppm for a 163-μm EPDM film (Meuleman, 1997).

On the other hand, the toluene flux increases linearly with the toluene concentration. Figure 7 shows the relative difference in water flux from the film model (J^{FM}) and the solution-diffusion model (J^{SD})[$=(J^{SD}-J^{FM})/J^{SD}$]. In the film model the water diffusion coefficient does not depend on the toluene present. In the SD-model the toluene concentration dependence has been incorporated by the Flory–Huggins interaction parameter. The maximum difference with the film theory is about 25%, which may be caused by the interaction

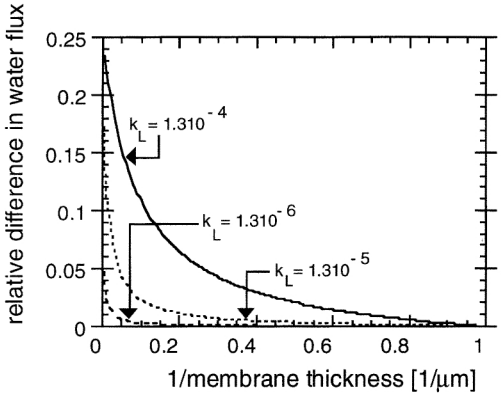

Figure 7. Difference in water fluxes when film model and SD-model are compared vs. the membrane thickness and k_L in m/s.

effects (ranged from the maximum amount of water that can be present with toluene and EPDM). Finally, Figure 8 represents the selectivity as a function of the membrane thickness and k_L value. It is clear that even for the highest mass-transfer coefficient the selectivity drops streeply for membranes thinner than 20 μm.

Conclusions

The resistances-in-series model with a modified solution-diffusion model, the Flory–Rehner theory, and the incorporated film theory have been used to calculate the diffusion coefficients of two components in a liquid feed that are separated by pervaporation. To predict the behavior of the pervaporative removal of toluene from water by EPDM some basic data from the literature were used (Nijhuis, 1990). The Flory–Rehner theory was used to calculate the activity. Both concentration-dependent and -independent diffusion coefficients have been determined by numerical methods. The difference between these coefficients was less than 1%, so it was decided to use a concentration-independent diffusion coefficient. A diffusion coefficient for toluene (D_1) of 3.2×10^{-12} m^2/s, and for water (D_2) of 1.4×10^{-11} m^2/s, was found. Concentration-dependent diffusion coefficients did not improve the results.

These values have been used to calculate the toluene and water fluxes in the case of a membrane thickness between 200 and 1 μm. Furthermore, the mass-transfer coefficient (k_L) was changed. It was shown that the toluene flux depends strongly on k_L. The toluene flux depends only on the membrane thickness for very high values of k_L ($>10^{-4}$ m/s). It can be concluded that $k_L = 10^{-5}$ m/s is too small, since the toluene can increase strongly at higher k_L.

The water flux increases (almost) linearly with the reciprocal value of the membrane thickness. It hardly changes for different k_L. This small difference for different feed toluene concentrations was actually found to occur (Meuleman, 1977). A simple film model is sufficient to describe the water flux.

Notation

a = activity
l = thickness of membrane, m
P = permeability, m^2/s
R = gas constant, J/mol·K

T = temperature, K
W = weight fraction
α = separation factor
β = enrichment factor
μ = thermodynamic potential, J/mol

Subscripts and Superscripts

b = bulk
$'$ = inside the membrane

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