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Prediction of permeation fluxes of small volatile components through starch-based films

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Abstract

Simple formulas for estimating the Maxwell–Stefan diffusion of trace volatile compounds through polymeric films in multicomponent mixtures are developed based on free-volume theory and Flory–Huggins–Maxwell–Stefan (FHMS) equation. The model includes the solution-diffusion theory, and predicts the order of magnitude of the permeation fluxes of diacetyl and carvone through starch films. The permeability of volatile components within starch films was dominated by the swelling of the matrix. The methodology required only some physical properties of the components sorption equilibrium.

Keywords: Starch; Barrier properties; Maxwell–Stefan; Flory–Huggins; Free-volume; Swelling; Multicomponent diffusion

1. Introduction

Quantitative prediction of permeation of volatile components through polymeric films is relevant for a great number of applications. Predictions of permeation of aroma compounds through food matrices can be important to develop suitable matrices for flavor encapsulation. Another important application is the permeation of drug molecules through matrixes for drug delivery (Majeti & Ravi Kumar, 2001). The transfer of compounds within the product and their release from it depends on the nature of the compounds, the composition and the structure of the matrix (Seuvre, Philippe, Rochard, & Voilley, 2006). Model predictions can be used to show the rate of release, or how the performance of the system will be affected by any change made to it. Furthermore, the use of predictive models of permeation allows the quantification of a rate of release of particular compound within a specific matrix.

The rate of permeation of small components through a polymeric matrix is affected by the size and geometry of the molecules as well as by their physical–chemical affinity to the polymer. A common approach used to describe the diffusion through matrices is the solution–diffusion model (Fornasiero, Krull, Prausnitz, & Radke, 2005), where the polymeric-matrix/solute system is considered to be a molecular solution in which solute transport is through diffusion only. Usually, the description of diffusion in these systems has been treated through three different approaches: by using the generalized Fick's law, the Maxwell–Stefan expression (MS), or via the thermodynamics of irreversible processes (Wesselingh & Krishna, 2000). Even though these formulations are formally equivalent, the MS description of diffusion is usually preferred (Taylor & Krishna, 1993) and is adopted in this work. The MS approach requires information about thermodynamic and kinetic components of the system. The thermodynamic part can be described using the Flory–Huggins theory (FH), which can be readily incorporated in the MS due to their similar treatment of the microscopic molecular structure (Schaetzel, Bendjama, Vauclair, & Nguyen, 2001).

The kinetic parameters can be obtained using the so-called free-volume theory (FV). This theory has been used to describe the mobility of small penetrant though rubbery polymer systems with good accuracy (Wang, Yamaguchi, & Nakao, 2001; Wesselingh & Bollen, 1997). In this

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Nomenclature

List of symbols

A	Avogadro constant (mol^{-1})
a	activity
c_{T}	total molar concentration ($\mathrm{mol\ m}^{-3}$)
d	molecular diameter (m)
$Đ$	Maxwell–Stefan diffusivity ($\mathrm{m}^2\ \mathrm{s}^{-1}$)
G	Gibbs free energy ($\mathrm{J\ mol}^{-1}$)
k	Boltzman constant ($\mathrm{J\ K}^{-1}$)
MW	molecular weight ($\mathrm{kg\ mol}^{-1}$)
N	molar flux ($\mathrm{mol\ m}^{-2}\ \mathrm{s}^{-1}$)
n	number of moles
P	pressure (Pa)
R	gas constant ($\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$)
T	temperature (K)
V	volume of pure component ($\mathrm{m}^3\ \mathrm{mol}^{-1}$)
$V^{\bullet}$	minimum (compressed) volume ($\mathrm{m}^3\ \mathrm{mol}^{-1}$)
V_c	critical volume ($\mathrm{m}^3\ \mathrm{mol}^{-1}$)
V_F	free volume (m^3)
χ	Flory–Huggins interaction parameter
x	molar fraction
x^{m}	mass fraction

Greek letters

ϕ	volume fraction
η	viscosity (Pa s)
σ	surface fraction
$\rho^{\bullet}$	maximum (compressed) density ($\mathrm{kg\ m}^{-3}$)
ξ	friction coefficients (($\mathrm{N\ mol}^{-1}$)/($\mathrm{m\ s}^{-1}$))
μ	chemical potential ($\mathrm{J\ mol}^{-1}$)

Subscripts

i, j, k	numbering of components (general)
$1, 2, 3, M$	numbering of components (specific)
eff	effective value
o	initial side of the film
e	final side of the film

approach the prediction of permeability values through polymeric films makes use of only physical data together with the sorption equilibrium for each component in the mixture. The model proposed in this study is based on the assumption that the diffusivity of each permeant depends uniquely on the total volume fraction occupied by the permeant molecules, whatever their nature. Combined with the Maxwell–Stefan/Flory–Huggins (MSFH) theory the model allows predictions of permeation values.

The aim of this paper is to describe the permeation rates of the volatile diffusive species through starch films and to relate these estimates to the structure and composition of the starch films. The model is first checked with permeation data reported in the literature for starch–volatile (Yilmaz, van Dijk, Jongboom, Feil, & Hennink, 2004) and then analyzed to explore its sensitivity to different parameters and produce guidelines for design of (edible) barriers.

2. Model

The simulations are based on Maxwell–Stefan, Flory–Huggins, and free-volume theories. The theoretical background and the assumptions considered in the present model are explained in the following section.

2.1. Basic considerations

The mathematical treatment of diffusion transport is based on the following assumptions:

- The system consists of: a model volatile compound being either Diacetyl (2,3-butanedione) or Carvone (*p*-menthe-6,8-dien-2-one) (component 1), Water (component 2), Glycerol (component 3), and Starch (component M).
- The matrix is considered as a homogeneous material.
- The diffusion process is considered to be isothermal and isobaric.
- The fluids on either side of the film are at equilibrium with the starch film at the interface. This assumption implies that there is a continuous gradient in chemical potential from one side of the film to the other. Thus, the rates of absorption and desorption at the matrix interface are much higher than the rate of diffusion through the film, i.e., diffusion through the film is the rate-determining step.
- The chemical potential gradient across the starch film is only a function of the composition.
- The FH interaction parameter χ was calculated using the solubility of the minor component, as outlined by Mulder (1996); Schaetzel et al. (2001) using the following expression:

$$\chi_{iM} = -\frac{\ln \phi_i + (1 - \phi_i)}{(1 - \phi_i)^2} \tag{1}$$

Solubility data were obtained from equilibrium experiments reported by Yilmaz et al. (2004). Using the formula for diacetyl-starch the χ values is 4.7 and 5.9 for carvone–starch. For water–starch, a constant value of 0.6 was taken from (van der Berg, 1981).

The fact that starch molecules are enormously larger than the other compounds induces large uncertainties in the model. However, in a mixture of polymers and low-molecular weight substances, the diffusion interaction will not be with the complete polymer chain, but only with portion of it. It is therefore usual to adapt the theory to avoid this. Different authors have proposed multiples strategies (Heintz & Stephan, 1994; Paul, 2004; Radke, Fornasiero, & Prausnitz, 2005; Wesselingh & Bollen, 1997). We adopted the strategy suggested by Wesselingh and Bollen, in which it is assumed that diffusion is caused by motion of the separate chain elements of the polymer. Thus, it is assumed that glucose constitutes the chain repeat element of starch. In addition, water is assumed to be associated (dimer).

3. The Maxwell–Stefan equation

The Maxwell–Stefan approach poses a force balance in which the driving forces acting on system balance a (linear) combination of the friction forces between the species in the system.

$$-\frac{x_i}{RT}\nabla_{T,P}\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j N_i - x_i N_j}{c_\mathrm{T} Đ_{ij}}, \quad i = 1,2,\ldots,n \tag{2}$$

where i is one of the diffusing species; c_T is the total molar concentration; $Đ_{ij}$ is the binary Maxwell–Stefan diffusivity; μ_i is the chemical potential; x_i is the molar fraction; N_i is the species molar flux. The MS diffusivity can be interpreted as the inverse of the intermolecular friction coefficient (Wesselingh & Krishna, 2000). The use of the MS equation requires the estimation of the binary MS diffusivities as well as the chemical potential for all the species. For the case of polymer-solvent mixtures, the chemical potential can be estimated using the Flory–Huggins theory, and the binary MS diffusivities can be predicted through the free-volume theory.

4. Free volume theory

Here, we will use the theory proposed by Wesselingh and Bollen (1997) to estimate the diffusion coefficients of the mixture. The free volume theory follows three basic assumptions. The first assumption is that the total free volume in a mixture is given by the contribution of the pure components:

$$V_F = \sum_{i=1}^{n} x_i V_{Fi} \tag{3}$$

The free volume of each component (V_{Fi}) can be calculated using two simple equations based on viscosity and molar volume data as was described by Wesselingh and Bollen (1997):

$$\eta_i = \sqrt{\frac{3\mathrm{MW}_i A^{1/3} kT}{\pi^2 (V_i^\bullet)^{4/3}}}\exp\left(0.7\frac{V_i^\bullet}{V_{Fi}}\right) \tag{4}$$

and

$$V_{Fi} = V_i^\bullet - V_i \tag{5}$$

The minimum (compressed) volume ($V_i^\bullet$) of each component can also be estimated using the critical volume (V_c) of component i according to Guggenheim equation (Wesselingh & Bollen, 1997). The minimum compress volume was then used as a starting value to solve Eqs. (4) and (5).

$$V_i^\bullet = 0.289 V_{ci} \tag{6}$$

The second assumption is that for molecules of different sizes, a better estimation of the free volume can be obtained if it is assumed that the free volume seen by each component is proportional to its surface fraction. When considering molecules to be spherical, the surface of a molecule scales to $V^{2/3}$. Therefore, the surface fractions of the component species are represented by:

$$\sigma_i = \frac{x_i (V_i)^{2/3}}{\sum_{k=1}^{n} x_k (V_k)^{2/3}} \tag{7}$$

The free volume for each species becomes now:

$$V_{Fi} = \frac{\sigma_i V_F}{x_i} \tag{8}$$

The third assumption relates to the density that we approximated as a mass averaged density:

$$\rho^\bullet = \sum_{k=1}^{n} \rho_k^\bullet x_k^m \tag{9}$$

Finally, the expression for the MS binary diffusivity is given by:

$$Đ_{ik} = \frac{RT}{\xi_{ik}} \tag{10}$$

where

$$\xi_{ik} = \frac{\xi_{i,\mathrm{eff}}\,\xi_{k,\mathrm{eff}}}{\sum_{m=1}^{n} x_m \xi_{m,\mathrm{eff}}} \quad i \neq k \tag{11}$$

and

$$\xi_{i,\mathrm{eff}} = 2A\sqrt{3kT\rho^\bullet d_i}\exp\left(0.7\frac{V_i^\bullet}{V_{Fi}}\right) \tag{12}$$

where $\xi_{i,\mathrm{eff}}$, and d_i can be calculated assuming that the compressed fluid has a cubic structure:

$$d_i = \left(\frac{V_i^\bullet}{A}\right)^{1/3} \tag{13}$$

5. The Maxwell–Stefan/Flory–Huggins equations (MSFH)

Following the Flory–Huggins theory for a quaternary system; the Gibbs energy of mixing (ΔG_M) is as follows:

$$\frac{\Delta G_M}{RT} = n_1\ln\phi_1 + n_2\ln\phi_2 + n_3\ln\phi_3 + n_3\ln\phi_M + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_1\phi_M\chi_{1M} + n_2\phi_3\chi_{23} + n_2\phi_M\chi_{2M} + n_3\phi_M\chi_{3M} \tag{14}$$

Differentiation with regard to each component gives the change in chemical potential upon mixing for that component:

$$\Delta\mu_i = RT\ln(a_i) = \left(\frac{\partial\Delta G_M}{\partial n_i}\right)_{P,T,n_j} \tag{15}$$

In which a_i is the activity.

We assume that the binary FH interaction parameters χ_{ij} are not concentration dependent. The latest assumption is justified, because we consider that for the low concentration range of the three non-polymeric components the binary parameters behave as constants. The resultant system is:

$$\begin{aligned}\ln(a_1) ={}& \ln\phi_1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 - \frac{V_1}{V_M}\phi_M \\ &+ (1-\phi_1)(1+\chi_{12}\phi_2+\chi_{13}\phi_3+\chi_{1M}\phi_M) \\ &- \frac{V_1}{V_2}\chi_{2M}\phi_2\phi_M - \frac{V_1}{V_2}\chi_{23}\phi_2\phi_3 - \frac{V_1}{V_M}\chi_{3M}\phi_3\phi_M \end{aligned} \quad (16A)$$

$$\begin{aligned}\ln(a_2) ={}& \frac{V_1}{V_2}\ln\phi_2 - \phi_1 - \frac{V_1}{V_3}\phi_3 - \frac{V_1}{V_M}\phi_M \\ &+ (1-\phi_2)\left(\frac{V_1}{V_2}+\chi_{12}\phi_1+\frac{V_1}{V_2}\chi_{23}\phi_3+\frac{V_1}{V_2}\chi_{2M}\phi_M\right) \\ &- \chi_{1M}\phi_1\phi_M - \chi_{13}\phi_1\phi_3 - \frac{V_1}{V_M}\chi_{3M}\phi_3\phi_M \end{aligned} \quad (16B)$$

$$\begin{aligned}\ln(a_3) ={}& \frac{V_1}{V_3}\ln\phi_3 - \phi_1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_M}\phi_M \\ &+ (1-\phi_3)\left(\frac{V_1}{V_3}+\chi_{13}\phi_1+\frac{V_1}{V_2}\chi_{23}\phi_2+\frac{V_1}{V_M}\chi_{3M}\phi_M\right) \\ &- \chi_{1M}\phi_1\phi_M - \chi_{12}\phi_1\phi_2 - \frac{V_1}{V_2}\chi_{2M}\phi_2\phi_M \end{aligned} \quad (16C)$$

$$\begin{aligned}\ln(a_M) ={}& \frac{V_1}{V_M}\ln\phi_M - \phi_1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 \\ &+ (1-\phi_M)\left(\frac{V_1}{V_M}+\chi_{1M}\phi_1+\frac{V_1}{V_2}\chi_{2M}\phi_2+\frac{V_1}{V_M}\chi_{3M}\phi_3\right) \\ &- \chi_{13}\phi_1\phi_3 - \chi_{12}\phi_1\phi_2 - \frac{V_1}{V_2}\chi_{23}\phi_2\phi_3 \end{aligned} \quad (16D)$$

The MS equation for a quaternary system in terms of volume fraction (considering unidirectional diffusion in the *z* axis) is as follows:

$$-\left(\frac{\mathrm{d}\ln(a_i)}{\mathrm{d}z}\right) = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\phi_j}{c_T V_j Đ_{ij}}\left(\frac{V_i N_i}{\phi_i} - \frac{V_j N_j}{\phi_j}\right), \quad i = 1,2,3,4 \qquad (17)$$

This equation extended for four components considering a zero value for the polymer flux (i.e., $N_M \cong 0$) are as follow:

$$\begin{aligned}-\left(\frac{\mathrm{d}\ln(a_1)}{\mathrm{d}z}\right) ={}& \frac{\phi_2}{c_T V_2 Đ_{12}}\left(\frac{V_1N_1}{\phi_1}-\frac{V_2N_2}{\phi_2}\right) \\ &+ \frac{\phi_3}{c_T V_3 Đ_{13}}\left(\frac{V_1N_1}{\phi_1}-\frac{V_3N_3}{\phi_3}\right) \\ &+ \frac{\phi_M}{c_T V_M Đ_{1M}}\left(\frac{V_1N_1}{\phi_1}\right), \end{aligned} \quad (18A)$$

$$\begin{aligned}-\left(\frac{\mathrm{d}\ln(a_2)}{\mathrm{d}z}\right) ={}& \frac{\phi_1}{c_T V_1 Đ_{12}}\left(\frac{V_2N_2}{\phi_2}-\frac{V_1N_1}{\phi_1}\right) \\ &+ \frac{\phi_3}{c_T V_3 Đ_{23}}\left(\frac{V_2N_2}{\phi_2}-\frac{V_3N_3}{\phi_3}\right) \\ &+ \frac{\phi_M}{c_T V_M Đ_{2M}}\left(\frac{V_2N_2}{\phi_2}\right), \end{aligned} \quad (18B)$$

$$\begin{aligned}-\left(\frac{\mathrm{d}\ln(a_3)}{\mathrm{d}z}\right) ={}& \frac{\phi_1}{c_T V_1 Đ_{13}}\left(\frac{V_3N_3}{\phi_3}-\frac{V_1N_1}{\phi_1}\right) \\ &+ \frac{\phi_2}{c_T V_2 Đ_{23}}\left(\frac{V_3N_3}{\phi_3}-\frac{V_2N_2}{\phi_2}\right) \\ &+ \frac{\phi_M}{c_T V_M Đ_{3M}}\left(\frac{V_3N_3}{\phi_3}\right), \end{aligned} \quad (18C)$$

$$\begin{aligned}\left(\frac{\mathrm{d}\ln(a_M)}{\mathrm{d}z}\right) ={}& \frac{\phi_1}{c_T V_1 Đ_{1M}}\left(-\frac{V_1N_1}{\phi_1}\right) \\ &+ \frac{\phi_2}{c_T V_2 Đ_{23}}\left(-\frac{V_2N_2}{\phi_2}\right) \\ &+ \frac{\phi_3}{c_T V_3 Đ_{3M}}\left(-\frac{V_3N_3}{\phi_3}\right), \end{aligned} \quad (18D)$$

The exact solution requires the numerical resolution of these equations, however, we have considered several further assumptions, which are physically acceptable that allow additional simplifications. They are:

- Glycerol acts as a plasticizer in the film, and it does not leave film. Therefore, we may assume its net diffusion to be negligible (i.e., $N_3 \cong 0$).
- The permeating species are present at low concentrations, thus we neglect coupling fluxes. Even though the interaction parameters between non-permeating species will have influence on the swelling value of the system, it is only the binary interaction between permeating species and the matrix (χ_{1M} and χ_{2M}) that is important for determining the flux.

The simplified equation resulting from application of these assumptions is similar to the one given by Schaetzel et al. (2001).

$$\begin{aligned}N_i = \frac{Đ_{iM}}{V_i^2 z_e}\Bigg[&\left(V_M - 2V_i - 2\chi_{iM}V_i + \frac{V_i^2}{V_M}\right)\cdot\frac{(\phi_{io}^2-\phi_{ie}^2)}{2} \\ &+ \frac{2}{3}\chi_{iM}(V_i - V_M)(\phi_{io}^3-\phi_{ie}^3) - V_i\ln\left(\frac{1-\phi_{io}}{1-\phi_{ie}}\right)\Bigg] \end{aligned} \quad (19)$$

The subscripts ‘o’ and ‘*e*’ refer to the initial and final side of the film, respectively, and Z_e is the thickness of the film.

To elucidate the driving parameter that governs permeation of hydrophobic compound through starch films, two simulations were performed with Mathcad (Mathsoft Engineering & Education, version 11.0, Cambridge, USA) following the steps described in previous paragraphs. Table 1 shows the parameters used for the simulations. Viscosity values are used to calculate the free volume, however for the contribution of trace components (such as the volatile components) free volumes are negligible, and thus their viscosity data do not need to be considered.

6. Results and discussion

6.1. Validation of the model

To verify the model, we used the experimental results reported by Yilmaz et al. (2004) concerning the permeation data of diacetyl and carvone through starch films at 20 °C. The experimental data extracted to verify the model are summarized in Table 2.

First of all, MS binary diffusivities were calculated using the procedure previously described. The estimated MS diffusivities are shown Fig. 1. Water concentration in the films turned out to be the main parameter in the diffusivities of all components. According to the FV theory, the diffusion coefficient is a strong function of the volume fractions of the individual species. For this reason, the addition of small molecules such as water or polar solutes results in increase in free volume, strongly increasing the molecular mobility of the mixture (plasticizing effect). This plasticizing effect upon starch films caused by water and glycerol is synergistic and enhances the diffusion rate, which facilitates the penetration of the volatile components as was also observed by Yilmaz et al. (2004) for this specific system. Another aspect observed is the effect of the size of the permeants in the diffusivities values. Thus, water is the smallest molecule in this system and consequently the fastest to diffuse. In contrast, carvone is the biggest and therefore the slowest diffusive species. Diacetyl and glycerol have similar molecular weights, and therefore their diffusion coefficients are similar. Figs. 2 and 3 show the fluxes

Table 1
Physical data used for the simulations

Code	Component	Molecular weight	Density (kg/m^3)	Viscosity (N s/m^2)
1	Diacetyl	86.1	981	–
	Carvone	150.22	961	–
2	Water	2×18.0^{b}	998	8.0×10^{-4}
3	Glycerol	92.09	1261	1.07×10^{0}
M	Glucose	180.16	1544	1.61×10^{11a}

Data taken from (Weast, 1973).

[a] Data generated using ASPEN Plus.

[b] Water is taken as a dimmer.

Table 2
Characteristics of different starch films[a] (Yilmaz et al., 2004)

Film No.	Film thickness (mm)	Solubility (mg cm^{-3})	Moisture contain after equilibration of the film (% mol/mol)	Flux (mol m^{-2} s^{-1})*10	Crystallinity (%)
1	0.351 ± 0.002	2.11 ± 0.04	32.2	42.3	19 ± 1
2a	0.164 ± 0.002	2.41 ± 0.03	47.7	153	20 ± 2
2b	0.348 ± 0.002	2.42 ± 0.02	47.1	71.9	22 ± 1
3[b]	0.353 ± 0.002	2.41 ± 0.02	56.8	117	17 ± 1
4[c]	0.356 ± 0.004	3.30 ± 0.03	66.5	169	21 ± 1
5	0.352 ± 0.005	3.14 ± 0.03	55.2	117	24 ± 1
6	0.354 ± 0.003	2.14 ± 0.02	56.8	36.1	31 ± 3
7	0.347 ± 0.007	2.18 ± 0.02	47.8	172	None
8a	0.165 ± 0.002	0.60 ± 0.03	47.7	13.7	19 ± 2
8b	0.351 ± 0.002	0.61 ± 0.03	47.1	5.18	21 ± 1
9	0.351 ± 0.003	0.43 ± 0.14	32.8	3.88	19 ± 2
10[b]	0.352 ± 0.002	0.62 ± 0.02	56.5	5.55	18 ± 1
11[c]	0.352 ± 0.005	0.63 ± 0.05	66.0	7.21	22 ± 2
12	0.348 ± 0.003	0.76 ± 0.02	54.4	10.2	24 ± 1
13	0.350 ± 0.004	0.57 ± 0.04	57.9	3.33	31 ± 2
14	0.351 ± 0.007	0.67 ± 0.01	47.1	12.8	None

[a] Films 1–7 were used for permeation experiments with diacetyl; films 8a–14 were used for the permeation experiments with carvone.

[b] Films where the permeation experiments were carried out at relative humidity (RH) of 60%.

[c] The permeation experiments were carried out at RH of 90%. All the rest films were equilibrated at RH of 30%.

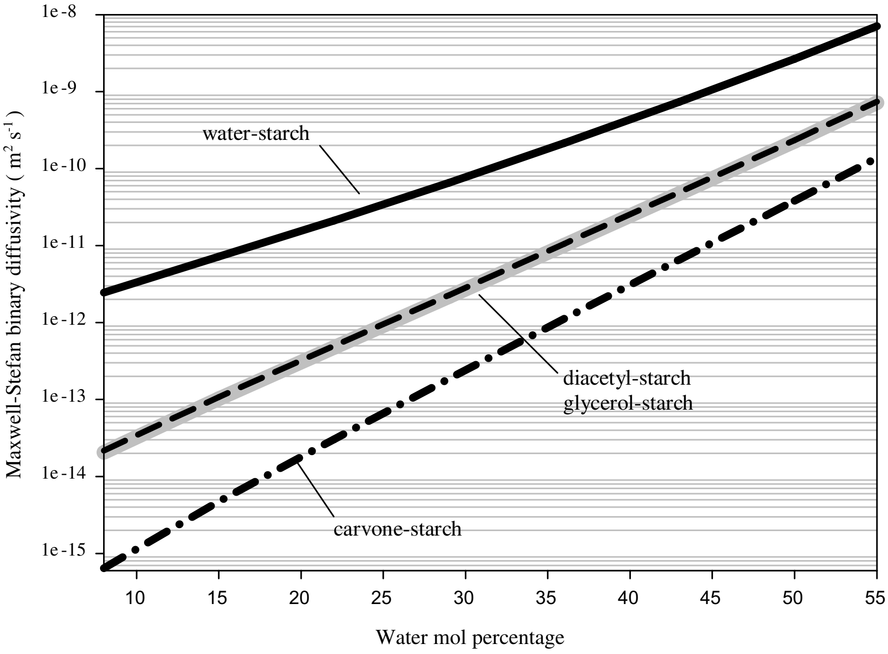

Fig. 1. Binary Maxwell–Stefan diffusivities at 20 °C.

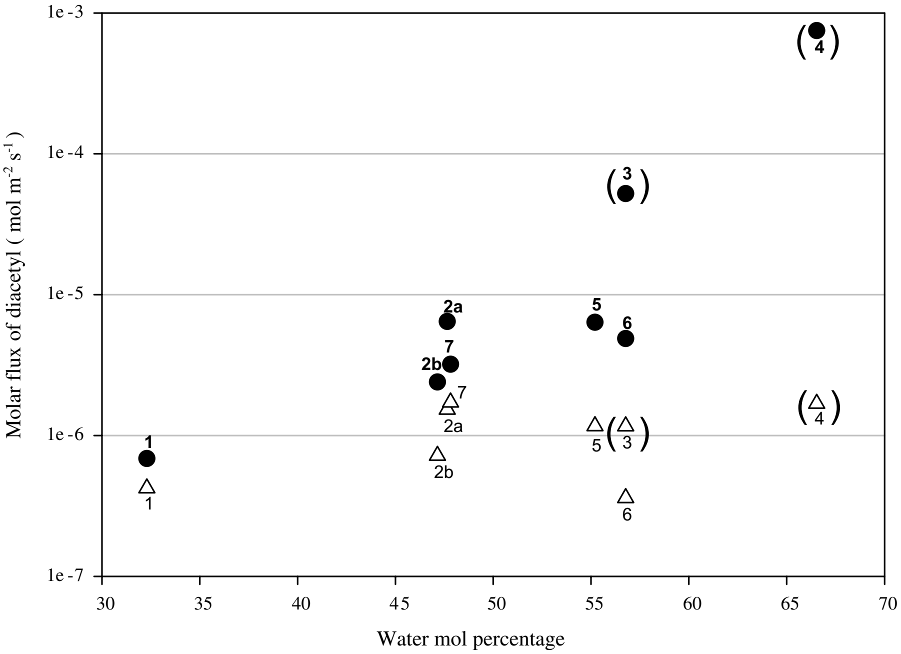

Fig. 2. Permeation flux of diacetyl through starch films (Nos. 1–7; Table 2) at 20 °C as a function of the water mol percentage. (△) experimental values, (●) simulated values.

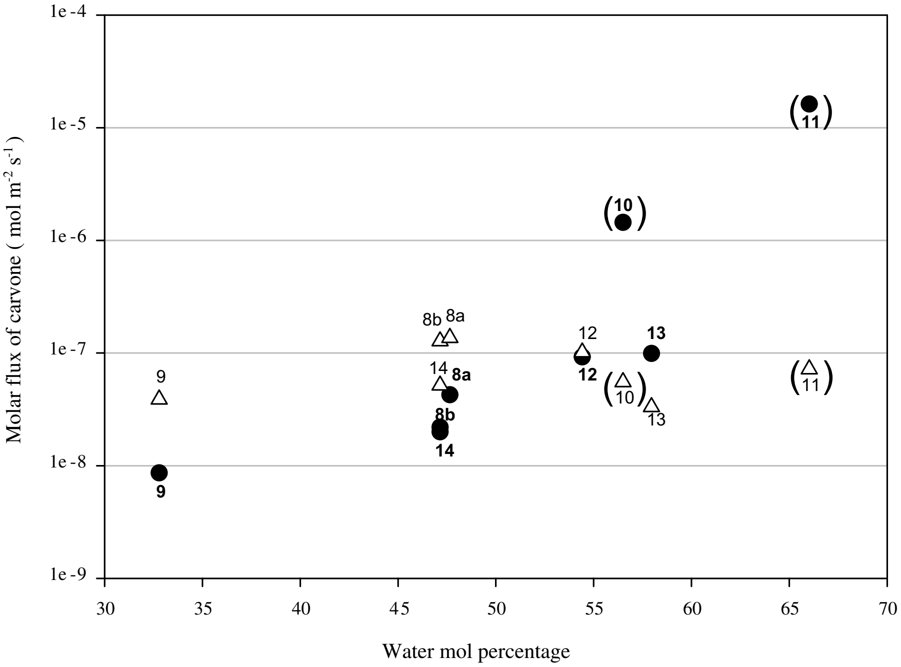

Fig. 3. Permeation flux of carvone through starch films (Nos. 8a–14; Table 2) at 20 °C as a function of the water mol percentage. (△) experimental values, (●) simulated values.

estimations for diacetyl and carvone. Most of the estimations are of the same order of magnitude as the experimental results. Furthermore, the flux of water shows concordance with the result for carvone and diacetyl, it increases when the water content in the film increases (Fig. 4). As a result, this model results very attractive to make predictions of diffusion of small components through starch-based films.

Some of the values for diacetyl show less precise predictions. The deviations from the experiments may be related to the effect of crystallinity, cross-linking, or other inhomogeneities that are not taken into consideration in the present model. For example, film 6 for diacetyl has the highest crystallinity and its prediction deviates strongly from the experimental results. A similar situation occurs with film 13 for carvone but, although a less pronounced effect.

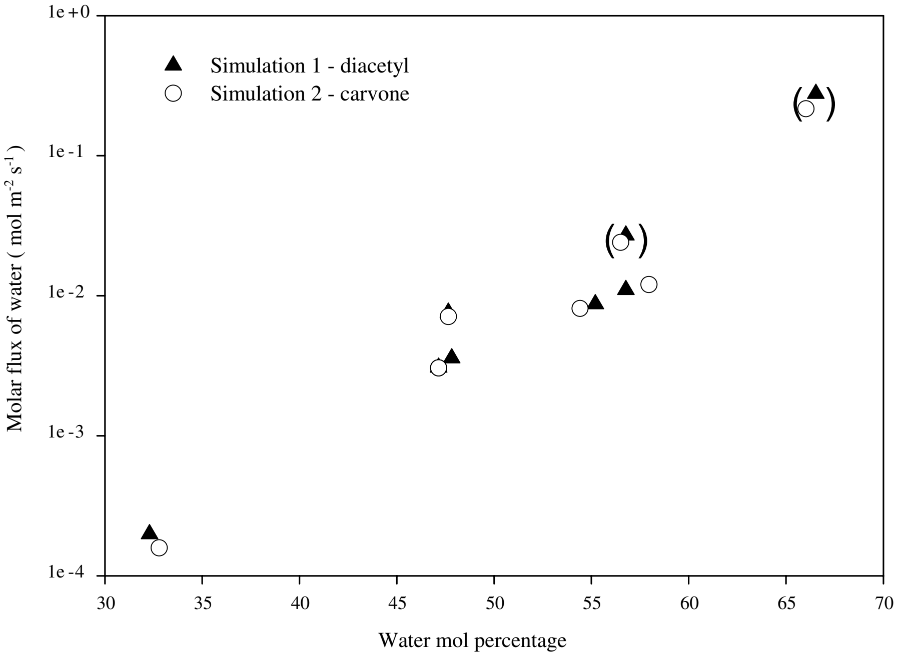

Fig. 4. Permeability of water through starch films at 20 °C.

Films 3–4 for diacetyl, and films 10–11 for carvone differ more than one order of magnitude from the experimental results. In addition, Fig. 4 shows that the highest water flux values correspond to the anomalous films mentioned above. Table 2 shows that the permeability experiments with these films were carried out at high relative humidity (60 and 90% RH), while they were prepared at low humidity (30% RH). In consequence, it is possible that the films were not measured at equilibrium conditions leading to a lower permeation values, violating the fourth assumption of our model. Hence, the model suggests that the relative independence of these experimental points on the water contains might be due to data obtained in non-equilibrium (non-steady state) conditions. This suggestion is supported by the results of Standing and co-workers who found a direct effect of the surrounding humidity on the film microstructure and permeability properties. They reported that for glycerol-plasticized amylose films, the network microstructure changed from dense and homogeneous to a more open structure with fluctuations in the pore size when the surrounding RH was increased (Stading, Rindlav-Westling, & Gatenholm, 2001). This change in morphology was attributed to plasticization of the amorphous areas due to the increased water content, leading to higher mobility in the network and subsequent higher permeability values. This observation supports our interpretation of the disagreement between model and experiments for these films.

In summary, the diacetyl/carvone permeation fluxes through starch films are satisfactorily predicted with the free-volume/Maxwell–Stefan/Flory–Huggins (FV-MSFH) equation without the need of any adjustable parameters. For the prediction, only a number of physical properties of the components sorption equilibrium values were required.

6.2. Consequences for film design

Now, the model can be used to explore the effect of film and permeant properties on the permeation, leading to insight how to change the film in order to modify the permeation properties.

The solubility of diacety/carvone in starch films is low (Table 2). An increase in water activity in the mixture however leads to swelling of the matrix and consequently to an increment in the permeation of the volatile molecules through the swollen polymer. As was previously shown, the steady state flux of diacetyl is higher than the flux of carvone. This can be ascribed to the higher diffusion coefficient as well as the higher solubility of diacetyl as compared with carvone (e.g Films 1–7 for diacetyl have a solubility almost four times higher than films 8a–10 for carvone – see Table 2). Fig. 5 shows three different calculations carried out by changing the solubility of diacetyl and water in comparison with the original calculations, referred as a base case. If the starch films are modified to be more hydrophobic (i.e., solubility of water decreases and solubility of hydrophobic compound increases), the resulting FH interaction parameter for diacetyl decreases (simulation refers as $\chi_{1M} = 4.4$) and the flux of water and diacetyl also decreases. In contrast, if the films are more hydrophilic (i.e., solubility of water increases and solubility of hydrophobic compound decreases), resulting in a higher FH interaction (i.e., $\chi_{1M} = 4.9$), the flux of water and diacetyl increase. Therefore, the hydrophobicity of the film determines the degree of swelling, which has a direct influence

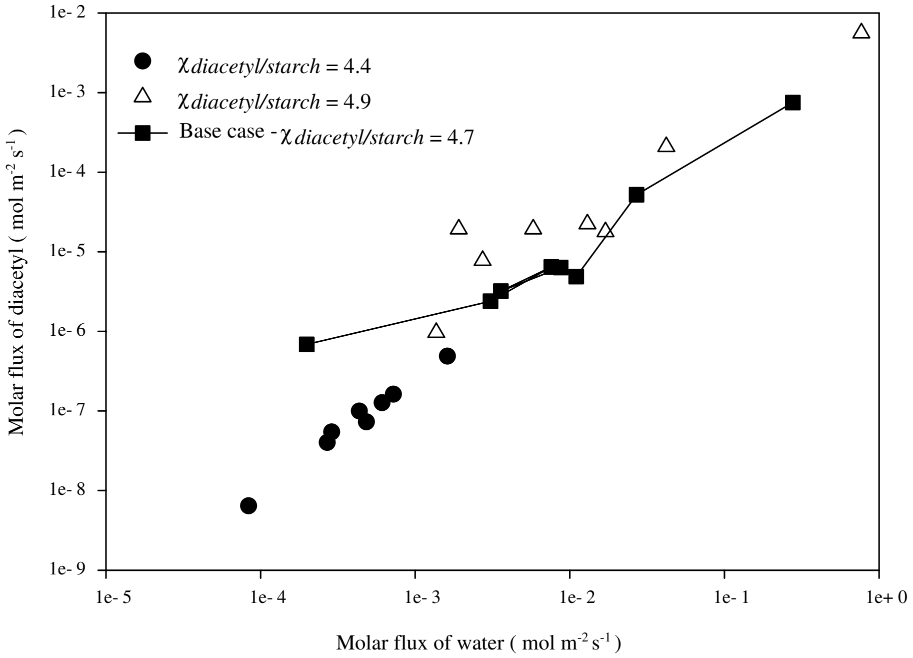

Fig. 5. Solubility effect on flux estimations.

on the flux of the diffusive species. Starch-based films are very hydrophilic and have a sorption capacity that increases with the water concentration. This sorption capacity is observed with the proportional increase of the diacetyl/carvone flux with the water concentration. As a result, the increment in the flux of the volatile component is the direct result of sorption effects, not by the flux coupling as their concentration are very low. This explanation is consistent with the assumption of negligible flux coupling between the species in their diffusion through the films. It should be noticed that having no coupling does not mean that a component in the mixture does not affect the flux of the other components. A component can affect the flux of the other components through sorption effects (Schaetzel, Vauclair, Nguyen, & Bouzerar, 2004).

In brief, the contra intuitive results obtained after change the hydrophobicity of the films show that swelling is more important that solubility. Therefore, to reduce the permeability, one should decrease the hydrophilicity of the matrix; even thought this will somewhat increase the sorption of the permeant species, it will reduce the swelling of the matrix.

In the case it is not possible to modify the starch, the inclusion of an additional phase with for example a more hydrophobic character, might be an option to influence the rate of permeation.

7. Conclusion

The present model coupling FV, FH and MS, was found to be adequate for the quantitative description of permeation fluxes of volatile trace components (diacetyl and carvone) and water through polymeric films. The permeability of diacetyl and carvone through starch films is dominated by swelling, i.e., permeability is mostly easily changed by changing the interaction with water. In consequence, the diffusion process of a particular volatile compound in trace concentration can be manipulated decreasing the degree of plastization of the film or via chemical or physical reduction of the hydrophilicity of starch. Even thought the absolute sorption of the trace component will be larger, the lower (equilibrium) moisture contain will result in a significantly lower permeation rate of the trace component.

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