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Comparison of various models for transport of binary mixtures through dense polymer membrane

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Abstract

The main aim of this work is the application of various models describing the transport of a penetrant during pervaporation process in the membrane and their comparison.

We experimentally determined sorption isotherms of pure components, diffusion coefficients, non-ideal sorption of liquid binary mixture in a membrane and the density of the membrane versus concentration composition. All mentioned dependencies were mathematically described and then introduced into a Flory–Rehner equations, UNIFAP model and modified Maxwell–Stefan equations. Models were used for description of the transport of liquid binary mixtures (pentan-1-ol, hexan-1-ol with toluene) through the low-density polyethylene membrane at 25 °C. Calculated pervaporation fluxes and separation diagrams were compared with the results of the experiments.

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Keywords: Modified Maxwell-Stefan equations; Flory–Rehner equations; UNIFAP model

1. Introduction and theory review

1.1. Flory–Rehner equation

The Flory–Huggins equation is valid only for free polymer chains in dilute solutions [1]. However, in case of solid polymers we deal with polymer network structures or semicrystalline polymers, in which solvent take-up is restricted by the resulting strain in the amorphous polymer chains. Their ends join either in crosslinkages or in crystallites.

Flory and Rehner [2] modified the Flory–Huggins equation and introduced an entropy term for elastic deformation of polymer chains in a rubber-like network structure. They applied an earlier work of Kuhn [3], who derived a distribution function for the distance between the ends of a polymer molecule. They assumed that the chain displacement length is dilated during swelling by a factor of $\varphi_M^{-1/3}$, while the extension of the polymer phase is isotropic. Flory [4] furthermore accounted for the degree of interlinking of the polymer chains and finally obtained the following equation for activity a_i of component i :

$$\ln a_i = \ln\left(\frac{p_i}{p_i^0}\right) = \ln(1-\varphi_M) + \varphi_M + \chi_i\varphi_M^2 + \frac{V_{mi}\rho_M}{M_c} \times\left(\varphi_M^{1/3} - \frac{1}{2}\varphi_M\right) \quad (1)$$

where p_i is partial pressure of component i in gaseous mixture, p_i^0 is the pressure of saturated vapors, φ_M[1] is volume fraction of polymer, V_{mi} is molar volume of the penetrant i, ρ_M is the density of the swollen polymer, χ_i is Flory–Huggins interaction parameter, M_c is molar mass of polymer chain between two network nodes or between two crystallic domains in polymer. Parameters χ_i and M_c are

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[1] The excessive free volume was neglected in calculation of volume fraction of polymer φ_M.

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Nomenclature

A	membrane area (m^2)
a_i	activity of component i
c	molar concentration ($mol\ m^{-3}$)
$\mathbf{D}$	diffusion coefficient ($m^2\ s^{-1}$)
D_0	diffusion coefficient at zero concentration ($m^2\ s^{-1}$)
$\bar{D}_{iM}$	average diffusion coefficient of a pure component i in the active layer of a membrane ($m^2\ s^{-1}$)
h	change in length of the quartz spring (m)
J	pervaporation flux ($g\ m^{-2}\ h^{-1}$)
k	constant of the spiral quartz balance ($g\ m^{-1}$)
L	membrane thickness (m)
M_i	molar mass of the component i ($g\ mol^{-1}$)
M_{Ci}	molar mass of polymer chain between two network nodes in polymer ($g\ mol^{-1}$)
m	mass of the swelled foil (kg)
m_o	mass of the dry polymer foil (kg)
m_t	mass uptake at time t (kg)
m_∞	mass uptake at equilibrium (kg)
p_i	partial pressure of component i in gaseous mixture (Pa)
p_i^0	pressure of saturated vapors at temperature 25 °C (Pa)
Q_e	equilibrium swelling degree $\{= (m - m_o)/m_o\}$
R	universal gas constant ($Pa\ m^3\ mol^{-1}\ K^{-1}$)
T	absolute temperature (K)
V_{mi}	molar volume of the component i ($m^3\ mol^{-1}$)
w_{1F}	weight fraction of the faster permeant 1 in the feed
w_{2P}	weight fraction of the slower permeant 2 in the permeate
w_1'	weight fractions of components 1 in a membrane
x_i^o	mole fraction of the component i before sorption
x_i	mole fraction of the component i in the equilibrium bulk liquid
$\Delta x_i = x_i^o - x_i$	experimentally determined change of solution concentration caused by the sorption

Greek letters

α	separation factor
δ_M	thickness of the membrane (m)
μ_i	chemical potential of component i
v_j	local velocities of the components ($m\ s^{-1}$)
ρ_A	density of an amorphous phase of the dry membrane ($kg\ m^{-3}$)
$\bar{\rho}_M$	mean density of the swollen membrane ($kg\ m^{-3}$)
Φ_j	volume fraction of component j
ϕ	crystallinity of the membrane
χ_i	Flory–Huggins interaction parameter
$\Omega_i(x_i)$	preferential sorption as a function of the bulk liquid composition
φ_M	volume fraction of membrane

calculated by Newton‘s iterative method from experimentally obtained vapor sorption isotherms of pure component i.

1.2. UNIFAP model

Today we have already a lot of contribution methods [5] that allow predicting the solubility of organic compound in a polymer without any experiment. One of the best methods that are able to describe the transport properties in the membrane is UNIFAP model [6]. This model is based on modified UNIFAC model for solutions, in which contribution approach and free-volume theory are connected.

The UNIFAC model by Fredenslund [7] is based on the assumption that molecules in the mixture can be split up into functional groups (parameters of which are tabulated) and their properties depend on the local composition of the functional groups and that their interactions. The activity of the penetrant i a_i can be described as a sum of the activities of each individual contribution:

$$\ln a_i = \ln a_i^{c} + \ln a_i^{vo} + \ln a_i^{int} + \ln a_i^{el} \qquad (2)$$

where upper indexes c, vo, int and el mean: combinatory, free-volume, interaction and elastic contributions. The first three terms on the right side of Eq. (2) are identical with

Table 1
Calculated fitting parameters in Flory–Rehner equations and UNIFAP model

Parameters	Flory–Rehner equations	UNIFAP model
χ_{Toluene}	1.58	1.50
$\chi_{\text{Hexan-1-ol}}$	4.57	4.54
$\chi_{\text{Pentan-1-ol}}$	4.73	4.69
$M_{\text{c,Toluene}}$ (g mol^{-1})	2290	2570
$M_{\text{c,Hexan-1-ol}}$ (g mol^{-1})	1410	1360
$M_{\text{c,Pentan-1-ol}}$ (g mol^{-1})	1310	1250

UNIFAC-FV model by Oishi and Prausnitz [8], the last term includes the influence of the crystallinity of the polymer material. It is assumed that the sorption takes place in an amorphous region only. The resultant form of the modified UNIFAP model used in that work for fitting the experimental values can be written [9,10]:

$$\ln a_i = \ln\left(\frac{p_i}{p_i^0}\right) = \ln(1-\varphi_M) + \varphi_M + \chi\varphi_M^2 + \left(\frac{\rho_A M_i}{\rho_M M_c}\right)\varphi_M^{1/3} \qquad (3)$$

where ρ_A is the density of an amorphous phase of the dry membrane.

The pervaporation flux of component i can be then calculated from activity of each component by Eq. (4):

$$J_i = -D_i\varphi_i \frac{\mathrm{d}\ln a_i}{\mathrm{d}z} \qquad (4)$$

1.3. Modified Maxwell–Stefan equations

The transport of components through a polymer during pervaporation is affected by many collisions among molecules. Therefore, it may be expected that the molecule i will during its movement through polymer experience a friction force resulting from combined interactions of all locally surrounding molecules [1].

Accordingly, the friction coefficient depends on the size and the shape of molecule i and on average frictional property of the local mixture. Based on this principle, the modified Maxwell–Stefan equation can be derived [1]:

$$\frac{\mathrm{d}\mu_i}{\mathrm{d}z} = \sum_{j=1}^{n} x_j(v_j - v_i)\frac{RT}{D_{ji}^0} \qquad (5)$$

where μ_i is the chemical potential of component i, $\mathrm{d}\mu_i/\mathrm{d}z$ is the gradient of the chemical potential of component i, x_j are the mole fractions of the components $j = 1, 2, \ldots, n$; v_j are the local velocities of the components j, RT/D_{ji}^0 has the meaning of a friction coefficient accounting for the frictional effect exerted by component j on component i.

The modified Maxwell–Stefan approach is for three components (binary liquid and membrane) in pervaporation process well described by Heintz [11]. We can introduce diffusive mass fluxes $J_i = \rho_i v_i$ and weight fraction of component i in a membrane w'_i instead of molar fractions x_i in Eq. (5) and we can also assume $D_{ij} = D_{ji}$. The following approximation, which for two permeating components through a membrane deals with difference equations rather than differential equations, can then be obtained [11]:

$$J_1 = \bar{D}_{1M}\left(\frac{\bar{D}_{2M}\bar{w}'_1 + D_{12}}{D_{12} + \bar{w}'_1\bar{D}_{2M} + \bar{w}'_2 D_{1M}}\right)\bar{\rho}_M\frac{\Delta w'_1}{\delta_M} + \bar{D}_{1M}\left(\frac{\bar{D}_{2M}\bar{w}'_1}{D_{12} + \bar{w}'_1\bar{D}_{2M} + \bar{w}'_2 D_{1M}}\right)\bar{\rho}_M\frac{\Delta w'_2}{\delta_M} \qquad (6a)$$

$$J_2 = \bar{D}_{2M}\left(\frac{\bar{D}_{1M}\bar{w}'_2 + D_{12}}{D_{12} + \bar{w}'_2\bar{D}_{1M} + \bar{w}'_1 D_{2M}}\right)\bar{\rho}_M\frac{\Delta w'_2}{\delta_M} + \bar{D}_{2M}\left(\frac{\bar{D}_{1M}\bar{w}'_2}{D_{12} + \bar{w}'_2\bar{D}_{1M} + \bar{w}'_1 D_{2M}}\right)\bar{\rho}_M\frac{\Delta w'_1}{\delta_M} \qquad (6b)$$

where $\bar{w}'_i = (w'_{iF} + w'_{iP})/2$, $\Delta w'_i = w'_{iF} - w'_{iP}$, w'_{iF} (denotes weight fraction of component i in feed in the membrane) and w'_{iP} weight fraction of component i in permeate in the membrane which is in the case of $\bar{D}_{iM}$, which is the average diffusion coefficient of a pure component i in the active layer of the membrane and is defined by:

$$\bar{D}_{iM} = \frac{\int_{w'_{iP}}^{w'_{iF}} D_{iM}(w'_i)\mathrm{d}w'_i}{w'_{iF} - w'_{iP}} \qquad (7)$$

$\bar{\rho}_M$ is the average density of the polymer membrane and is defined by:

$$\bar{\rho}_M = \frac{\int_{w'_{iP}}^{w'_{iF}} \rho_M(w'_i)\mathrm{d}w'_i}{w'_{iF} - w'_{iP}} \qquad (8)$$

D_{12} can be adjusted to the experimental partial fluxes. The permeate weight fraction w_{1P} is given by Eq. (9):

$$w_{1P} = \frac{J_1}{J_1 + J_2} = \frac{1}{1 + J_2/J_1} \qquad (9)$$

In order to obtain consistent results for the permeate composition (w_{1P}, w_{2P}) and partial pervaporation fluxes from Eqs. (6a), (6b) and (9), Newton's iteration process, during which we optimize the adjustable parameter D_{12}, has to be repeated until w_{1P} values fulfill Eq. (9).

To calculate partial fluxes of the permeating components through dense membrane by a Flory–Rehner, UNIFAP model and the modified Maxwell–Stefan equations, we need to know concentration dependence of the diffusion coefficients of pure component i in the membrane, weight fraction of component i in the membrane w'_{iF} from the feed side, the thickness of the membrane δ_M and concentration dependence of the membrane densityρ_M.

Table 2
Calculated diffusion coupling coefficients in modified Maxwell–Stefan equations

Measured system	Diffusion coupling coefficient $D_{12} \times 10^{13}$ ($m^2 s^{-1}$)
Pentan-1-ol + Toluene	1.50
Hexan-1-ol + Toluene	95.02

Partial pervaporation fluxes have to be determined experimentally and then compared with calculated values. In the modified Maxwell–Stefan equations these data are used for iterative calculation of coupled diffusion coefficient D_{ij}. In case of Flory–Rehner and UNIFAP models two sets of adjustable parameters ($\chi_i, M_{ci}, \chi_j, M_{cj}$) are iteratively calculated from sorption isotherms of pure components.

Then we can successfully solve Eqs. (1), (3), (4), (6a), (6b) and (9) by Newton's iterative method to fit experimentally obtained data. All fitting parameters are in Tables 1 and 2.

2. Experimental

Two liquid binary mixtures (pentan-1-ol, hexan-1-ol with toluene) and polyethylene membrane were measured at 25 °C.

2.1. Chemicals and the membrane

Pentan-1-ol, hexan-1-ol and toluene were analytical grade and synthetic Zeolite type A4 was used for their dehydration. Binary mixtures used for experiments were prepared by weighting.

The membrane used for experiments is a high-pressure, low-density, linear Polyethylene-Bralen FB2-30 from Slovnaft Bratislava, Slovakia (denoted PE in the text) in the form of foil (50 μm thick). Antistatic PE foil has a melting index ITT = (1.7–2.3)/600 s. Its density ($\rho = 919 \pm 2$ kg m^{-3}) is determined with mercury pycnometer. The density corresponds to the volume fraction of crystalline phase, $\phi = 0.455$ and glass transition temperature $T_g = -120$ °C. Prior to experiments, the foil is washed in distilled water, dried in the drying box for 12 h at 60 °C and then kept in vacuum desiccator over magnesium perchlorate.

2.2. Swelling of polymer membrane

We measured the extension of the polymer membrane during swelling in liquid organic solutions [12]. Therefore a special device was developed at the Department of Physical Chemistry of the Institute of Chemical-Technology in Prague [13,14].

The device is able to measure the extension of the polymer membrane during swelling continuously, while the membrane is immersed in liquid. The device has photo-electric sensors that are rolling above the membrane in two vertical directions (this is important especially for anisotropic materials).

Experiments with swelling show that the density of polyethylene membrane is concentration dependent. This information can improve the accuracy of the results of all used models.

From the results of our measurements we found out that PE membrane during swelling in solvents extends in three dimensions. Thus we were able to calculate the density of the membrane that depends on the concentration of the feed [12].

We described the dependence of the PE membrane density on concentration of solvent with accuracy up to 2% by polynomial equation of the second order ($\rho_M = \rho_M^0 + b\rho_M + a\rho_M^2$). The density of dry PE membrane (ρ_M^0) was experimentally measured by mercury pycnometer.

2.3. Solubility measurements of binary liquid mixtures in PE membrane

The application of all mentioned models for predicting fluxes through PE membrane requires knowledge of sorption isotherms. Sorption data (namely the preferential sorption and the equilibrium swelling degree) were determined by two different experiments.

Measurements of the preferential sorption in binary liquid solutions over the whole concentration range at constant temperature yield the isotherm of concentration change (composite isotherm):

$$\Omega_i(x_i) = \frac{N_o}{m_o} \Delta x_i \tag{10}$$

where m_o is the mass of dry polymer brought in contact with N_o moles of binary solution, $\Delta x_i = x_i^o - x_i$ is the experimentally determined change of solution concentration caused by sorption, $\Omega_i(x_i)$ denotes the preferential sorption as a function of the bulk liquid composition, x_i^o is the mole fraction of the component i before sorption, x_i is the mole fraction of the component i after the equilibrium in bulk liquid is reached.

The composition of the sorbed liquid in the membrane is obtained by combining the data about preferential sorption with the information about total amount of liquid sorbed by the polymer, that are both gained from the liquid sorption experiments:

$$x_i^s = \frac{Q_e x_i + \Omega_i M_j}{Q_e + \Omega_i (M_i - M_j)} \tag{11}$$

where $Q_e = (m - m_o)/m_o$ is the equilibrium swelling degree, m_o is the mass of the dry polymer foil, m is the mass of the swelled foil, M_i and M_j are the molar masses of the components i and j, respectively.

The concentration of x_i^o and x_i is determined by comparing

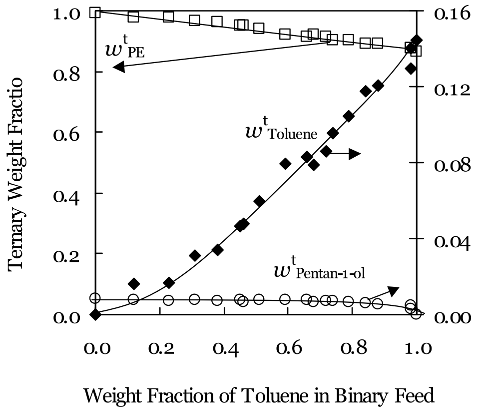

Fig. 1. Sorption diagram of the ternary system pentan-1-ol + toluene + PE membrane at 25 °C.

the reading of the interferometer with the calibration curve, constructed in the vicinity of each measuring point. The interferometer is very convenient for this type of measurement, because it is able to detect even a very small concentration differences and the change in solution concentration is obtained directly in a single measurement. For practical purposes we recalculated mole fractions to weight ones. The dependence of weight fractions of component i in a membrane (w_i^l) on weight fractions of preferable component (toluene) is in Figs. 1 and 2.

The amount of sorbed liquid is very small. Weighing of the swelled sample, after it has been dried between two sheets of filter paper, gave therefore entirely unreliable results. For that reason a special gravimetric method must be used [15].

The foil is transferred into a tightly closed weighing bottle inlaid by filter paper. The foil must be fixed in a position, in which only its edges touch the paper (the dimensions of the weighing bottle must correspond to the dimensions of the foil sample). After 3 h, during which the paper has drained off the excess liquid from the foil and the equilibrium in the bottle is established, the full bottle is weighed. The foil is then taken out quickly and the bottle with the wet paper is weighed again. The difference represents the weight of the swollen membrane. This procedure is found to be reproducible within 2%.

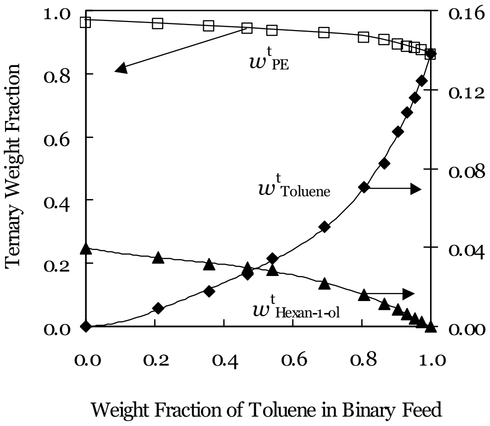

Fig. 2. Sorption diagram of the ternary system hexan-1-ol + toluene + PE membrane at 25 °C.

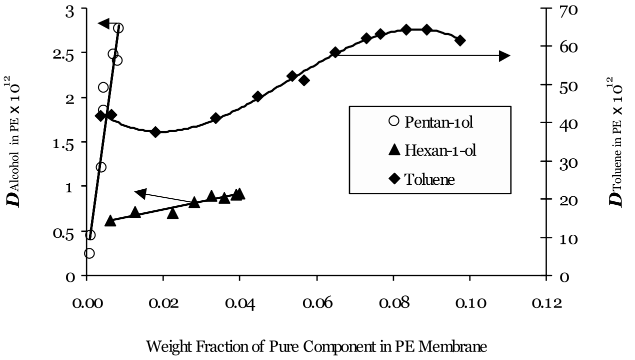

Fig. 4. Experimental data of the diffusion coefficient D_i (Hittorf frame of reference) as a function of the weight fraction of pure component i in the PE membrane at 25 °C.

2.4. Determination of diffusion coefficient by sorption method

The solution of the second Fick's law [16,17] for the membrane of finite dimensions bounded by planes $z = \delta_M/2$ and $z = -\delta_M/2$ (where δ_M is the membrane thickness) is given by:

$$\frac{\partial c_i}{\partial t} = D_i\left(\frac{\partial^2 c_i}{\partial z^2}\right) \tag{12}$$

under the initial and boundary conditions

$$\begin{array}{lll} -\delta_M/2 < z < \delta_M/2 & t = 0 & c = 0 \\ z = \delta_M/2 & t \geq 0 & c = c_1 \\ z = -\delta_M/2 & t \geq 0 & c = c_1 \end{array}$$

leads to infinite series given by Eq. (13):

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{n=\infty} \times\left[\frac{1}{(2n+1)^2}\exp\left(-D_i\frac{(2n+1)^2\pi^2 t}{\delta_M^2}\right)\right] \tag{13}$$

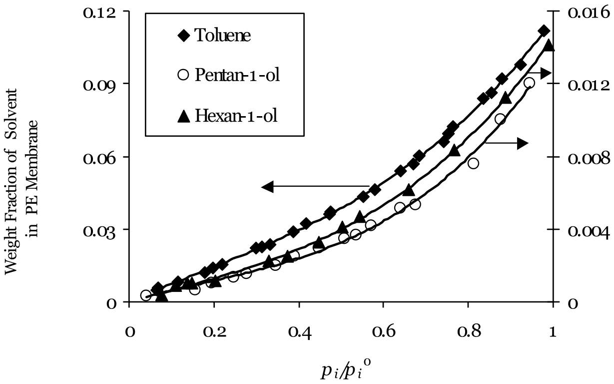

Fig. 3. Sorption isotherms of solvents in the PE membrane at 25 °C.

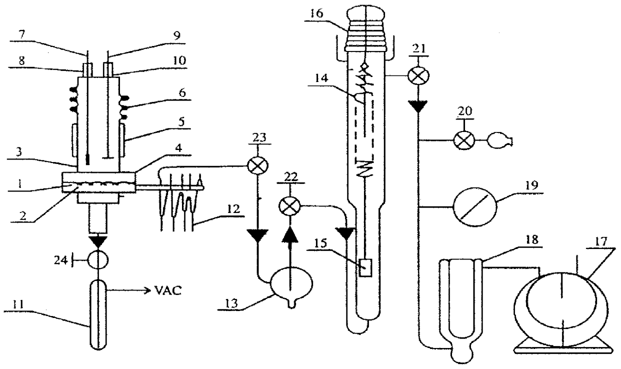

Fig. 5. Scheme of the pervaporation apparatus: 1—membrane, 2—support layer, 3 and 4—cell from stainless, 5—electric heater, 6—water cooler, 7—thermometer, 8 and 10 slots for thermometer and stirrer, 9—stirrer, 11 and 13—glass cold trap, 12—channel, 14—spiral quartz balance, 15—absorbent (active carbon), 16—glass coat, 17—oil rotating pump, 18—cold trap for oil vapor, 19—vacuometer, 20—24 valves with Teflon core.

where m_t is the mass uptake at time t, m_∞ is the mass uptake at equilibrium.

If the ratio $m_t/m_\infty > 0.5$ we can apply Eq. (14) for the determination of D_i with sufficient accuracy [16]:

$$\ln\left(1 - \frac{m_t}{m_\infty}\right) = -\frac{\pi^2 D_i}{\delta_M^2} t + \ln\left(\frac{8}{\pi^2}\right) \tag{14}$$

The appropriate value of diffusion coefficient D_i can be calculated from the linear part of the curve which is obtained by plotting $\ln(1 - m_t/m_\infty)$ versus time. The measured vapor sorption isotherms and dependence of pure diffusion coefficient of pentan-1-ol, hexan-1-ol and toluene in PE membrane at 25 °C are shown in Figs. 3 and 4.

2.5. Pervaporation experiments

Our pervaporation apparatus was designed to achieve a rapid desorption of the permeates at the downstream surface of the membrane in order to reduce their activities in the subjacent layer of the operating barrier to a virtually zero value. The pervaporation apparatus, constructed at the Department of Physical–Chemistry of the Institute of Chemical-Technology in Prague, allows sensitive measurement of very small pervaporation fluxes by sorption method.

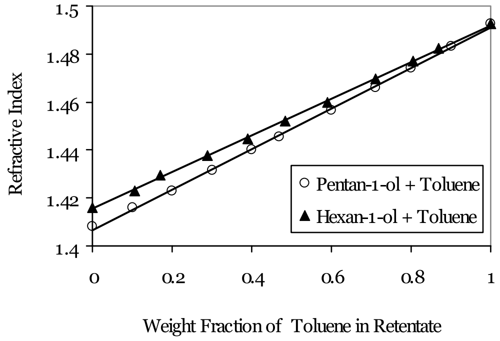

Fig. 6. Dependence of refractive index on weight fraction of toluene at 25 °C.

We measured pervaporation flux by the gravimetric method using the spiral quartz balances [12].

The apparatus (Fig. 5) is evacuated prior to every experiment. The permeate is condensed in the cold trap (refer to Fig. 5 part 11), until steady state is reached within the apparatus. The measurement of the pervaporation flux is carried out in duplicate. It is necessary to regenerate active carbon by heating it to 200 °C for 10 min in a reheating furnace. Opening of the valves 21, 22 and 23 allows the pervaporation flux to enter into the evacuated apparatus.

The permeate then travels along the apparatus to the cold trap 13, where it is condensed. The time required for it depends on the feed concentration of the initial binary system. The liquid nitrogen source surrounding the cold trap 13 is removed, which allows warming of the cold trap by surrounding atmosphere and a return of the condensed permeate to the vapor state. Valve 22 is opened and the permeate proceeds into the evacuated apparatus, where it is absorbed by active carbon suspended on the quartz spring. A cathetometer is used to read the change its length. When the reading comes to a constant value, absorption is completed.

The previous procedure is repeated until, when liquid permeate is obtained. At this point a sample is extracted for analysis. Valve 22 is removed and the sample is extracted using a syringe. Measurement of weight fraction of toluene in the retentate can then proceed.

Pervaporation flux is given by relationship:

$$J = \frac{m}{At} \tag{15}$$

where

$$m = kh \tag{16}$$

where m is weight of the permeate passing through the membrane area A during the time t and it is determined by the change in length of the quartz spring balance with cathetometer, k is constant of the spiral quartz balance, h is change in length of the quartz spring.

Partial pervaporation flux is given by relations:

$$J_i = J w_{iP} \tag{17}$$

$$J_j = J - J_i \tag{18}$$

where J_i is partial pervaporation flux of component i, J_j is partial pervaporation flux of component j, J is total pervaporation flux, w_{iP} is weight fraction of component i in the permeate.

The analysis of retentate and permeate is performed by the refractometric method. The calibration curve, that express the dependence of refractive index versus weight fraction of binary mixture, was measured at 25 °C (Fig. 6). Weight fraction values of retentate and permeate obtained from calibration curves are then substituted into Eqs. (17) and (19) for the determination of partial pervaporation flux

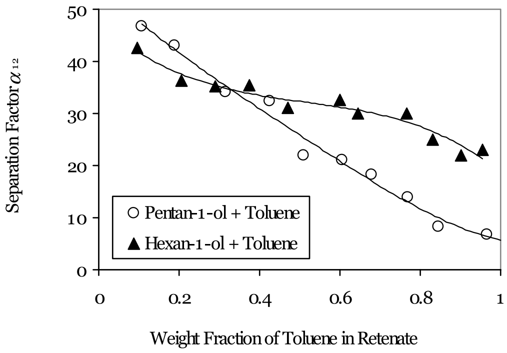

Fig. 7. Dependence of separation factor on the weight fraction of toluene in feed at 25 °C.

and separation factor of the membrane:

$$\alpha_{12} = \frac{w_{1P}/w_{2P}}{w_{1F}/w_{2F}} \tag{19}$$

The selectivity of separation binary mixtures is represented by the dependence of separation factor and weight fraction of toluene in permeate on weight fraction of toluene in feed (Figs. 7–9).

3. Discussion of the results

In both measured systems (pentan-1-ol, hexan-1-ol with toluene) the solubility of toluene in PE membrane increases with higher concentration of toluene in the binary liquid mixtures. On the contrary, the solubility of pentan-1-ol and hexan-1-ol decreases with higher concentration of toluene. Toluene is in one order of magnitude more soluble in PE membrane than pentan-1-ol and four times more than hexan-1-ol. We described the solubility of component i versus binary weight fraction of toluene in liquid by polynomial equations of the third order and used it in all equations, where activity and diffusion coefficient are concentration dependent (Eqs. (1), (3), (4), (6), (7) and (8)).

All measured sorption isotherms increased exponentially with increasing relative partial pressure of the solvent (Fig. 3). It is obvious that weight fraction of toluene in PE membrane is in one order of magnitude higher than weight fractions of aliphatic alcohols.

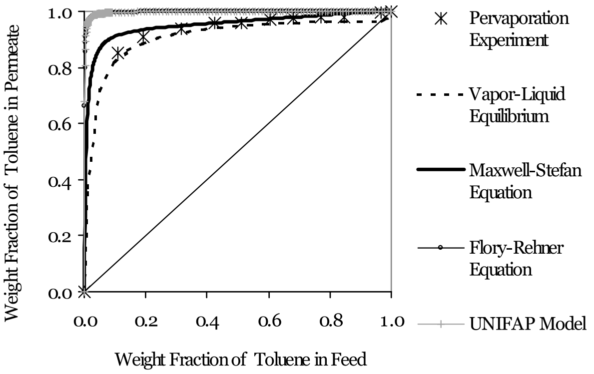

Fig. 8. Separation diagram for the system pentan-1-ol + toluene + PE membrane at 25 °C.

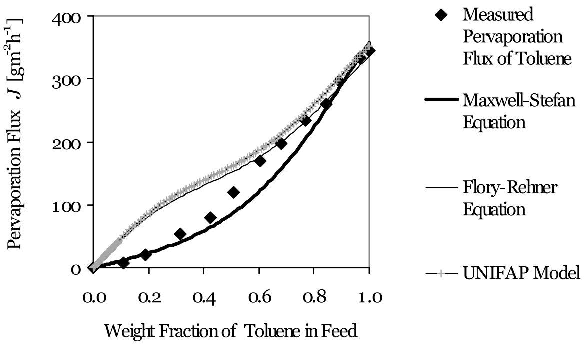

Fig. 10. Partial fluxes of toluene for the system pentan-1-ol + toluene + PE membrane at 25 °C.

On the basis of our measurements we can say that the diffusion coefficients of aliphatic alcohols rise with an increase of their concentration in the membrane (Fig. 4). The diffusion coefficient of toluene D_{Toluene} passes the maximum in its dependence on concentration in the membrane. A similar behavior was observed by Lützow in the system toluene + linear low-density polyethylene ($\phi = 0.45$, $\rho_{70\,^\circ\mathrm{C}} = 0.9097$) at 70 °C [18]. We described the dependence of D_{Toluene} on weight fraction of toluene in the membrane by polynomial equations of the third order,[2] which give the best fit for our experimental data.

From the measured data we calculated fitting parameters for Flory–Rehner equation, UNIFAP model (see Table 1) and for modified Maxwell–Stefan equations (see Table 2). From Figs. 8–13 we can observe that modified Maxwell–Stefan equations give the best fit for experimental data. The main advantage of this model is only one adjustable parameter (coupled diffusion coefficient D_{ij}). Flory–Huggins parameter for toluene χ_i in Flory–Rehner equation and UNIFAP model has the lowest value in comparison with parameters of measured alcohols ($\chi_{\mathrm{Toluene}} < \chi_{\mathrm{Hexan\text{-}1\text{-}ol}} < \chi_{\mathrm{Pentan\text{-}1\text{-}ol}}$). The lower the value of Flory–Huggins parameter χ_i, the greater is the interaction of component i with polymer.

Molar mass of polymer chain between two network nodes or between two crystallic domains in polymer M_C increases with better solubility of component i in the membrane ($M_{\mathrm{c\ Toluene}} > M_{\mathrm{c\ Hexan\text{-}1\text{-}ol}} > M_{\mathrm{c\ Pentan\text{-}1\text{-}ol}}$). It can be caused by bigger extension of polymer chains during swelling of the polymer network. However, it should be pointed out that the physical meaning of the χ_i and M_{ci} parameters should not be taken too seriously. In some cases different sets of parameters lead to similar results, in other ones even small changes may result in remarkable differences in the calculated fluxes and separation diagrams.

The dependence of the weight fraction of toluene in the

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[2] Personal discussion with Dr Marcel Mulder during the 41st Microsymposium of Polymer Membranes, (16.7.2001–19.7.2001), Prague, Czech Republic.

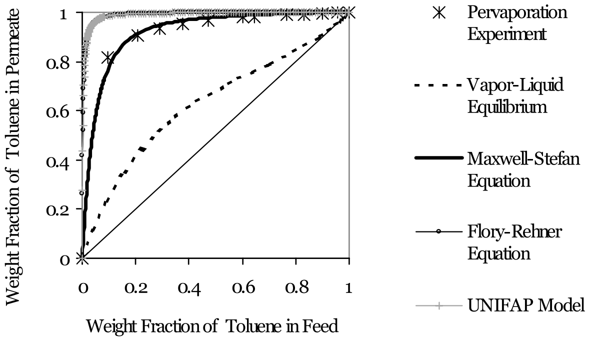

Fig. 9. Separation diagram for the system hexan-1-ol + toluene + PE membrane at 25 °C.

permeate (Figs. 8 and 9), of partial fluxes (Figs. 10–13) and of separation factor (Fig. 7) on the weight fraction of toluene in the feed was evaluated from vacuum pervaporation experiments with the binary liquid mixtures pentan-1-ol and hexan-1-ol with toluene through a PE membrane. These azeotropic mixtures were separated by pervaporation in the whole concentration range. In Figs. 8–13 we compared all three models with pervaporation experiments.

We can see that modified Maxwell–Stefan equations can describe the experiment very well in all cases. Flory–Rehner equation and UNIFAP model gave identical results (the calculated curves overlap in Figs. 8 and 9) for separation diagrams, where they highly over predict the separation. According to these models, the curves reflecting the dependence of partial fluxes of aliphatic alcohols on the weight fraction of toluene in the feed, overlap, too (Figs. 12 and 13). Both models also highly underestimate the non-ideal pervaporation. Total pervaporation flux through the PE membrane increased exponentially, when the concentration of toluene in the feed increased. The reason for it is the fact that partial pervaporation flux of toluene is in two orders of magnitude higher than fluxes of aliphatic alcohols.

The separation factor was decreasing with increasing concentration of toluene in the feed for both systems. Separation factor reached the highest values in cases, where there was a small amount of toluene in alcohol (Fig. 7).

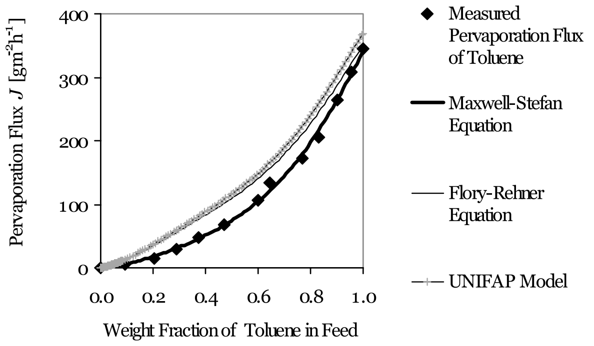

Fig. 11. Partial fluxes of toluene for the system hexan-1-ol + toluene + PE membrane at 25 °C.

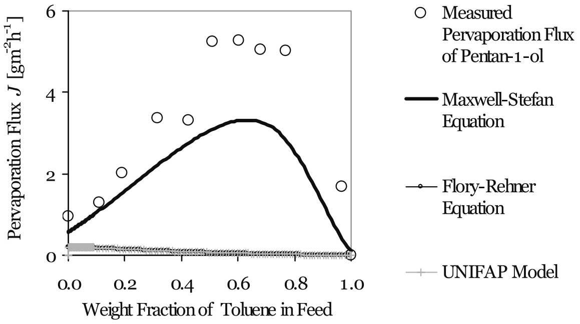

Fig. 12. Partial fluxes of pentan-1-ol for the system pentan-1-ol + toluene + PE membrane at 25 °C.

4. Conclusions

We used three different models (Flory–Rehner equation, UNIFAP model, and modified Maxwell–Stefan equations) for the description of pervaporation characteristics for two ternary systems (pentan-1-ol and hexan-1-ol + toluene + PE membrane at 25 °C).

Pervaporation of liquid binary mixtures through non-porous membrane is a complex process, which is influenced by many factors. It is especially the strong non-ideal solubility and diffusivity behavior of measured liquid binary mixture components in polyethylene membrane and diffusive coupling effects that play the important role in the pervaporation process (above all in cases of less permeating components). All used models were able to semi-quantitatively describe pervaporation fluxes and separation ability.

Flory–Rehner equation and UNIFAP model have four parameters for binary system (Flory–Huggins interaction parameter χ_i, χ_j and molar mass of polymer chain between two network nodes in polymer M_{Ci}, M_{Cj}). Nevertheless, if there are more than two parameters, different sets of them lead to similar results and their physical meaning can therefore be questionable.

Flory–Rehner equation and UNIFAP model gave almost identical results for separation diagrams and for partial pervaporation fluxes. These two models cannot describe the pervaporation process precisely, because they do not take into consideration coupled diffusion, during which much more rapidly permeating toluene drags molecules of

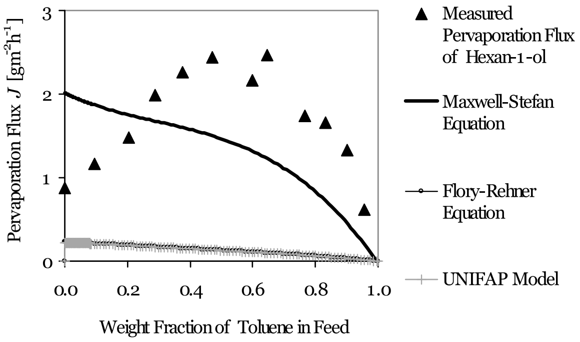

Fig. 13. Partial fluxes of hexan-1-ol for the system hexan-1-ol + toluene + PE membrane at 25 °C.

pentan-1-ol or hexan-1-ol that otherwise would be many times slower.

On the basis of our results and experience for very precise description of pervaporation processes, during which coupled diffusion may occur (usually one component permeating much faster than other ones) we recommend the use of modified Maxwell–Stefan equations. Their advantage is also in the use of only one adjustable parameter (coupled diffusion coefficient D_{ij}). However, from the technological point of view, Flory–Rehner equation and UNIFAP model should be sufficient in situations, when it is necessary to know dominant pervaporation flux and when the pervaporation data are unknown.

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References

[1] Bitter JGA. Transport mechanism in membrane separation processes. Edited Koninklijke Shell Laboratorium. Postbus, Amsterdam, The Netherlands.

[2] Flory PJ, Rehner J. J Chem Phys 1943;11:512.

[3] Kuhn W. Kolloid-ZZ Polym 1934;68(1):1.

[4] Flory PJ. J Chem Phys 1950;18:108.

[5] Goydan R, Reid RC, Tseng HS. Estimation of the solubilities of organic compounds in polymers by group-contribution methods. Ind Engng Chem Res 1989;28:445.

[6] Saure R, Schlünder EU. Sorption isotherms for methanol, benzene and ethanol on polyvinyl acetate. Chem Engng Proc 1995;34:305.

[7] Fredenslund A, Gmeling J, Prausnitz JM. Group-contribution estimation of activity coefficients in non-ideal liquid mixtures. AIChE J 1975;21:1086.

[8] Oishi T, Prausnitz JM. Estimation of solvent activities in polymer solution using a group contribution method. Ind Engng Chem Process Des Dev 1978;17:333.

[9] Castro EF, Gonzo EE, Gottifredi JC. The analysis of sorption data of organic vapors in polymeric membranes through novel theories. J Membr Sci 1996;113:57–64.

[10] Vicente MS, Gottifredi JC. Estimation of solvent activities in polymer solution using a group contribution method. Sep Purif Tech 2001;22–23:671–9.

[11] Heintz A, Stephan W. A generalized solution-diffusion model of the pervaporation process through composite membranes Part II. Concentration polarization, coupled diffusion of the porous support layer. J Membr Sci 1994;89:153–69.

[12] Izák P, Bartovská L, Friess K, Šípek M, Uchytil P. Description of binary liquid mixtures transport through non-porous membrane by modified Maxwell–Stefan equations. J Membr Sci 2003;5540:1–17.

[13] Bartovský T, Šišková M. Sorption properties of polymeric membrane materials, 36. Mikrosymposium "HIGH-SWELLING GELS", Praha, 10.7.1995–14.7.1995.

[14] Bartovská L, Bartovský T, Šišková M. Solubility in systems Polymeric foil—mixtures of organic solvents. 49. Sjezd chemickúch spolec̑ností, Bratislava, 4.9.1995–7.9.1995.

[15] Bartovská L, Šišková M. Poživilová O. Sorption properties of polymeric Pervaporation Membranes. 12th International Congress CHISA'96, Prague 25.8.1996–30.8.1996.

[16] Crank J, Park GS. Diffusion in polymers. London: Academia Press; 1968.

[17] Crank J. The mathematics of diffusion, Second edition. Oxford: Claredon Press; 1975.

[18] Lützow N, Tihminlioglu A, Danner RP, Duda JL, De Haan A, Warnier G, Zielinski JM. Diffusion of toluene and *n*-heptane in polyethylenes of different crystallinity. Polymer 1999;40:2797–803.