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Effective moisture diffusivity modelling versus food structure and hygroscopicity

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Abstract

Effective moisture diffusivities (D_{eff}) for model food systems presenting distinct structure and water sensibility were identified at various levels of hydration. Experimental moisture sorption kinetics with a controlled atmosphere microbalance were analyzed using distinct Fickian models with specific assumptions. Taking into account the deformation and the external resistance to mass transfer, higher values of D_{eff} were identified specially for hygroscopic dense products in the range of high water activity. The difference of impact of the model assumptions on D_{eff} depending on the investigated water activity range and food material was related to the structure and the equilibrium moisture sorption properties.

Keywords: Effective moisture diffusivity; Moisture sorption isotherm; Food structure

1. Introduction

The determination of the water diffusion coefficient in food products is based on the processing of experimental data. Moisture diffusivity is identified by adjusting to experimental moisture contents the calculated ones, using an appropriate Fickian model with specific boundary conditions representing water transport in the studied food system. As Fickian models are not strictly representative of the various prevailing mechanisms of water transport in food products, the identified diffusion coefficient is considered as an apparent or effective diffusivity (D_{eff}). Several experimental sets-up can be performed to generate water flow, with various water sources, temperatures conditions and sample sizes and geometries, as presented in the literature (Boudhrioua, Bonazzi, & Daudin, 2003; Doulia, Tzia, & Gekas, 2000; Zogzas, Maroulis, & Marinos-Kouris, 1994). Water migration in food products are then characterized by following the global flow rate as a function of time, or by following the local moisture content as a function of distance and time (concentration profiles methods). This diversity of experimental sets-ups and methods for water flow characterization are proved to give rise to serious variations of identified values of D_{eff}, even for a same product (Zogzas, Maroulis, & Marinos-Kouris, 1996). Another aspect affecting D_{eff} is the deformation or the changes of texture and chemical composition of materials induced during water migration, particularly in the case of desorption at high temperature experiments (drying). These structural changes are not always taken into account in the models.

Among all the investigated techniques, evaluation of moisture sorption or desorption kinetics under constant

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Nomenclature

a_w	water activity
D_{eff}	effective moisture diffusivity (m^2/s)
ξ	Lagrangian coordinate (m)
k_{mass}	external mass transfer coefficient (m/s)
L	thickness of the slab (m)
M_W	molar mass of water (18×10^{-3} kg mol^{-1})
η	modified space coordinate (m)
p_{va}	water vapour pressure of air (Pa)
p_{vsat}	saturated water vapour pressure (Pa)
R	perfect gas constant (8.314 J mol^{-1} K^{-1})
ρ^0_{dm}	dry matter density (kg m^{-3})
ρ^0_x	water density (kg m^{-3})
t	time (s)
T	temperature (K)
X	moisture content (kg kg^{-1} dry matter)
X_∞	equilibrium moisture content (kg kg^{-1} dry matter)
X_0	initial moisture content (kg kg^{-1} dry matter)
x	Eulerian coordinate (m)

water vapour concentration using controlled atmosphere microbalances offers the advantage of inducing very little alterations of materials. Indeed, materials are submitted to gentle temperature conditions and low water flow, leading to little degradation and deformation, but also to little air velocity, which can enhance a significant external resistance to mass transfer. Using controlled atmosphere microbalances, D_{eff} of varying food products were successfully identified from analytical resolution of Fick's second law (Guillard, Broyart, Bonazzi, Guilbert, & Gontard, 2003; Roman-Gutierrez et al., 2002). Analytical resolutions of Fick's second law have been largely used for D_{eff} estimation in food products. They involve simplifying assumptions, like simple material geometries without deformation, classical boundary conditions (i.e. negligible external mass transfer resistance at the interface) and constant or linear variations of D_{eff} (Crank, 1975). Nevertheless, some studies pointed out that these assumptions may influence significantly the predicted D_{eff}, even using the same experimental data. Zogzas and Maroulis (1996) observed important differences on the analysis of experimental drying data depending on the assumptions of the models used, with best predictions for more detailed models. Similar observations were done by Teixeira and Tobinaga (1998) determining D_{eff} in squid mantle with a numerical solution accounting for shrinkage. Other important assumptions affecting effective moisture diffusivity values concern boundary conditions. Gaston, Abalone, Giner, and Bruce (2004) described better predictions of wheat drying kinetics with a mathematical model considering time-varying surface moisture content as compared to a model assuming instantaneous equilibrium of the material surface. Indeed, when neglecting the external mass transfer coefficient, the resulting calculated moisture diffusion coefficients account both for internal and external resistance to moisture transfer, leading to lower values. Theses studies prove the importance of using models describing accurately the specific interfacial conditions or matrix deformation for D_{eff} determination. In addition, it is well-known that the physical and physicochemical structure of food products also plays a decisive role on water transport mechanisms and on D_{eff} (Aguilera, 2005). Saravacos and Maroulis (2001) reported typical values of D_{eff} depending on the food structure and hygroscopicity, varying from 50 to 0.01×10^{-10} m^2/s.

As simplifying assumptions made in analytical resolutions of Fick's second law may not be sufficient for the processing of water sorption experiments using a controlled atmosphere microbalance, more detailed models should be developed for D_{eff} determination. With this objective, the dependence of D_{eff} on two specific assumptions was evaluated: the hypothesis made for the description of product deformation and the hypothesis made for external mass transport phenomena. The validity of these hypotheses of water transport has been investigated at various levels of hydration for model food systems presenting distinct structure and water sensibility:

- Dense liquid-crystalline lipidic products.
- Dense amorphous hydrophilic products.
- Solid dispersion in a dense matrix.
- Porous products.

2. Materials and methods

2.1. Model food systems

Four model food systems were investigated, with varying structure and water sorption behaviours:

- *Dense liquid-crystal lipidic system*, modelled by an acetylated monoglycerides matrix (density 890 ± 43 kg dry matter/m^3; Danisco Ingredients, Trappes, France). The material was melted at 70 °C over 10 min, laminated at thickness 0.20 ± 0.02 mm using a film-making apparatus (Braive instrument, Chévy, France) onto a hot steel plate covered with greaseproof paper sheets and solidified at room temperature.
- *Dense amorphous hydrophilic system*, simulated by a wheat gluten network. A solution was elaborated, constituted of wheat gluten (concentration: 15 g/100 ml-vital wheat gluten, Amylum Aquitaine, Bordeaux, France), of ethanol (concentration: 32 ml/100 ml – 95%, Carlo Erba, Val de Reuil, France), glycerol (concentration:

3 g/100 ml – 95%, Merck, Darmstadt, Germany), acetic acid (100%, Carlo Erba) to adjust pH of the solution to 4 and distilled water. It was poured onto polyvinyl chloride plates, dispersed with a film-making casting knife and dried at room temperature. Average thickness of wheat gluten systems equilibrated at a_w 0 was 0.053 ± 0.007 mm and density 995 ± 38 kg dry matter/m^3.

- *Solid dispersion in a dense matrix*, represented by dark chocolate (Barry Callebaut, Meulan, France). It was constituted of cocoa liquor (17.4 g/100 g wet basis (w.b.)), sugar (36.7 g/100 g w.b.), cocoa butter (45 g/100 g w.b.), emulsifier (<1 g/100 g w.b.) and vanillin (<1 g/100 g w.b.). The paste was tempered as described by Biquet and Labuza (1988), laminated at 31 °C onto a steel plate at room temperature covered with grease-proof paper sheets and solidified at room temperature. Average thickness of dark chocolate systems equilibrated at a_w 0 was 0.45 ± 0.05 mm and density 1750 kg dry matter/m^3.
- *Porous hydrophilic system*, simulated by a laboratory-made sponge cake. Sponge cakes were constituted of flour (100 g flour-T45; Moulin de Sauret, Montpellier, France), of sugar (100 g-Beghin Say, Thumeries, France), of whole egg powder (40 g-Igreca, Seiches-sur-le-Loir, France), of water (86.6 g) and of salt (1.3 g). Sponge cakes were prepared as described by in recent literature (Roca, Broyart, Guillard, Guilbert, & Gontard, 2007). They were baked in an electric oven for 20 min at 180 °C and were allowed to cool at 20 °C for 1 h. They were frozen at −18 °C for long-term storage (4–6 months) in water-impermeable, polyvinylidene chloride bags (Avenir Complexage Service, St.-Varent, France) and before experiments, they were slowly thawed to 5 °C and kept for 7 days at 5 °C to allow moisture redistribution. Average thickness of sponge cake slices equilibrated at a_w 0 was 2.84 ± 0.09 mm and density 190 ± 4 kg dry matter/m^3.

2.2. Scanning electron microscopy (SEM)

The structure of the model food systems was observed by Scanning Electronic Microscopy (JSM-6300-F, JEOL, Japan). The samples were dried over P_2O_5 for at least 5 days. They were mounted into 13 mm diameter aluminium stubs using double-sided adhesives tape and coated with 5–10 nm thick metal (platinum). They were scanned by a focused electron beam, which intensity was adjusted for better contrast of the images (15 kV for sponge cake and 5 kV for temperature-sensitive materials). Magnification was adjusted to each product according to their structure: 1000× for dense materials and 20× for sponge cake.

2.3. Moisture sorption kinetics

Moisture sorption kinetics experiments were performed at 20 °C using a controlled atmosphere microbalance (Dynamic Vapour Sorption (DVS) apparatus; Surface Measurement System Ltd., London, UK) as previously described in the literature (Guillard et al., 2003; Roca et al., 2007). The DVS apparatus allows recording of mass evolution with time as a function of relative humidity of air. In practice, successive relative humidity steps (from 0 to 98%, with 10% step up to 70% and 5% step beyond) were performed for a same product sample and the remoistening kinetics was followed step by step until equilibrium between material and surrounding atmosphere was reached. Moisture sorption isotherms were determined from the equilibrium moisture contents at each relative humidity step. Constant values of effective moisture diffusivity at each relative humidity step were identified from experimental sorption kinetics by minimizing the root mean square deviations between simulated and experimental results using the Levenberg–Marquardt procedure (Gill, Murra, & Wright, 1981). Effective moisture diffusivity was assumed to be constant along each relative humidity step since differences between relative humidity from one stage to another were small.

2.4. Modelling moisture transport phenomena

Depending of the assumptions made for the description of product deformation and external mass transfer phenomena, four alternative models were developed in order to predict moisture migration inside products and between products and environment and hence to determine the effective moisture diffusivity.

Considering the description of the influence of water uptake upon the state of deformation of the product, two different assumptions were made. First, the volume of the product was assumed to remain constant during water sorption (no deformation hypothesis). Second, the solid structure of the product was assumed to instantaneously swell depending on the local value of moisture content (simplified deformation hypothesis): in this case, the volume occupied by both liquid and solid phases was assumed to be equal to the sum of partial volume occupied by each phase. The thermodynamic state of the product is assumed independent of its state of mechanical stress. Equations describing mass transport phenomena were hence written in a referential (ξ,t) moving at the velocity of the solid phase. Lagrangian coordinate ξ is related to the dry matter on the main direction of mass transport (Boudhrioua et al., 2003).

Considering the description of external moisture transfer (between the product surface and the surrounding environment), two different assumptions were made. First, the external resistance to mass transfer was neglected. The product surface moisture content was hence assumed constant during water sorption and equal to the equilibrium moisture content for the relative humidity of air (no external resistance hypothesis). Second, the external resistance to mass transfer was taken into account using an external mass transfer coefficient (k_{mass}, in m/s) expressing the resistance of diffusion through the mass transfer boundary layer for the vapour emitted by the product surface (external resistance hypothesis). The external mass transfer coefficient was chosen equal to 8.165×10^{-3} m/s ($\pm 0.487 \times 10^{-3}$) as described by Roca et al. (2007).

Combining these different assumptions, four models were developed for describing mass transport during moisture sorption experiments:

Model (1): no deformation and no external resistance to mass transfer.
Model (2): deformation but no external resistance to mass transfer.
Model (3): external resistance to mass transfer but no deformation.
Model (4): deformation and external resistance to mass transfer.

For all the models, the system is assumed to be composed of a continuous aqueous phase moving through a solid phase (so called dry matter). A Fickian formalism with a constant moisture apparent diffusivity is used. Whatever the hypotheses chosen for describing product deformation and product external mass transfer, the mass conservation equation in our system can be written as:

$$\left(\frac{\partial X}{\partial t}\right) = \frac{\partial}{\partial \eta}\left(D^{*}_{\text{eff}}\frac{\partial X}{\partial \eta}\right) \quad \text{for } 0 \leqslant \eta \leqslant \eta_{\max}\ \forall t \tag{1}$$

$$-D^{*}_{\text{eff}}\left(\frac{\partial X}{\partial \eta}\right) = 0 \quad \text{for } \eta = 0\ \forall t \tag{2}$$

where η and D^{*}_{eff} are respectively the modified space coordinate (m) and modified apparent diffusivity (m^2/s) whose expressions depend on the hypothesis chosen to describe the product deformation. The hypothesis chosen to describe the external mass transfer phenomena influence the nature of the boundary condition at $\eta = \eta_{\max}$. For the four mass transport models developed, the expressions for η and for the boundary condition at the surface of the product can be found in Table 1. Deff stands for the effective diffusivity (m^2/s) and ρ_{dm}, ρ^0_{dm} and ρ^0_{x} stand, respectively, for dry matter concentration in the binary mixture (kg m^{-3}), pure dry matter and pure water intrinsic densities (kg m^{-3}). When the hypothesis of simplified deformation is retained, the Eulerian coordinates x_i corresponding to Lagrangian coordinate ξ_i is recalculated following:

$$x_{\text{i}} = \int_0^{\xi_i}\left(1 + \frac{\rho^0_{\text{dm}}}{\rho^0_{\text{x}}}X\right)\mathrm{d}\xi \tag{3}$$

2.5. Solving procedure

Concerning model (1), with assumption of no deformation and no external resistance to mass transfer, Eq. (1) can be solved analytically for the case of an infinite slab and the evolution of moisture contents with time is given by Crank (1975):

$$\frac{X - X_\infty}{X_0 - X_\infty} = \frac{8}{\pi^2}\sum_{\text{n}=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\frac{\pi^2 D_{\text{eff}}t}{L_2}\right] \tag{4}$$

where X is moisture content (g/g), X_∞ equilibrium moisture content (g/g), X_0 initial moisture content (g/g), D_{eff} effective moisture diffusivity (m^2/s), t time (s) et L thickness of the slab (m).

If moisture transport occurs only from one surface of the slab, the thickness must be substituted by $2L$.

Concerning models (2), (3) and (4), with assumption of deformation and/or external resistance, Eq. (1) was solved numerically. The domain $0 \leqslant \eta \leqslant \eta_{\max}$ is divided into, respectively, N sub regions of equal thickness $\Delta\eta = \eta_{\max}/N$. The first and second-order spatial derivatives of the previous system of equations are then discretized using three-point central difference formula (Ozisik, 1994). For example, the second-order derivation in Eq. (1), once discretized, takes the form:

$$\frac{\mathrm{d}X_{\text{i}}}{\mathrm{d}t} = \frac{D^{*}_{\text{eff,i}-1} + D^{*}_{\text{eff,i}}}{2\Delta\eta^2}(X_{i-1} - X_{\text{i}}) + \frac{D^{*}_{\text{eff},i} + D^{*}_{\text{eff,i}+1}}{2\Delta\eta^2} \times (X_{i+1} - X_i) \tag{5}$$

The previous system of partial differential equations consist now of a differential-algebraic system of N equations

Table 1
Assumptions of the investigated models for effective moisture diffusivity estimation

Model 1	Model 2	Model 3	Model 4
Nature of hypotheses			
No deformation	Simplified deformation	No deformation	Simplified deformation
No external resistance	No external resistance	External resistance	External resistance
$\eta = x$	$\eta = \xi$	$\eta = x$	$\eta = \xi$
Eulerian coordinate	Lagragian coordinate	Eulerian coordinate	Lagragian coordinate
$D^{*}_{\text{eff}} = D_{\text{eff}}$	$D^{*}_{\text{eff}} = \frac{D_{\text{eff}}}{(1+(\rho^0_{\text{dm}}/\rho^0_{\text{x}})X)^2}$	$D^{*}_{\text{eff}} = D_{\text{eff}}$	$D^{*}_{\text{eff}} = \frac{D_{\text{eff}}}{(1+(\rho^0_{\text{dm}}/\rho^0_{\text{x}})X)^2}$
Boundary condition at $\eta = \eta_{\max}\ \forall t$			
$X = X_\infty$	$X = X_\infty$	$-\rho_{\text{dm}}D_{\text{eff}}(\partial X/\partial x) = \cdots\frac{h_{\text{m}}M}{RT}(a_{\text{w}}p_{\text{vsat}} - p_{\text{va}})$	$\frac{-\rho^0_{\text{dm}}D_{\text{eff}}(\partial X/\partial\xi)}{(1+(\rho^0_{\text{dm}}/\rho^0_{\text{x}})X)^2} = \cdots\frac{h_{\text{m}}M}{RT}(a_w p_{\text{vsat}} - p_{\text{va}})$
Mathematical resolution			
Analytical solution	Numerical solution	Numerical solution	Numerical solution

solved using a specific algorithm developed in Matlab® and dedicated to the solving of this type of system of equations (corresponding Matlab built-in function *ode15s*).

3. Results

3.1. Characterization of the model food systems

Moisture sorption isotherms of the investigated model food systems were determined at 20 °C using a controlled atmosphere microbalance. Results are presented in Fig. 1. The four materials investigated were representative of 3 classes of food products according to their equilibrium moisture sorption properties (Iglesias & Chirife, 1982). Sponge cake and wheat gluten presented the classical sigmoid shape of moisture sorption isotherms of hydrocolloid-based products, with high adsorption for water activity above 0.90. Similar curves were observed for cereal-based food products (Kim, Kim, Kim, Shin, & Chang, 1999; Roca, Guillard, Guilbert, & Gontard, 2006). Acetylated monoglycerides presented little increase of equilibrium moisture contents with water activity, as observed for others hydrophobic materials like by Donhowe and Fennema (1992) and by Bourlieu et al. (2006). Dark chocolate was representative of high sugar content products and presented the typical moisture sorption curve of those products, with very low water adsorption at low water activity up to the dissolution of the sugar crystals and then sharp increase of equilibrium moisture contents, as observed for chocolate products by Morillon, Debeaufort, Capelle, Blond, and Voilley (2000).

The dry structure of the investigated model food systems, observed by scanning electronic microscopy, is presented in Fig. 2, confirming the specific structure of the four model food systems. Acetylated monoglycerides and wheat gluten were characterized by a dense and continuous matrix, and in the case of acetylated monoglycerides with some visible fat crystals at the surface. Dark chocolate presented a rough surface, indicating the presence of dispersed solid (sugar crystals and cocoa solids) within a dense matrix. The porous structure of sponge cake was observed at lower magnification due to the presence of very large pores (0.1–2 mm).

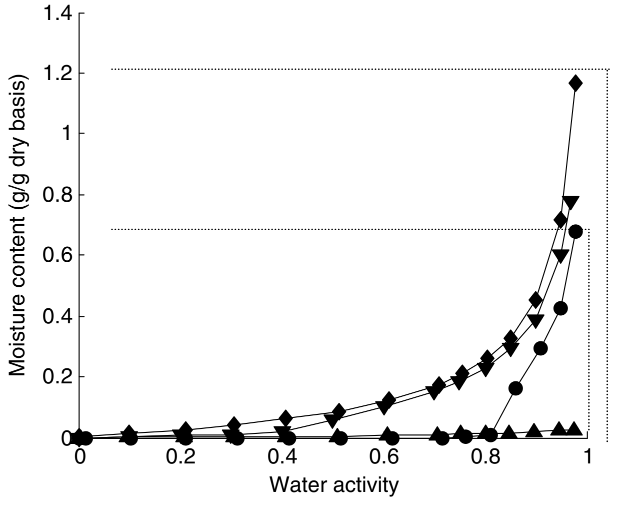

Fig. 1. Experimental moisture sorption of acetylated monoglycerides (▲), dark chocolate (●), wheat gluten (♦) and sponge cake (▼).

3.2. Modelling hypothesis: taking into account deformation

D_{eff} of the four model food systems were determined at 20 °C using successively the four mathematical models developed and the same set of experimental data. Since hygroscopicity of the investigated materials was distinct, D_{eff} are plotted versus materials average water activity, as presented in Fig. 3. D_{eff} curves are presented for water activity ranging from 0.50 to 0.98. The impact of the assumptions made for deformation or external resistance was evaluated by comparing the calculated D_{eff} using the analytical solution (no deformation no external resistance) or the numerical solutions with either the deformation hypothesis and/or the external resistance hypothesis. To facilitate comparison between all food systems and water transport models, average estimated values of D_{eff} for all the investigated water activity ranges are given in Table 2. The calculated differences of D_{eff} taking or not into account deformation or external resistance are presented in Fig. 4 (model 1 versus model 2) and Fig. 5 (model 1 versus model 3) for distinct ranges of water activities (0.50–0.70, 0.75–0.90 and 0.95–098).

Predictions of moisture content evolution were adjusted to experimental moisture contents kinetics in order to obtain optimal D_{eff} values. All models were able to fit with good accuracy experimental data, but large differences in the resulting values of D_{eff} were observed depending on the considered model. Hypotheses made on deformation and/or external mass transfer coefficient at the interface significantly influenced the predicted values of D_{eff}, even if the same experimental moisture sorption data was used. On the whole, D_{eff} were higher when estimated with the numerical models, presenting more detailed assumptions (deformation and/or external resistance hypotheses) as compared to the analytical model.

The effect of deformation hypothesis was different depending on the model food systems. Negligible influence of deformation hypothesis was observed for acetylated monoglycerides and sponge cake. On the contrary, it had a strong impact on D_{eff} for dark chocolate and wheat gluten: D_{eff} were higher when calculated with the model with deformation assumption, respectively, increasing from 0.9×10^{-11} to 1.4×10^{-11} m^2/s and from 0.9×10^{-12} to 1.3×10^{-12} m^2/s (Table 2). This difference can be explained by the fact that the analytical solution to Fick's second law, assuming no swelling of the solid matrix, underestimates the thickness of the product when water activity increases from one stage to another. Teixeira and Tobinaga (1998) observed similar impact of a deformation assumption, with an average deviation of 20% of effective moisture diffusivity

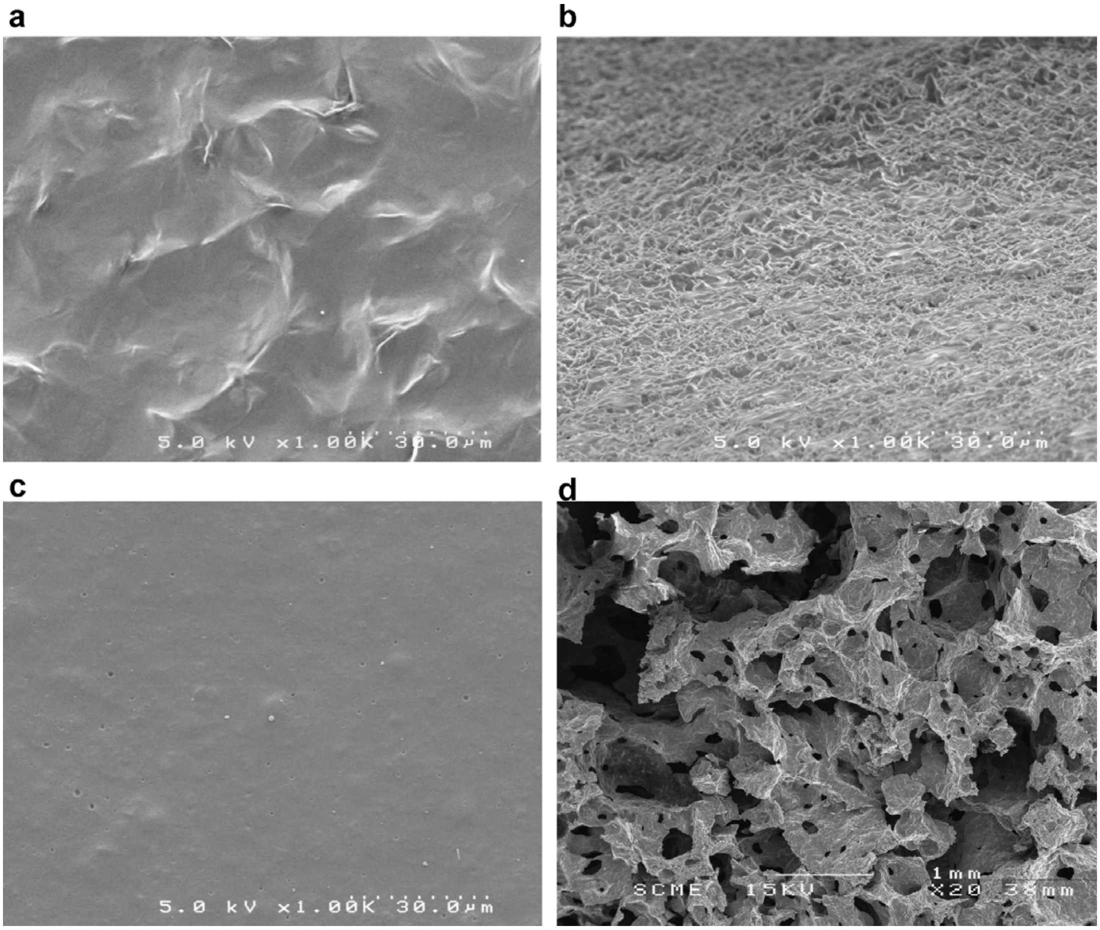

Fig. 2. Observation of the surface of acetylated monoglycerides (a), dark chocolate (b), wheat gluten (c) and sponge cake (d) at water activity 0 by scanning electron microscopy (magnification: acetylated monoglycerides 1000×; dark chocolate 1000×; wheat gluten 1000×; sponge cake 20×).

values in squid mantle taking into account shrinkage. Nevertheless, it can be seen in Fig. 4 that the effect of deformation hypothesis was not the same depending on the investigated range of water activity: taking into account deformation mainly affected D_{eff} for water activity above 0.75 for dark chocolate and wheat gluten, whereas no significant effect was observed for acetylated monoglycerides and sponge cake whatever the investigated range of water activity.

This difference depending on the investigated food material and water activity range was related to their moisture sorption isotherm and structure. The deformation criterion was calculated by addition of the partial volumes of water and of dry material, explaining that it affected mainly products with important water uptake. Results for calculated swelling ratio (thickness versus initial thickness) of the investigated model food systems are presented in Fig. 5. As water intake of acetylated monoglycerides was very low, very little swelling was calculated (increase of thickness lower than 5 μm) and no significant increase of D_{eff} was hence observed. An important swelling ratio of wheat gluten was calculated (1.6 at a_w 0.98), increasing with water activities above 0.75 in accordance with moisture sorption isotherm. Swelling of 70–100% for gluten-based materials by immersion in distilled water were also reported in the literature (Pommet, Redl, Guilbert, & Morel, 2005; Tropini, Lens, Mulder, & Silvestre, 2004). In spite of similar water sorption isotherm between sponge cake and wheat gluten, the impact of swelling on D_{eff} for sponge cake was negligible. This was related to the different structure of sponge cake as compared to wheat gluten. Although the absorbed water quantity at water activity 0.98 was high (0.8 g/g dry basis versus 1.2 g/g dry basis for wheat gluten), swelling ratio remained lower than 1.2 (versus 1.6 for wheat gluten), in accordance with previous experimental observations (Roca et al., 2007). This could be explained by the sponge cake density (190 kg dry matter/m^3), five times lower than wheat gluten density (995 kg dry matter/m^3) and than pure water density (1000.52 kg/ m^3). Therefore, considering a constant mass of sponge cake and wheat gluten, sponge cake volume is five times higher than wheat gluten one. The addition of a small volume of water will be then important when compared to the low volume of wheat gluten and small when compared to the great volume of sponge cake. Besides, in the case of porous materials, moisture is assumed to migrate inside the porous structure of the product and fill at various levels its porosity without any modification of the apparent volume, as observed experimentally

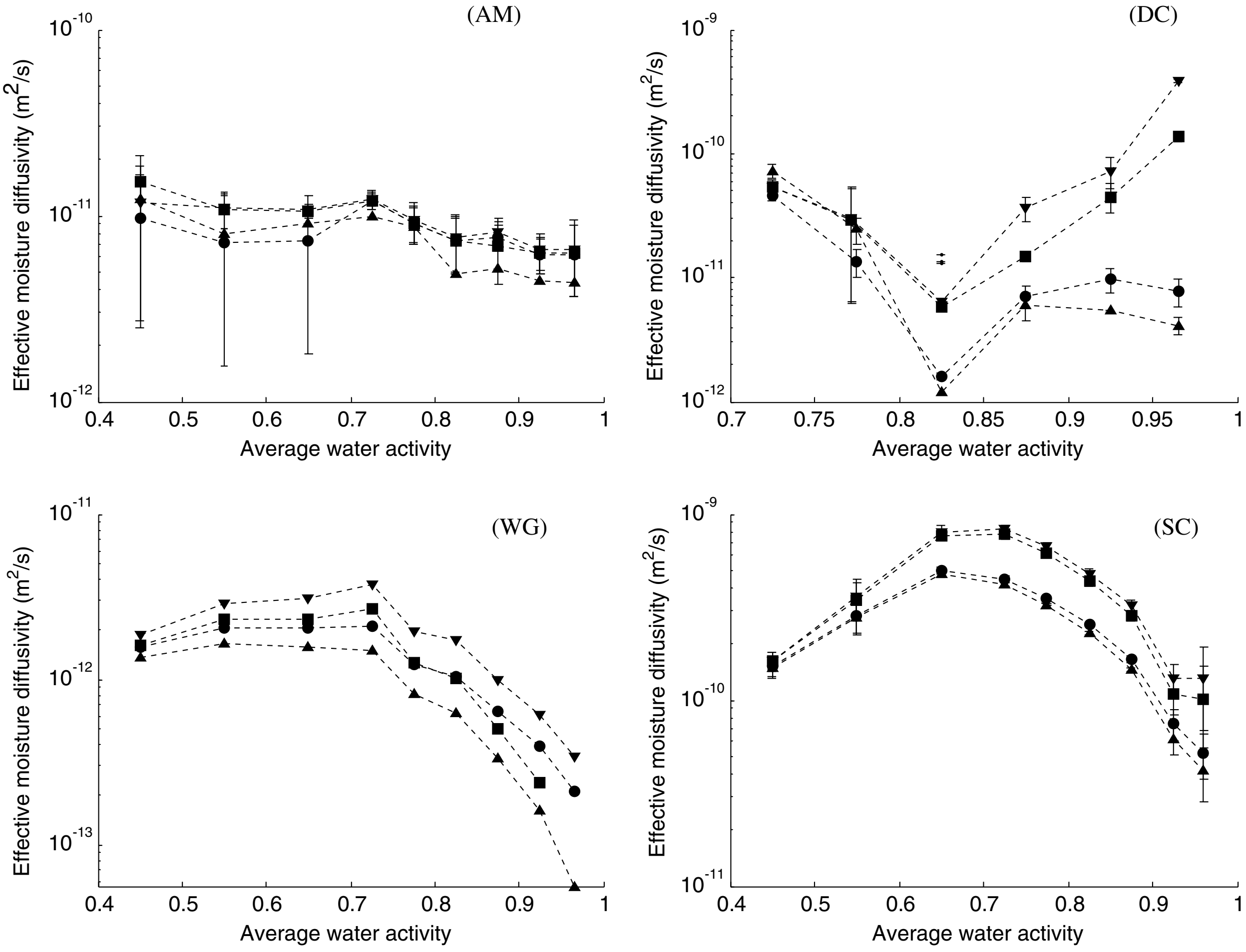

Fig. 3. Evolution of effective moisture diffusivity with average water activity in acetylated monoglycerides (AM), dark chocolate (DC), wheat gluten (WG) and sponge cake (SC), using four Fickian model with varying assumptions: no deformation and no external resistance (▲), deformation and no external resistance (●), external resistance and no deformation (■), deformation and external resistance (▼). Vertical bars stand for 95% confident intervals.

by Guillard et al. (2003). As a consequence, in the case of porous materials such as sponge cake, the hypothesis of addivity of partial volumes of water and dry matter may not be representative of the experimental swelling but permits to calculate a low swelling and thus be in accordance with experimental observations.

Another artefact can be induced by the presence of high amounts of sugar crystals as observed for the investigated dark chocolate. Indeed, the deformation hypothesis used in this study may not be representative of high-sugar content products such as dark chocolate. Softening of chocolate products was observed in the range of high water activities and is generally attributed to the swelling of the hydrophilic particles like milk powder and cocoa powder (Ghosh, Ziegler, & Anantheswaran, 2005). As regards to the high amount of sugar (36.7%) of the investigated dark chocolate, adsorbed water may rather contribute to the dissolution of sugar crystals without any modification of volume (Ghosh, Ziegler, & Anantheswaran, 2002). Supporting this hypothesis, the disruption of the moisture sorption curve for dark chocolate at water activities above 0.80 corresponds to the one observed for sucrose (Iglesias & Chirife, 1982). This was also reported by Morillon et al. (2000) who noticed that the shape of the water sorption isotherm of chocolate edible films is mainly due to sucrose, with a slight influence of cocoa powder. The main part of the adsorbed water may then not directly influence the volume of the material and our deformation hypothesis, based on the additivity of the partial volumes of dry matter and water, would overestimate the dark chocolate swelling. A more efficient swelling calculation would improve the predictive model, like for example combining the dissolution of sugars to the deformation hypothesis used in this study. It should be also noted that, in consideration of the sorption isotherm of the dark chocolate obtained in this study, at high hydration degree, water is almost free and able to act as a simple plasticizer decreasing hardness and cohesiveness in the product.

3.3. Modelling hypothesis: taking into account external resistance

The external resistance hypothesis affected strongly estimated D_{eff} as it can be seen on Fig. 3, but its impact varied

Table 2
Impact of deformation and external resistance hypotheses on the estimated effective moisture diffusivity for the investigated model food systems

Model food system	Model 1	Model 2	Model 3	Model 4
	Natures of hypotheses			
	No deformation, no external resistance	Deformation hypothesis	External resistance hypothesis	Deformation and external resistance hypothesis
Acetylated monoglycerides	7.4×10^{-12} (3.0×10^{-12})	8.05×10^{-12} (3.0×10^{-12})	9.4×10^{-12} (1.8×10^{-12})	9.3×10^{-12} (2.4×10^{-12})
Dark chocolate	0.9×10^{-11} (0.4×10^{-11})	1.4×10^{-11} (0.2×10^{-11})	4.5×10^{-11} (1.2×10^{-11})	9.8×10^{-11} (3.2×10^{-11})
Wheat gluten	0.9×10^{-12} (–)	1.3×10^{-12} (–)	1.5×10^{-12} (–)	1.9×10^{-12} (–)
Sponge cake	2.4×10^{-10} (0.2×10^{-10})	2.5×10^{-10} (0.2×10^{-10})	4.0×10^{-10} (0.4×10^{-10})	4.3×10^{-10} (0.4×10^{-10})

depending also on the investigated food materials and water activity range. D_{eff} increased from 0.9×10^{-11} to 4.5×10^{-11} m^2/s for dark chocolate, from 0.9×10^{-12} to 1.5×10^{-12} m^2/s for wheat gluten and from 2.4×10^{-10} to 4.0×10^{-10} m^2/s for sponge cake (Table 2). When external resistance to mass transfer is considered negligible, calculated D_{eff} generally account for both internal and external resistance, leading to lower values. Gaston et al. (2004) observed similar insufficiency of an analytical solution of Fick's second law with prescribed constant moisture constant boundary condition to accurately describe the shape of the drying curve of wheat grain. As presented in Fig. 6, the effect of the external resistance hypothesis was drastic for the materials presenting sharp slope of their moisture sorption curve: this effect was more pronounced for water activity above 0.95 for dark chocolate, increased regularly for water activity ranging from 0.50 to 0.98 for wheat gluten and sponge cake, and was negligible for acetylated monoglycerides whatever the water activity. This discrepancy can be related to the assumptions made for the surface water activity of the materials. For the analyt-

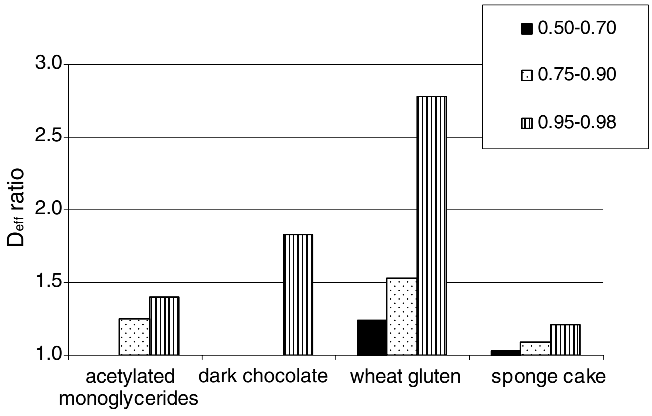

Fig. 4. Effective moisture diffusivity ratio comparing models with and without deformation hypothesis, for water activity ranges of 0.50–0.70 (black), 0.75–0.90 (spotted) and 0.95–0.98 (striped).

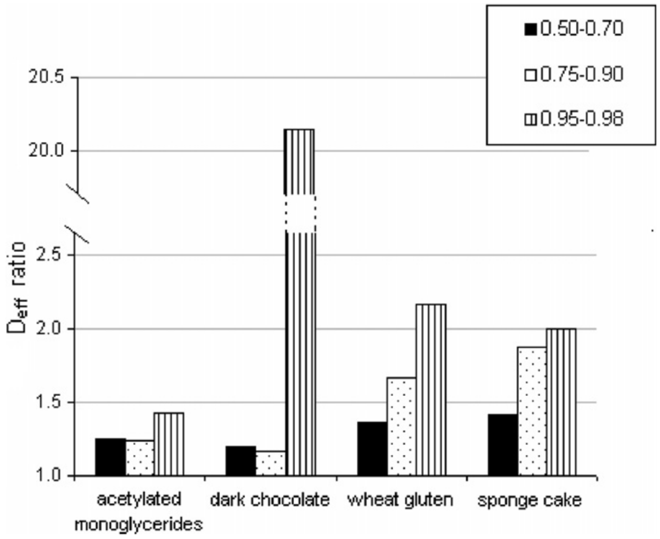

Fig. 5. Calculated swelling of acetylated monoglycerides, dark chocolate, wheat gluten and sponge cake, using the Fickian model with deformation hypothesis.

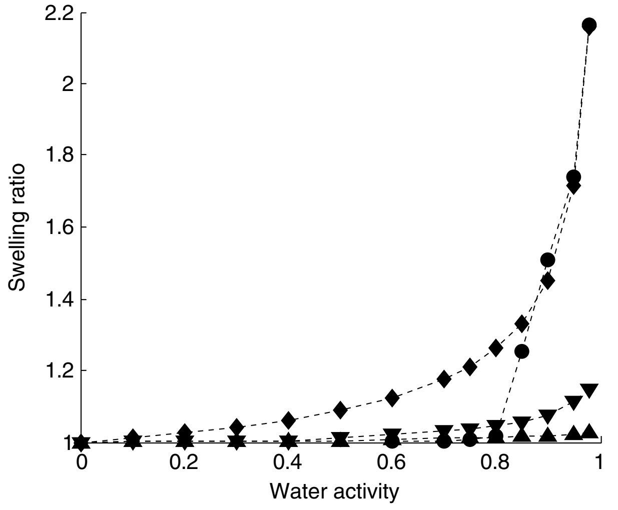

Fig. 6. Effective moisture diffusivity ratio comparing models with and without external resistance hypothesis, for water activity ranges of 0.50–0.70 (black), 0.75–0.90 (spotted) and 0.95–0.98 (striped).

ical solution of Fick's second law, instantaneous equilibrium of the surface water activity was assumed. This approximation was acceptable as far as hydrophobic materials are concerned, since the water uptake in these products remained very low, leading to few variations of equilibrium moisture contents from one water activity to another. On the contrary, in the case of hydrophilic products, small differences of water activity led to important variations of moisture contents as a consequence of the sharp slope of the moisture sorption curves. Therefore, approximation of the surface water activity made for the analytical solution led to under-estimate D_{eff}. Consequently, a particular attention should be paid on the external mass transfer coefficient, particularly for controlled atmosphere microbalances kinetics involving low air flow conditions. In practice, the external mass transfer coefficient should be determined with precision and the development of a standard method its estimation is of main interest.

4. Conclusion

This study outlines the significant impact of assumptions made for moisture transport predictive models for D_{eff} determination depending on the structure and hygroscopicity of food products. In the literature, analytical solutions of Fick's second law are mainly used whatever the food material considered, because they are simpler in term of encoding and no knowledge about the material properties are required. Even if these simplified models can be used for prediction of the global moisture transport, more precise models with assumptions representative of the specific conditions of the investigated experimental set up are needed for accurate estimation of D_{eff}. This could be facilitated by the use of powerful computers. Nevertheless, the knowledge of the sorption behaviour and the structure properties of the investigated materials would allow better adjustment of hypotheses made for deformation phenomena and boundary conditions.

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