ELSEVIER

Journal of Food Engineering 56 (2003) 401–410

JOURNAL OF
FOOD
ENGINEERING

www.elsevier.com/locate/jfoodeng

A model for determination of multicomponent diffusion coefficients in foods

Patricia E. Gerla [a], Amelia C. Rubiolo [b,*]

[a] *Facultad de Ingeniería, Instituto de Ingeniería Química, Comisión Sectorial de Investigación Científica, Universidad de la República, J. Herrera y Reissig 565, 11300 Montevideo, Uruguay*

[b] *Instituto de Desarrollo Tecnológico para la Industria Química, Consejo Nacional de Investigaciones Científicas y Técnicas, Universidad Nacional del Litoral, Güemes 3450, S3000GLN Santa Fe, Argentina*

Received 17 September 1998; received in revised form 3 October 2001; accepted 12 March 2002

Abstract

The simultaneous diffusion of NaCl, lactic acid and water in cheese during brining, were experimentally and theoretically evaluated using multicomponent and pseudobinary mass transport models. The average concentration data of each solute in the solid at different process times were correlated with theoretical models determining the diffusion coefficients values for each solute. Applying a ternary model, main and cross diffusion coefficient values for NaCl and lactic acid showed a non-reciprocal flux interaction. The NaCl diffusion rate resulted independent of the lactic acid concentration gradient, while the lactic acid diffusion rate was increased 12 times due to NaCl concentration changes in the cheese. The results established the importance of using multicomponent mass transport models to evaluate the flux variation of solute in the global flux value.

Keywords: Multicomponent diffusion; Diffusion coefficients; Diffusion in foods; Lactic acid; Brining; Pategras cheese.

1. Introduction

In the food processing the transfer of solutes between solid and liquid is used to modify food characteristics such as taste, colour, nutritional value, and preservation capacity. Thereby soaking products in aqueous solutions to leach or infuse solutes in the foodstuffs, is an usual manufacturing operation in food elaboration process. The mass transport between the solid food and the soaking solution, is generally controlled by the diffusion rate of solutes in the foodstuff. Diffusion velocities are calculated using effective diffusion coefficients of solutes in the solid (Luna & Bressan, 1986; Schwartzberg & Chao, 1982; Turhan & Kaletunç, 1992).

Models of solute diffusion in solid–liquid systems were generally developed for the component with larger concentration or for a group of solutes considered as one pseudocomponent, without considering the minor solutes. According to this, pseudobinary diffusion models of the mass transfer process were used to calculate the main solute flux and the diffusion coefficient as a binary solute–solid system (Bailey, 1975; Bressan, Carroad, Merson, & Dunkley, 1981).

Mostly solid foods showed complex structure with cellulosic or proteic framework that occludes an aqueous solution with major and minor components. Minor concentration solutes have an important role in the food characteristics, which are associated to the quality of the product and its preservation. However, the diffusion rate for the components in minor quantities during leaching or infusion processes in foods was almost not modelled.

Multicomponent mass transfer in cheese during brining is a case of interest. In this process, not only the water content in cheese is reduced and the salt concentration is increased but also the lactic acid concentration is modified. The lactic acid concentration change in the cheese during salting process (Lawrence & Gilles, 1982) and its detection in the brine can be explained by the lactic acid diffusion. The final acid concentration in cheese after brining influences physicochemical and microbiological changes in the cheese and consequently the quality of the product (Fox, 1987). Lactic acid is formed

---

[*] Corresponding author. Tel.: +54-342-455-9176; fax: +54-342-455-0944.

E-mail addresses: gerla@fing.edu.uy (P.E. Gerla), arubiolo@intec.unl.edu.ar (A.C. Rubiolo).

0260-8774/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0260-8774(02)00213-3

Nomenclature

a_i	relation defined by Eq. (7)
b_{ji}	relation defined by Eq. (8)
Bi	Biot number
C_n	parameter of the ternary model mass transport defined by Eq. (A.16)
D_{ij}	diffusion coefficient of solutes (i) in a multicomponent system, cm^2/s
$D_{i\mathrm{b}}$	diffusion coefficient of solute (i) in a binary systems, cm^2/s
$D_{i\mathrm{pb}}$	pseudobinary diffusion coefficient of solute (i) in a multicomponent system, cm^2/s
d_i	deviation for solute (i), defined by Eq. (14)
J_i	diffusion flux of solute (i), g/cm^2 s
$J_{i\mathrm{b}}$	diffusion flux of solute (i) in a binary system, g/cm^2 s
k_i	partition factor of solute (i)
L	liquid phase length, cm
m	number of experimental data
N	number of species
q_n	relation defined by Eq. (A.18)
r	axial coordinate, cm
S	solid slab half thickness, cm
V_L	liquid phase volume, cm^3
V_S	solid phase volume, cm^3
x	punctual concentration, g/cm^3
$\bar{x}$	average concentration, g/cm^3
α_i	partition relation, defined as $k_i(V_\mathrm{L}/V_\mathrm{S})$
β_n	relation defined by Eq. (A.17)
δ_{ij}	delta de Kronecker
λ	eigenvalue
θ	time, s
ψ	transformation variable
ϕ	diameter of the cylindrical samples

Superscript

–	bulk average

Subscripts

b	binary system
i, j	solutes i and j
pb	pseudobinary model
0	at initial time
∞	at infinite time or equilibrium conditions
k	auxiliary subindex

Operators

Δ	increment operator
∇	gradient operator
∇^2	Laplace operator
$\vert\ \vert$	determinant
erfc	complementary error function
eerfc	exponential complementary error function defined by Eq. (A.20)

by milk bacterias from the milk lactose remained in the water hold by the curd. In spite of this, lactic acid diffusion in cheese during brining has not been presented yet. Reported models for solutes transfer in cheese have considered movement of salts (NaCl; NaCl–KCl) and water without considering components in minor concentration as lactic acid which is present in a small weight fraction (1% w/w) (Geurts, Walstra, & Mulder, 1980; Luna & Bressan, 1986; Turhan & Kaletunç, 1992; Zorrilla & Rubiolo, 1994).

In addition, studies on pH changes in biological systems, as serum albumin gels soaked in aqueous solutions, have pointed out that gel lactic acid loss is increased in presence of NaCl (Chu, Speiss, & Wolf, 1992). This fact suggests a possible interaction between both solute fluxes in the mass transport process. Interaction effects in the transfer rate of each solute in ternary or multicomponent systems, were theoretically and experimentally studied for gases and liquid mixtures (Cussler & Lightfoot, 1963; Toor, 1964). The second Fick's law generalized form developed by Onsager was the constitutive equation of the solute mass fluxes used to model the diffusion process. For diffusion in solids Zorrilla and Rubiolo (1994) considered a ternary model in cheese salting with equal concentration of NaCl and KCl in brine. In this case solute sizes, properties and concentrations are similar, then, the diffusion coefficient determined using a diffusion cell showed that there were no strong interactions between solutes.

The aim of this work was to study the multicomponent mass transport in a solid–liquid system, and defined physical model equations to determine the main and cross effective diffusion coefficients of each solute, for simultaneous diffusion with interactions between fluxes in a complex solid like foodstuff.

Cheese brining process was the experimental system to determine lactic acid and NaCl effective main and cross diffusion coefficients in order to predict acid concentration changes during salting time in cheeses for different conditions.

2. Theory

The general form of the second Fick's law for multicomponent systems was considered as the constitutive equation for the flux J_i of the solute i, with the concentration gradients ∇x_i and constant diffusion coefficients. The following equations express the mass flux of the $(N-1)$ solutes and the solvent, in a solid in contact with a well stirred solution, when homogeneous and rigid solid structure, no chemical reaction and negligible convective mass flux, were assumed (Cussler, 1976).

$$J_i = -\sum_{j=1}^{N-1} D_{ij} \nabla x_j \tag{1}$$

Diffusion coefficients D_{ii} and D_{ij}, respectively called main and cross coefficients, are independent of concentration gradients, ∇x_i, of any one solute in the system. This equation can be applied in solids where the mass density is constant. Therefore, the mass average velocity is taken as reference and one of the N components is chosen as solvent.

In Eq. (1) the term that includes the main coefficient D_{ii} is the contribution to the total diffusive flux of solute i, originated by its own concentration gradient. The terms with cross coefficients D_{ij} represent the contribution of the concentration gradients of the other solutes in the system to the J_i flux.

In the case of one diffusing solute, i, the system is binary, the diffusion coefficient $D_{i\mathrm{b}}$ is the main coefficient, D_{ii} in Eq. (1), and the flux $J_{i\mathrm{b}}$ of the solute according to Fick's law is:

$$J_{i\mathrm{b}} = -D_{i\mathrm{b}} \nabla x_i \quad i = 1, \ldots, N-1 \tag{2}$$

Then, Eq. (1) can be evaluated in function of Eq. (2) as follows:

$$J_i = J_{i\mathrm{b}} + \sum_{j=1}^{N-1} J_{j\mathrm{b}} \frac{D_{ij}}{D_{j\mathrm{b}}} \quad i, j = 1, \ldots, N-1, \; i \neq j \tag{3}$$

A pseudobinary model in which the diffusive flux of the solute i is exclusively associated to its own concentration gradient can be apply in a multicomponent system. For this model the pseudobinary diffusion coefficient of the solute i, $D_{i\mathrm{pb}}$, results functionally dependent on the flux of the other solutes in the system. According to the second Fick's law in a pseudobinary system, the expression to relate each solute flux with its concentration gradients is:

$$J_i = -D_{i\mathrm{pb}} \nabla x_i \quad i = 1, \ldots, N-1 \tag{4}$$

2.1. Ternary diffusion model

The diffusion model for mass transport in a solid–liquid system was developed in terms of solute concentration in the solid as a whole (Schwartzberg & Chao, 1982). A partial differential equation (PDE) system was obtained for the variation with the time of local concentration, x_i, of each solute, in function of every solute gradients, after applying the continuity equation with Eq. (1). For three components, the PDE system is given by Eqs. (A.1)–(A.5) and the method for solving by Eqs. (A.6)–(A.14) in the appendix. The solution for calculating the concentration of each solute in the solid, at any particular position and time, using Eqs. (A.11)–(A.14) results:

$$\Delta x_i = \sum_{j=1}^{2} \left[\left[\sum_{k=1}^{2} f(\lambda_k) \frac{\prod_{\substack{j=1 \\ j\neq k}}^{2} (\lambda_j \delta_{ij} - D_{ij})}{\prod_{\substack{j=1 \\ j\neq k}}^{2} (\lambda_j - \lambda_k)} \right] \Delta x_{j_0} \right] \quad i = 1, 2 \tag{5}$$

where the eigenvalues λ_i are expressed in function of the D_{ij} coefficients by:

$$\lambda_i = \frac{1}{2} \left(D_{11} + D_{22} \pm \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}} \right) \quad i = 1, 2 \tag{6}$$

Defining a_i and b_{ji} as:

$$a_i = \frac{D_{ii} - \lambda_j + b_{ji} D_{ij}}{\lambda_i - \lambda_j} \quad i, j = 1, 2; \; i \neq j \tag{7}$$

$$b_{ji} = \frac{\Delta x_{j_0}}{\Delta x_{i_0}} \quad i, j = 1, 2; \; i \neq j \tag{8}$$

then, the explicit expression for solutes concentration which is Eq. (5) results:

$$\frac{\Delta x_i}{\Delta x_{i_0}} = a_i f(\lambda_i) + (1 - a_i) f(\lambda_j) \quad i, j = 1, 2; \; i \neq j \tag{9}$$

The solvent concentration (third component) in the solid with a constant density and volume, is obtained from the mass balance, by:

$$\sum_{i=1}^{3} (\Delta x_i - \Delta x_{i\infty}) = 0 \tag{10}$$

and using Eq. (10) in Eq. (9), the variation of solvent concentration is:

$$\frac{\Delta x_3}{\Delta x_{3_0}} = \sum_{i=1}^{2} [a_i f(\lambda_i) + (1 - a_i) f(\lambda_j)] \frac{1}{(1 + b_{ji})} \quad i, j = 1, 2; \; i \neq j \tag{11}$$

Considering a non-homogeneous microstructure of food products, equations to calculate the average concentration for each solute and the solvent in a solid volume after different immersion times are necessary. Average concentrations of the solute i in the whole solid volume, $\bar{x}_i$ and $\Delta\bar{x}_i = \bar{x}_i - \bar{x}_{i\infty}$ values, were obtained integrating Eqs. (9) and (11) over the thickness of the slab, when the mass transfer is in one-dimension. The solutions values were obtained replacing $f(\lambda_i)$ by its average values, $\bar{f}(\lambda_i)$, calculated by:

$$\bar{f}(\lambda_i) = \frac{1}{L} \int_0^L f(\lambda_i) \, \mathrm{d}r \tag{12}$$

For the case of infinite Biot Number, $(Bi \to \infty)$ and a finite value of the partition relation α_i, the solution for $\bar{f}(\lambda_i)$ is given by Eqs. (A.15)–(A.20) and ternary explicit solutions for concentrations in a solid slab in contact with a well stirred liquid, are showed in the appendix (Eqs. (A.21)–(A.24)).

2.2. Pseudobinary diffusion model

For a system of three components, when is assuming the pseudobinary mass transfer model, the correspondent set of PDE equations, results after applying the continuity equation with Eq. (4).

For these case, the explicit solution for average solutes and solvent concentrations can be directly obtained from the ternary model solutions (Eqs. (A.21)–(A.24) of appendix) substituting $a_i = 1$ and $\lambda_i = D_{i\mathrm{pb}}$.

2.3. Binary diffusion model

For a system of one solute in a solvent, the flux is given by Eq. (2) with a diffusion coefficient $D_{i\mathrm{b}}$. For this case $D_{i\mathrm{b}} = D_{i\mathrm{pb}} = D_{ii}$. Equations are those with this change and $a_i = 1$.

3. Experimental and computational method

The experimental system to estimate the lactic acid and NaCl diffusion coefficients, was Pategras cheese. The cheese was elaborated in a commercial factory with lactic ferments (*Streptococcus thermophilus* and *Lactobacillus bulgaricus*) and the curd in 33 cm × 12 cm × 12 cm sieved moulds transported to the laboratory. The moulds were kept in a humidity saturated chamber at 20 °C during 24 h, to reproduce industrial lag conditions before salting, Initial cheese composition was determined. Fat content was assessed using the Standard International Dairy Federation method (IDF 5A, 1969). Total protein content was determined with an automatic digestor model 430, a distillation unit model 322 (Büchi, Flawil, Switzerland). NaCl concentration, was determined following the method indicated by Fox (1963), using an automatic titrator DL40RC (Mettler Instrument AG, Greifensee, Switzerland). Moisture was determined using a microwave oven CEM AVC 80 (CEM, Mattheus, NC, USA) according to the equipment specifications. Cheese samples were assayed for lactic acid, lactose, galactose and glucose by high pressure liquid chromatography (HPLC) (Waters, Millipore, MA, USA) (Gerla, 1994) modifying the technique proposed by Marsili, Ostapenko, Simmons, and Green (1985). All measurements were carried out by triplicate.

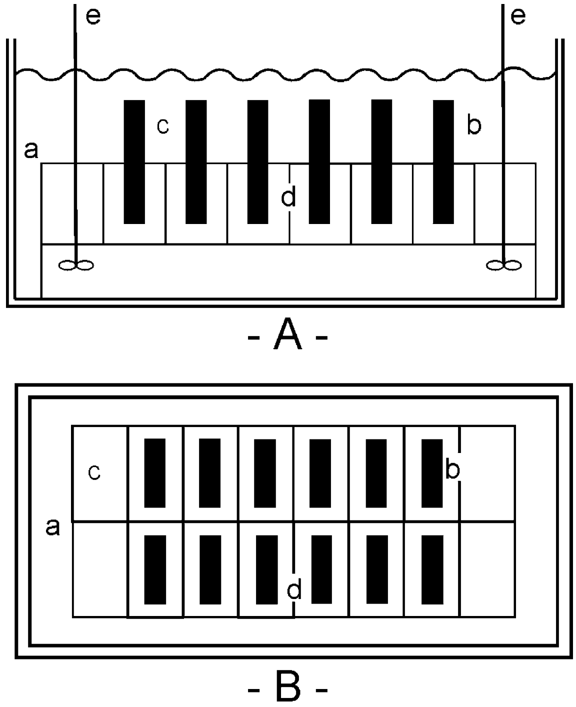

Fig. 1. (A) Schematic cross section view of the experimental A, B and C systems. (B) Schematic upper view of the same experimental systems: (a) immersion bath, (b) foodstuff slabs, (c) solution, (d) support for the foodstuff slabs, (e) agitation system.

Cheeses were cut into rectangular slices (11.1 cm × 9.4 cm) of 1.9 cm thickness (V_S). Cheese slices were immersed in a volume of specific solution five times the solid volume. $CaCl_2$ was added to the correspondent solution in order to get the same concentration of Ca^{2+} that the cheese initially had and the superficial rigidity of the cheese structure during the brining without loss of Ca^{2+} (Geurts et al., 1980). Cl^- contribution from the stirred solution is negligible since the charge equilibrium is maintained. Fig. 1 shows the arrangement used in the experimental system.

The solute concentration in cheese samples was determined at different times. A cheese slice was taken out, cutting from the central zone two cylindrical samples ($\phi = 2$ cm) with a length equal to the thickness of the slice. Cylindrical samples had only two parallel faces that were change solutes with the solution during the immersion time. The remaining slice was returned to the bath to maintain approximated solution level. Simultaneously, a solution volume five times the volume of cylindrical cheese samples, was withdrawn from the bath to keep the relation between solid and solution volumes in the system equal five $(V_L/V_S = 5)$.

Each slice dimension was measured before sampling, verifying that the cheese slab maintains its shape during the brining.

Three tests, A, B and C, with different initial concentrations of solutes in the cheese slices and in the solution were performed in a thermostatic chamber at 13 °C and 90 relative humidity.

For experience A, 13 unsalted cheese slices were immersed for 48 h in a salting solution similar to the industrial process brine (NaCl 20% w/w, $CaCl_2$ 0.5% w/w) and pH = 5.3. The NaCl, lactic acid and were determined.

Experience B was exactly performed as experience A, but without NaCl in the solution being lactic acid and water the principal diffusion components. Concentration values of lactic acid and water in cheese were obtained.

Experience C was performed with the same solution used in experience A but with washed cheese slices (free of lactic acid). These slices, obtained by immersion in water with $CaCl_2$ during 48 h, were salted in the brining solution, so that the diffusion components were NaCl and water. The concentration values of NaCl and water in cheese were determined.

Cylindrical samples from the slab were grounded and assayed for moisture, lactic acid and NaCl average concentration. HPLC determinations in cheese before salting confirmed the absence of sugars (lactose, galactose and glucose) and acids (except lactic acid) in significant concentration and allowed to verify the total lactose hydrolysis and lactic fermentation of sugars before the brining stage in this type of cheese.

Mass transport of solutes is considered one-direction diffusion process in the solid rigid medium for the experimental conditions and with the sampling procedure applied.

Using average concentrations the number of variables was reduced, applying simpler expressions for theoretical models. Another simplification was achieved since both solutes were completely dissolved in the aqueous solution entrapped in the proteic framework of the solid and in the immersion solution. In this case, the partition relation for the solutes i and j results of equal value, $\alpha_i = \alpha_j = \alpha$. Therefore, the number of parameters in equations is reduced to the diffusion coefficients and the partition relation value. Computational programs were developed for non-linear multiparametric regression using the Simplex method based in the Nelder–Mead algorithm for optimization (Kuester & Mize, 1973; Reklaitis, Ravnidran, & Ragsdell, 1983).

Table 1
Average initial composition of cheeses

Component	% (w/w)	Standard deviation
Moisture	45.58	0.01
Protein	27.50	0.36
Fat	23.60	0.15
NaCl	0.14	0.01
Lactic acid	1.31	0.04
Lactose	Not detected	–
Galactose	Not detected	–
Glucose	Not detected	–

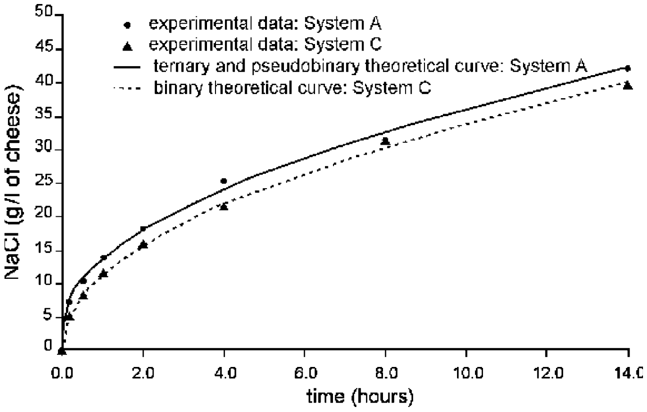

Fig. 2. Experimental data and fitting curve of theoretical models for variation of NaCl average concentration in cheese with immersion time, in ternary and binary systems (A and C). In system A, the theoretical curves for both model are superposed.

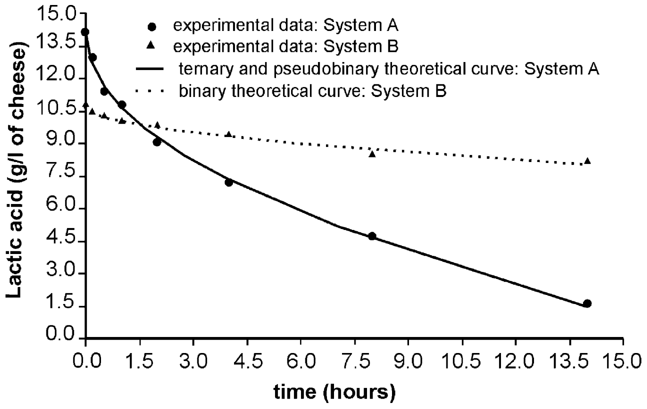

Fig. 3. Experimental data and fitting curve of theoretical models for variation of lactic acid average concentration in cheese with immersion time, in ternary and binary systems (A and B). In system A, the theoretical curves for both model are superposed.

4. Results and discussion

Table 1 shows the initial cheese composition. Figs. 2–4 indicate experimental and theoretical values for solutes and solvent. Table 2 presents the optimization parameters of experiences A, B and C calculated with the corresponding solution equation models for each system. Diffusion coefficients and partition relation values for the ternary and binary experimental systems were obtained after fitness. NaCl diffusion coefficients determined (Table 2) were similar to corresponding values of 3.8×10^{-6} cm^2/s, estimated using cheese composition (Geurts, Walstra, & Mulder, 1974).

The solid size and density variations were detectable after relatively long immersion times. After 72 h, experiences showed maximum difference of 6% in the volume

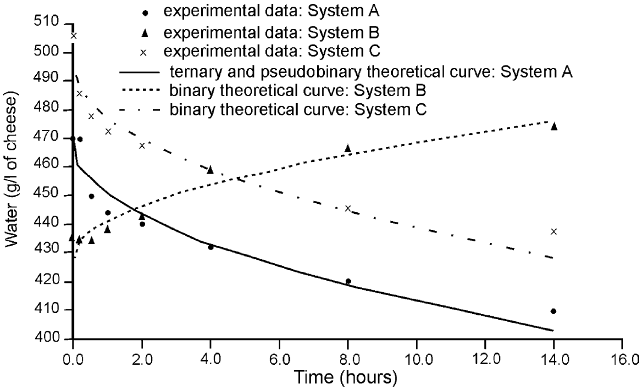

Fig. 4. Experimental data and fitting curve of theoretical models for variation of the solvent (water) average concentration in cheese with immersion time in binary and ternary systems (A, B and C). In system A, the theoretical curves for both model are superposed.

of slices while the density varies less than 2%. When the equilibrium conditions were reached, at least 72 h, the solid volume was different to the initial value, and therefore partition relation. For times shorter than 14 h, the solid thickness ($2S$) is constant. Consequently, in that period the solid is rigid and the density practically constant for diffusion direction.

Table 2 shows a small variation of the partition relation (α), according to effusion or infusion in the solid during different experiences. However, α does not affect the diffusion coefficient since solutions are independent from α values when $\alpha > 10$ (Schwartzberg & Chao, 1982).

The Simplex direct search method was more adequate for fitness than the gradient optimization method or the combination of both. The problem in the last methods were that ternary model solutions converge for infinite trivial solutions when $D_{11} = D_{22}$ and $D_{12} = D_{21} = 0$.

Table 3 shows the equilibrium values obtained from mass balance of solutes in the solid–liquid system with the liquid concentration which variation is practically negligible after 72 h of immersion and α values obtained from the model.

Less than 4% deviations between predicted and experimental values of solutes and solvent average concentrations were obtained. The percent deviation were calculated by:

$$\%d_i = 100\sqrt{\sum_{k=1}^{m}\left[\left(\frac{\bar{x}_{i,\text{calc.}} - \bar{x}_{i,\text{exp.}}}{\bar{x}_{i\,\text{exp.}}}\right)_k\right]^2 \frac{1}{m-1}} \qquad i = 1,2,3 \tag{13}$$

where m is the number of experimental data.

Similar values for solutes and solvent concentrations, calculated through short time solution could be obtained with the function series, when more than 30 terms were used.

A negative value for the cross diffusion coefficient D_{12} and 10^{10} times smaller than the other solutes coefficients (D_{11}, D_{22} and D_{21}) was obtained. Therefore, D_{12} is considered zero with negative sign.

The effective diffusion coefficient for NaCl ($i = 1$) and for lactic acid ($i = 2$) in the solid, shows that:

(1) $(D_{11})_{\text{exp.A}} \approx (D_{1\text{pb}})_{\text{exp.A}};\ (D_{12})_{\text{exp.A}} \to 0^-$
$(D_{22})_{\text{exp.A}} \neq (D_{2\text{pb}})_{\text{exp.A}};\ (D_{21})_{\text{exp.A}} < 0$

(2) $(D_{1\text{b}})_{\text{exp.C}} \approx (D_{11})_{\text{exp.A}}$

(3) $(D_{2\text{b}})_{\text{exp.B}} \approx (D_{22})_{\text{exp.A}}$

Table 2
Diffusion coefficients determined with corresponding theoretical models and different experimental systems[a]

Experimental system	Theoretical model	Percent deviation ($\%d_i$)		Diffusion coefficients ($\times 10^6$ cm^2/s)		Partition relation (α)
		Series solution[b]	Short time solution[c]	Series solution[b]	Short time solution[c]	
A: cheese–brine	Ternary	$\%d_1 = 4.9$	$\%d_1 = 3.2$	$D_{11} = 3.20$	$D_{11} = 3.51$	14.0
		$\%d_2 = 2.4$	$\%d_2 = 3.9$	$D_{22} = 0.93$	$D_{22} = 0.99$	
		$\%d_3 = 1.2$	$\%d_3 = 1.5$	$D_{12} = -0.00$	$D_{12} = -0.00$	
				$D_{21} = -1.15$	$D_{21} = -1.26$	
	Pseudobinary[d]	$\%d_1 = 5.4$	$\%d_1 = 2.7$	$D_{1\text{pb}} = 3.20$	$D_{1\text{pb}} = 3.51$	14.0
		$\%d_2 = 1.7$	$\%d_2 = 3.2$	$D_{2\text{pb}} = 12.8$	$D_{2\text{pb}} = 12.9$	
		$\%d_3 = 1.2$	$\%d_3 = 1.2$			
B: cheese–water	Binary[e]	$\%d_2 = 1.4$	$\%d_2 = 1.4$	$D_{2\text{b}} = 0.96$	$D_{2\text{b}} = 1.09$	12.2
		$\%d_3 = 0.7$	$\%d_3 = 0.7$			
C: washed cheese–brine	Binary[e]	$\%d_1 = 2.6$	$\%d_1 = 2.1$	$D_{1\text{b}} = 3.25$	$D_{1\text{b}} = 3.79$	14.6
		$\%d_3 = 1.1$	$\%d_3 = 1.0$			

[a] 1: NaCl; 2: lactic acid and 3: solvent (water).
[b] Series solutions truncated at 30 terms (Eq. (A.21)).
[c] Short time solution (Eq. (A.23)).
[d] Pseudobinary solution: $a_i = 1$, $\lambda_i = D_{i\text{pb}}$ in Eq. (A.21) or Eq. (A.23).
[e] Binary solution: $a_i = 1$, $\lambda_i = D_{i\text{b}}$ in Eq. (A.21) or Eq. (A.23).

Table 3
Equilibrium concentrations in solid and liquid phases of the experimental systems

Experimental system	Solutes and solvent equilibrium concentrations 10^3 (g/cm^3)						Partition factor k^a
	Solid phase			Liquid phase			
	NaCl	Lactic acid	Water	NaCl	Lactic acid	Water	
A: cheese–brine	81.2	0.94	308.5	226.8	2.64	948.5	2.80
B: cheese–water	–	0.92	601.1	–	2.23	998.1	2.46
C: washed cheese–brine	76.7	–	367.9	224.3	–	942.9	2.92

[a] $k = \alpha/(V_L/V_S)$; (g solute in liquid phase/cm^3 of liquid solution)/(g solute in solid phase/cm^3 of solid).

The NaCl diffusion coefficients values that results for A ($D_{11} = D_{1pb}$; $D_{12} \rightarrow 0$) indicate that the NaCl diffusion occurs exclusively under its own concentration gradient showing similar values of D_{11} and D_{1b}. NaCl concentration changes in experiences A and C (Fig. 2), indicates that the solute behaviour is practically equal in both systems.

D_{21}, the negative interaction coefficient for lactic acid, and the main lactic acid diffusion coefficient, D_{22}, are values of the same order. Therefore, due to the NaCl large concentration gradient, the counter-diffusion process is an important contribution to the lactic acid total flux.

The experimental system A, is a non-reciprocal interaction case, since only acid lactic flux, J_2, is changed due to the gradient of NaCl in the system, ∇x_1. The concentration gradients, ∇x_1 and ∇x_2, have opposite signs, then, in the total flux the terms J_{1b} and J_{2b} have opposite directions.

Results in Fig. 3, shows a diffusion rate of the lactic acid in system A higher than in system B. This experimental conclusion is in agreement with the multicomponent diffusion theory, that relates the main and cross diffusion coefficients for ternary model, D_{22} and D_{21}, with the coefficient for pseudobinary model, D_{2pb}, by the following expression obtained from Eqs. (1)–(4):

$$D_{2pb} = D_{21}\frac{\nabla x_1}{\nabla x_2} + D_{22} \qquad (14)$$

Therefore, D_{2pb} was 12 times higher than D_{22} in experimental system A, or D_{2b} in experimental system B, which are diffusion coefficients of lactic acid flux exclusively under its own gradient.

The lactic acid concentration in the cheese used in experience B (Fig. 3) was smaller in the beginning of salting (short time test) because water in these cheese was also smaller than in the samples of experience A. The whey remained in the curd after pressing was different, 43.5% w/w in experience B and 46.9% w/w in experience A, according loading on the cheeses in the production process. Therefore lactic acid concentrations in the solid moisture were very similar, 24.9 and 29.6 g/l respectively, but different in the whole solid for the different cheeses.

In Eq. (14) the negative gradient ratio is multiply by the negative cross diffusion coefficient D_{21}, while D_{22} is always positive, resulting for system A that $D_{2pb} > D_{22} > 0$. The increase in the lactic acid diffusion rate was also detected by Chu et al. (1992), although not determined, in the study of the pH influence in the lactic fermentation of gels containing NaCl.

Results obtained from systems A and C show that the diffusion rate of NaCl is independent from the lactic acid gradient in the solid and there were no errors for salt concentration estimated with a binary model.

For the flux of water, common solvent to both phases, the mass balance in system A is:

$$J_3 = -(J_1 + J_2) \qquad (15)$$

The solvent net flux, J_3, is opposite to the net flux, $J_1 + J_2$, of the solutes 1 and 2. In system A, solutes are in counter diffusion and therefore, J_3 is opposite to the highest solute flux. In the counter-diffusion process during cheese salting studied in this work, the NaCl concentration gradient is clearly higher than the lactic acid gradient and the NaCl flux is which determines the water variation in the solid. Fig. 4 shows theoretical curves and experimental values for the water concentration variation in cheese at experience A, B and C.

5. Conclusions

Solutes effective diffusion coefficients in the solid were obtained. The effect of their interactions among solutes in the flux on the ternary system A was determined. There was a strong interaction of NaCl on lactic acid flux but, a reciprocal effect was not detected. Therefore, D_{2pb} is strongly dependent on the NaCl concentration gradient, ∇x_1 but the cross coefficient D_{12} is zero, then, D_{11}, D_{1pb} and D_{1b}, for NaCl are almost equal and independent of the lactic acid concentration gradient, ∇x_2 and consequently independent of gradients of all solutes in the system.

The main and cross effective diffusion coefficients for NaCl and lactic acid, D_{11}, D_{22}, D_{12} and D_{21}, determined by the ternary models can be used to predict concentrations for similar systems with different initial conditions and fluxes.

The experimental process considered in this work showed that a solute in low concentration as lactic acid, presented a larger variation due to the driving force of another solute gradient, which is in a high concentration in the system. Therefore, in processes involving simultaneous diffusion of solutes, the largest solute gradient can cause concentration changes on the minor solutes, which are important for the sensorial properties of the food product.

The method, based on the use of average experimental concentrations data with multicomponent equation models fitted with a computational optimization system, described in this work, allows to obtain the diffusion coefficients and a phenomenological description of the mass transfer process, specially for minor components, being able to apply it in other solid–liquid systems.

Appendix A

For ternary mass transfer model, the PDE system is:

$$\partial x_i/\partial\theta = \sum_{j=1}^{2} D_{ij}\nabla^2 x_j \quad i,j = 1,2 \tag{A.1}$$

considering D_{ij} independent of the concentration.

For one-dimensional diffusion in a solid slab of thickness $2S$, $-S \leqslant r \leqslant S$, in a solution volume limited by $-S-L < r < -S$ and $S < r < S+L$, Eq. (A.1) becomes:

$$\partial x_i/\partial\theta = \sum_{j=1}^{2} D_{ij}\partial^2 x_j/\partial^2 r \quad -S < r < S,\ \theta > 0,\quad i,j = 1,2 \tag{A.2}$$

with the following initial and boundary conditions:

$$x_i = x_{i_0} \quad -S < r < S,\ \theta = 0,\ i = 1,2 \tag{A.3}$$

$$\alpha_i(\partial x_i/\partial\theta) = \pm\sum_{j=1}^{2}(D_{ij}/S)(\partial x_i/\partial r) \quad r = \pm S,\ \theta > 0,\quad i = 1,2 \tag{A.4}$$

$$\partial x_i/\partial r = 0 \quad r = 0,\ \theta > 0,\ i = 1,2 \tag{A.5}$$

where the partition relation, α_i, is k_i (V_L/V_S), being V_S and V_L the solid and solution volumes for a rigid solid with constant density and k_i the solute partition factor.

The PDE, can be transformed using the eigenvalue and eigenvector matrixes method developed by Toor (1964), resulting a PDE linearized system in transformed variables ψ_i, equivalent to a set of binary uncoupled problems for each value of i, as follows:

$$\partial\psi_i/\partial\theta = \lambda_i\partial^2\psi_i/\partial r^2 \quad i = 1,2 \tag{A.6}$$

with the transformed initial and boundary conditions:

$$\psi_i = \psi_{i_0} \quad -S < r < S,\ \theta = 0,\ i = 1,2 \tag{A.7}$$

$$\alpha_i(\partial\psi_i/\partial\theta) = \pm(\lambda_i/S)(\partial\psi_i/\partial r) \quad r = \pm S,\ \theta > 0,\ i = 1,2 \tag{A.8}$$

$$\partial\psi_i/\partial r = 0 \quad r = 0,\ \theta > 0,\ i = 1,2 \tag{A.9}$$

where λ_i are the eigenvalues associated to the matrix of elements D_{ij}, that verifies:

$$|D_{ij} - \lambda_i\delta_{ij}| = 0 \tag{A.10}$$

where δ_{ij} is Kronecker's delta.

The solution of PDE system in the original variables (concentrations and diffusion coefficients D_{ij}), is obtained by the inverse transformation of the solution $\psi_i = f_i(\lambda_i)$ of the problem (Eqs. (A.6)–(A.9)), which is achieved multiplying the ψ_i solution by the eigenvector matrix associated with the diffusion coefficients matrix. The general solution in the original variables is given by:

$$\Delta x_i = \sum_{j=1}^{2} f_i(D_{ij})\Delta x_{i_0} \quad i,j = 1,2 \tag{A.11}$$

where

$$\Delta x_i = x_i - x_{i_\infty} \quad i = 1,2 \tag{A.12}$$

$$\Delta x_{i_0} = x_{i_0} - x_{i_\infty} \quad i = 1,2 \tag{A.13}$$

identifying with subscripts "0" and "∞" the initial and the equilibrium conditions respectively.

If the eigenvalues λ_i are different, the function $f_i(D_{ij})$ in Eq. (9) is obtained applying the Sylvester's theorem to the solutions $f_i(\lambda_i)$ of the set of binary problems Eqs. (A.6)–(A.9) (Frazer & Collar, 1965):

$$f_i(D_{ij}) = \sum_{k=1}^{2} f(\lambda_k)\frac{\prod_{\substack{j=1\\ j\neq k}}^{2}(\lambda_j\delta_{ij} - D_{ij})}{\prod_{\substack{j=1\\ j\neq k}}^{2}(\lambda_j - \lambda_k)} \quad i = 1,2 \tag{A.14}$$

where k is a auxiliary subindex.

In a similar form it can be obtained the average solution $\bar{f}_i(D_{ij})$ by substituing in Eq. (A.14) $f(\lambda_k)$ by its average value $\bar{f}(\lambda_k)$. The coefficients of $\bar{f}(\lambda_k)$ will be the same and named a_k. The solution in the transform variables is (Carslaw & Jaeger, 1959; Crank, 1975):

$$\bar{f}(\lambda_i) = \sum_{n=1}^{\infty} C_{n_i}\mathrm{e}^{-\lambda_i\beta_{n_i}\theta} \quad i = 1,2 \tag{A.15}$$

where

$$C_{n_i} = \frac{2\alpha_i(1+\alpha_i)}{1+\alpha_i+\alpha_i^2 q_{n_i}^2} \quad i = 1,2;\ n = 1,\ldots,\infty \tag{A.16}$$

$$\beta_{n_i} = q_{n_i}^2/S^2 \quad i = 1,2; \; n = 1,\ldots,\infty \tag{A.17}$$

$$\tan q_{n_i} = -\alpha_i q_{n_i} \quad i = 1,2; \; n = 1,\ldots,\infty \tag{A.18}$$

being q_{n_i} the non-zero positive roots of Eq. (A.18).

An alternative solution with the advantage of fast convergence for short salting times, is:

$$\bar{f}(\lambda_i) = 1 - (1+\alpha_i)\left[1 - \mathrm{eerfc}\sqrt{\lambda_i\theta/(\alpha_i S)^2}\right] \quad i = 1,2 \tag{A.19}$$

where

$$\mathrm{eerfc} = \mathrm{e}^{z^2}\mathrm{erfc}(z) \quad \text{with} \quad z = \sqrt{\lambda_i\theta/(\alpha_i S)^2} \tag{A.20}$$

and substituting in the integrated form of the Eq. (A.11), the explicit solution for the average concentration of each solutes is obtained as:

$$\frac{\Delta\bar{x}_i}{\Delta\bar{x}_{i_0}} = a_i\sum_{n=1}^{\infty} C_{n_i}\mathrm{e}^{-\lambda_i\beta_{n_i}\theta} + (1-a_i)\sum_{n=1}^{\infty} C_{n_j}\mathrm{e}^{-\lambda_j\beta_{n_j}\theta}$$
$$i,j = 1,2; \; i \neq j \tag{A.21}$$

and for the solvent results:

$$\frac{\Delta\bar{x}_3}{\Delta\bar{x}_{3_0}} = \sum_{i=1}^{2}\left[a_i\sum_{n=1}^{\infty} C_{n_i}\mathrm{e}^{-\lambda_i\beta_{n_i}\theta} + (1-a_i)\sum_{n=1}^{\infty} C_{n_j}\mathrm{e}^{-\lambda_j\beta_{n_j}\theta}\right] \times \frac{1}{(1+b_{ji})} \quad i,j = 1,2; \; i \neq j \tag{A.22}$$

The alternative explicit expressions of average concentration solutions for short process times are obtained by susbstituing Eq. (A.19) in the integrated form of Eq. (A.11), resulting:

$$\frac{\Delta\bar{x}_i}{\Delta\bar{x}_{i_0}} = a_i\left[1 - (1+\alpha_i)\left[1 - \mathrm{eerfc}\sqrt{\lambda_i\theta/(\alpha_i S)^2}\right]\right] + (1-a_i)\left[1 - (1+\alpha_j)\left[1 - \mathrm{eerfc}\sqrt{\lambda_j\theta/(\alpha_j S)^2}\right]\right]$$
$$i,j = 1,2; \; i \neq j \tag{A.23}$$

$$\frac{\Delta\bar{x}_3}{\Delta\bar{x}_{3_0}} = \sum_{i=1}^{2}\left[a_i\left[1 - (1+\alpha_i)\left[1 - \mathrm{eerfc}\sqrt{\lambda_i\theta/(\alpha_i S)^2}\right]\right] + (1-a_i)\left[1 - (1+\alpha_j)\left[1 - \mathrm{eerfc}\sqrt{\lambda_j\theta/(\alpha_j S)^2}\right]\right]\right] \times \frac{1}{(1+b_{ji})} \quad i,j = 1,2; \; i \neq j \tag{A.24}$$

For pseudobinary-diffusion mass transfer model, the PDE system is:

$$\partial x_i/\partial\theta = D_{i\mathrm{pb}}\nabla^2 x_i \quad i = 1,2 \tag{A.25}$$

where $D_{i\mathrm{pb}}$ is assumed constant by the model, but it is strictly function of the concentration gradients of the others solutes in the system.

The PDE system is formally equal to the one expressed in Eqs. (A.6)–(A.9). They are two independent problems with the same functional form for the both solutes, and consequently the pseudobinary problem solution will be the same, when the following substitutions are made:

$\psi_i, \psi_{i0}, \psi_{i\infty}$ by $x_i, x_{i0}, x_{i\infty}$ $\quad i = 1,2$

$\bar{\psi}_i,$ by $\bar{x}_i$ $\quad i = 1,2$

λ_i by $D_{i\mathrm{pb}}$ $\quad i = 1,2$

The solution of the pseudobinary model for the ternary system average concentrations, can be directly obtained from Eq. (A.15) or Eq. (A.19) changing the corresponding variables.

References

Bailey, J. E. (1975). Diffusion of grouped multicomponent mixtures in uniform and nonuniform media. *American Institute of Chemical Engineering Journal, 21*, 192–194.

Bressan, J. A., Carroad, P. A., Merson, L., & Dunkley, W. L. (1981). Modelling of isothermal diffusion of whey components from small curd Cottage cheese during washing. *Journal of Food Science, 47*, 84–88.

Carslaw, H. S., & Jaeger, J. C. (1959). *Conduction of heat in solids*. London: Clarendon Press.

Chu, C. L., Speiss, W. E., & Wolf, E. (1992). Diffusion of lactic acid in gels. *Lebensmittel Wissenschaft und Technology, 25*, 470–475.

Crank, J. (1975). *The mathematics of diffusion*. London: Oxford University Press.

Cussler, E. L., & Lightfoot, E. N. (1963). Multicomponent diffusion in semi-infinite systems. *American Institute of Chemical Engineering Journal, 9*, 783–785.

Cussler, E. L. (1976). *Multicomponent diffusion*. Amsterdam: Elsevier.

Fox, P. F. (1963). Potentiometric determination of salt in cheese. *Journal of Dairy Science, 46*, 744–745.

Fox, P. F. (1987). *Cheese chemistry, physics and microbiology: general aspects* (Vol. 1). London: Elsevier.

Frazer, R. A., & Collar, A. R. (1965). *Elementary matrix and its applications to dynamics and differential equations*. London: Cambridge University Press.

Gerla, P. (1994). *Modelado del cambio de concentración de ácido láctico, cloruro de sodio y agua en el salado de queso.* Ph.D. Thesis, Universidad Nacional del Litoral, Santa Fe.

Geurts, T. J., Walstra, P., & Mulder, H. (1974). Transport of salt and water during salting of cheese. 1. Analysis of the processes involved. *Netherlands Milk Dairy Journal, 28*, 102–129.

Geurts, T. J., Walstra, P., & Mulder, H. (1980). Transport of salt and water during salting of cheese. 2. Quantities of salt taken up and of moisture lost. *Netherlands Milk Dairy Journal, 34*, 229–254.

IDF (1969). Determination of the fat content of cheese and of processed cheese products. *IDF Standard 5A*. Brussels, Belgium: International Dairy Federation.

Kuester, J. L., & Mize, J. H. (1973). *Optimization techniques with fortran*. New York: MacGraw-Hill.

Luna, J., & Bressan, J. (1986). Mass transfer during brining of Cuartirolo Argentino cheese. *Journal of Food Science, 51*, 829–831.

Lawrence, R. C., & Gilles, J. (1982). Factors that determine the pH of young Cheddar cheese. *New Zealand Journal of Dairy Science Technology, 17*, 1–14.

Marsili, R., Ostapenko, H., Simmons, R. E., & Green, D. E. (1985). High performance liquid chromatographic determination of organic acids in dairy products. *Journal of Food Science, 46*, 52–57.

Reklaitis, G., Ravnidran, A., & Ragsdell, K. M. (1983). *Engineering optimization: methods and applications*. New York: John Wiley & Sons.

Schwartzberg, H. G., & Chao, R. Y. (1982). Solute diffusivities in leaching processes. *Food Technology, 36*, 73–86.

Toor, H. L. (1964). Solution of the linearized equations of multicomponent mass transfer: II. Matrix methods. *American Institute of Chemical Engineering Journal, 10*, 460–465.

Turhan, M., & Kaletunç, G. (1992). Modelling the salt diffusion during long-term brining. *Journal of Food Science, 57*, 1082–1085.

Zorrilla, S. E., & Rubiolo, A. C. (1994). A model for using the diffusion cell in the determination of multicomponent diffusion coefficients in gels or foods. *Chemical Engineering Science, 49*, 2123–2128.