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Determination of the diffusion coefficients of small solutes in cheese: A review

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Abstract – In cheese technology, the mass transfer of small solutes, such as salt, moisture and metabolites during brining and ripening, is very important for the final quality of the cheese. This paper has the following objectives: (i) to review the data concerning the diffusion coefficients of solutes in different cheese types; (ii) to review the experimental methods available to model the mass transfer properties of small solutes in complex matrices such as cheese; and (iii) to consider some potential alternative approaches. Numerous studies have reported the transfer of salt in cheese during brining and ripening. Regardless of the type of cheese and its composition, the effective diffusion coefficients of salt have been reported to be between 1 and $5.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ at 10–15 °C. However, few papers have dealt with the mass transfer properties of other small solutes in cheese. Most of the reported effective diffusion coefficient values have been obtained by macroscopic and destructive concentration profile methods. More recently, some other promising techniques, such as nuclear magnetic resonance, magnetic resonance imaging or fluorescence recovery after photobleaching, are currently being developed to measure the mass transfer properties of solutes in heterogeneous media at microscopic scales. However, these methods are still difficult to apply to complex matrices such as cheese. Further research needs to focus on: (i) the development of non-destructive techniques to determine the mass transfer properties of small solutes at a microscopic level in complex matrices such as cheese; and (ii) the determination of the mass transfer properties of metabolites that are involved in enzymatic reactions during cheese ripening.

cheese / mass transfer / diffusion / modelling / solute

摘要 – 干酪中少量溶质扩散系数的测定-综述。在干酪技术中，通过盐渍和成熟过程的控制来调整少量溶质（盐、水分和代谢产物）的传质，将对最终干酪的质量具有非常重要的作用。本文综述了溶质在不同类型干酪中的扩散系数，以及综述了少量溶质在干酪这一复杂基质中质量传递的数学模型。关于盐渍和成熟过程盐的迁移已有大量的文献报道，无论是何种类型的干酪，盐的有效扩散系数在 $1 \sim 5.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ (10 ~ 15 °C) 范围内。但是关于干酪中其他少量溶质传质特性的报道非常有限。大多数的有效扩散系数是通过显微镜或者破坏性浓度分布曲线的方法获得。一些新的测定技术，如核磁共振、磁共振成像或者光脱色荧光恢复技术等已经在显微技术的水平下用于测定不同介质中溶质的质量传递特性。然而，这些技术还很难应用于象干酪这样复杂的介质中。将来的研究将主要在：(i) 基于干酪这一复杂介质，在显微水平下采用非破坏性分析技术测定少量溶质的质量传递性质；(ii) 测定干酪成熟过程中代谢产物的质量传递特性。

干酪 / 质量传递 / 扩散 / 模型 / 溶质

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Résumé – Détermination des coefficients de diffusion de petits solutés dans le fromage : une synthèse. En technologie fromagère, le transfert de petits solutés, tels que le sel, l'eau et les métabolites au cours du saumurage et de l'affinage, joue un rôle majeur sur la qualité finale du fromage. Cette revue bibliographique a pour objectifs principaux : (i) de faire le bilan des valeurs publiées des coefficients de diffusion de différents solutés dans les fromages ; (ii) de passer en revue les méthodes expérimentales disponibles pour déterminer les propriétés de transfert des petits solutés dans des milieux complexes comme le fromage ; (iii) de considérer les méthodes alternatives potentiellement applicables aux fromages. Dans la littérature, de nombreuses études ont été publiées au sujet du transfert de sel dans les fromages au cours du saumurage et de l'affinage. En fonction du type de fromage et de sa composition, les coefficients de diffusion effectifs du sel sont compris entre 1 et $5,3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ à des températures comprises entre 10 et 15 °C. Très peu d'études concernant les propriétés de transfert d'autres petits solutés dans les fromages ont été publiées. La plupart des coefficients de diffusion effectifs ont été obtenus à l'aide de la méthode classique dite « des profils de concentration », méthode macroscopique présentant l'inconvénient d'être destructive. D'autres techniques, telles que la résonance magnétique nucléaire, l'imagerie par résonance magnétique ou la redistribution de fluorescence après photo-blanchiment sont actuellement développées pour mesurer des propriétés de transfert de matière de solutés à une échelle microscopique. Cependant, elles sont encore difficilement applicables aux matrices complexes comme le fromage. Les perspectives en matière de recherche dans ce domaine sont donc les suivantes : (i) le développement de nouvelles techniques expérimentales pour modéliser à l'échelle microscopique les propriétés de transfert de solutés dans des milieux complexes comme le fromage ; (ii) la détermination des propriétés de transfert des métabolites impliqués dans les réactions enzymatiques pendant l'affinage du fromage.

fromage / transfert de matière / diffusion / modélisation / soluté

1. INTRODUCTION

In cheese, transport of water and aqueous solutes has a crucial role during cheese making and cheese ripening (NaCl, transfer of substrates or reaction products like lactic acid). Cheese ripening is the result of bacterial activity of immobilized colonies in the lipoproteic matrix. Substrates have to diffuse in the matrix to reach bacterial colonies, and produced metabolites have then to diffuse from the bacterial colonies into the proteinic network. In case of diffusional limitations, microgradients of concentration, pH or water activity can be created around and in between the immobilized colonies, modifying bacterial and enzymatic activities.

Diffusion properties of cheese solutes can depend on (i) their physicochemical characteristics and (ii) the composition and microstructure of the matrix. In food matrices and notably in cheese, transfers of small molecules can occur between two

heterogeneous phases of the matrix, heterogeneous in terms of composition or physical state (liquid, solid or gaseous). To measure these transfers, diffusion coefficients (D) must be modelled [80].

Analysis of the literature reveals a strong lack of data concerning the migration rates of key molecules in cheese, such as sugars, organic acids and peptides, which can be decisive in the ripening process. Most of the data related to mass transport of small solutes in cheese deal with the salting process. Indeed, salt concentration distribution is an important parameter affecting cheese quality and acceptability. Salt affects the water activity of cheese, the growth and survival of bacteria and the activity of cheese enzymes [7].

Many different mechanisms can be involved during cheese processing, like multicomponent diffusion of solutes and water during salting. Due to technical difficulties to follow solute migration and modelling

difficulties inherent to the physical model chosen, working out diffusion properties of solutes is a complicated task, especially in complex heterogeneous matrices like cheese.

After a theoretical reminder concerning mass transfer phenomena, this paper reviews different methods available in the literature to determine diffusion coefficients of small solutes in cheese products. Values of the diffusion coefficients are then discussed for solutes in different cheese types, with details concerning the modelling methods. Finally, alternative techniques potentially applicable to cheese are presented.

2. THEORY OF MASS TRANSFER

2.1. Definitions

Mass transfer by diffusion is the transport of molecules caused by a random molecular motion in a region where composition gradient exists [82].

2.1.1. Steady-state diffusion

In a macroscopic, motionless (without internal movement and deformation), homogeneous (made up of one phase) and isotropic medium (uniform structure in all directions), solutes diffuse in the direction of their decreasing chemical potentials, until thermodynamic equilibrium is reached. Fick's first law links the diffusive flux to the concentration field, by postulating that the flux goes from high-concentrated regions to low-concentrated regions, with a magnitude that is proportional to the concentration gradient (spatial derivative). In one spatial dimension, this leads to

$$J_i = -D_{im} \cdot \frac{\partial C_i}{\partial x}, \quad (1)$$

where J_i is the molar diffusion flux of component i (kg or $\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$), C_i is the concentration of component i (kg or

$\text{mol} \cdot \text{m}^{-3}$), x is the position (m) and D_{im} is the diffusion coefficient of component i in the medium ($\text{m}^2 \cdot \text{s}^{-1}$). J_i measures the amount of substance that will flow through a small area during a short time interval.

The driving force for the one-dimensional diffusion is the quantity $-\frac{\partial C_i}{\partial x}$. To solve transfer equations, a simplification is generally made, considering chemical potential as a concentration or partial pressure (in the gas phase).

In two or more dimensions, the gradient operator ∇ can be used. This leads to

$$J_i = -D_{im} \cdot \nabla C_i. \quad (2)$$

Molecular diffusion coefficient D_{im} at a constant temperature may be adequately predicted in very diluted solutions using the well-known Stokes-Einstein equation, provided the molecular radius of the solute, solvent viscosity and absolute temperature are known [19]:

$$D_{im} = \frac{k_B T}{6\pi\mu R_0}, \quad (3)$$

where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the absolute temperature (K), μ is the viscosity of the phase ($\text{Pa} \cdot \text{s}$) and R_0 is the radius of the diffusing molecule (m).

The Stokes-Einstein equation (equation (3)) does not take the intermolecular interactions between solutes and between solvent and solute molecules into account (that may be significant for small solutes). Diffusion through a heterogeneous matrix is more complicated. Solute will have to diffuse in the liquid or gas phase contained within that porous matrix. Subsequently, the Stokes-Einstein equation has little use in the prediction of diffusion properties in food [77].

Some phenomena that cannot be distinguished from molecular diffusion must also be considered in heterogeneous matrices in terms of composition and structure, such as

capillary or Knudsen diffusion, diffusion modification due to matrix changes (obstruction, retraction, etc.) or interactions of the solute with other components. The term “apparent” or “effective diffusion” is then generally preferred to “diffusion” alone. Effective diffusivities are the most convenient way to describe mass transfer process through porous matrices, which have an intricate network of pores where diffusing species take a tortuous path [77].

If we consider liquid diffusion through porous matrices in which the pores are large, Fick’s diffusion model is able to correctly describe the mass transfer within the liquid contained in the pores. The flux can be described in terms of an effective diffusion coefficient D_{eff} ($\text{m}^2 \cdot \text{s}^{-1}$), defined as

$$D_{\text{eff}} = \frac{\varepsilon}{\tau} D_{im}, \quad (4)$$

where D_{im} is the diffusion coefficient of i in the medium m ($\text{m}^2 \cdot \text{s}^{-1}$), τ is the tortuosity and ε is the porosity [82].

In a porous matrix, the effective diffusion coefficient D_{eff} is then significantly smaller than the molecular diffusion coefficient D_{im} because of (i) tortuosity effects (the more tortuous the region the more devious the route between two points) and (ii) interactions between the solute and the matrix if they are both charged (ionic strength, hydrophobic and electrostatic interactions) [69, 77]. Note that equation (4) does not take chemical or electrostatic interactions into account, but only structural incidence of the matrix on solute diffusion properties.

Various alternative equations have been subsequently developed incorporating factors for molecular interactions and physical interferences [67]. To consider charged molecules, a general flux model can be used [38]:

$$J_i = D_{\text{eff}} \frac{C}{RT} \left(\frac{\partial \mu_i(x, t)}{\partial x} \right), \quad (5)$$

where D_{eff} is the effective diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), which does not depend on the electrostatic forces. μ_i is the chemical potential of the solute ($\text{J} \cdot \text{mol}^{-1}$), which is a function of solute concentration, ionic strength and pH. The charge dependence is thus moved from the diffusion coefficient to the chemical potential. Neglecting pressure and temperature contributions, the chemical potential is defined by [83]

$$\mu_i = \mu_i^0 + RT \ln a + \mu_{el}, \quad (6)$$

where a is the activity and μ_{el} is the contribution of the electrostatic charges to the chemical potential. In dilute solutions, the activity can be replaced by the concentration and if no electrical charges are present, $\frac{\partial \mu_{el}}{\partial x} = 0$, leading to Fick’s law according to equation (1).

However, due to the difficulty in quantifying such factors in real food matrices, equation (5) has poor prediction accuracy [77].

2.1.2. Unsteady-state diffusion

In order to be able to predict the concentration profiles of solutes in the matrix, Fick’s first law is associated to a local mass balance to obtain Fick’s second law

$$\frac{\partial C_i}{\partial t} = \nabla(D_{im} \cdot \nabla(C_i)). \quad (7)$$

Considering both unidirectional mass transfer along the x axis and a constant diffusion coefficient value, the previous equation becomes

$$\frac{\partial C_i(x, t)}{\partial t} = D_{im} \cdot \frac{\partial^2 (C_i(x, t))}{\partial x^2}. \quad (8)$$

Analogous equations can be written in spherical or cylindrical shapes, and two or three dimensions, in order to find the solute concentration as a function of time and position [17].

2.2. Using Fick's law solutions to estimate diffusion coefficients

Most research publications on mass transfer in cheese are using Fick's model with some specific geometries [10]. Diffusion coefficients in food matrices can be evaluated by different methods involving defined geometries and well-defined experimental conditions (steady or transient state and boundary conditions). To determine the diffusion coefficient of a solute in a given matrix, an experimental device generating a flux of the diffusing substance is set up. An average flux (mass variation) or a profile of concentration of the diffusing substance is measured, using either a destructive (slicing and analyzing samples) or a non-destructive method (nuclear magnetic resonance, NMR; fluorescence recovery after photobleaching, FRAP; radioactive tracer; etc.). A mathematical method, adapted to the experiment and generally based on Fick's laws, gives an average diffusion coefficient or diffusion coefficient versus concentration. Table I presents a summary of the principles, advantages and drawbacks of some existing methods for the determination of diffusion properties in cheese-like matrices.

The majority of macroscopic model studies can be divided into measurements in a diffusion cell (steady-state diffusion type of studies) and in cheese cylinders (transient diffusion type of studies).

2.2.1. Steady state

Zorrilla and Rubiolo [88] used the diffusion cell model developed by Djelveh et al. [20]. The diffusion cell consists of two compartments where perfectly mixed solutions A and B of equal volume V but different solute concentrations are separated by a matrix slab with thickness L and cross-section S . The solute migrates through the slab from the higher concentration

solution A to the lower concentration solution B.

Assuming a one-dimensional diffusion process through the slab and perfectly mixed compartments, the effective diffusion coefficient of the migrating solute can be modelled thanks to Fick's model. Equation (1) is transformed into equation (9) by applying a mass balance, assuming that there is no change in volume and that the effective diffusion coefficient is constant

$$V_A \frac{\partial C_A}{\partial t} = -D_{\text{eff}} \cdot S \cdot \frac{C_A - C_B}{L}, \quad (9)$$

where D_{eff} is the effective diffusion coefficient of the solute ($\text{m}^2 \cdot \text{s}^{-1}$), V_A is the liquid volume in the compartment from which the solute diffuses (m^3), S is the matrix area through which the diffusion takes place (m^2) and C_A and C_B are the solute concentrations, respectively, in the upper and lower compartments A and B (mol or $\text{kg} \cdot \text{m}^{-3}$).

By measuring the solute concentration in the upper compartment A and, via a mass balance, calculating the concentration in the lower compartment B at different times, an effective diffusion coefficient can be calculated by fitting equation (9) to the experimental data.

2.2.2. Unsteady or transient state

Gros and Rüegg [29] reviewed the various experimental techniques and appropriate mathematical treatments proposed to obtain effective diffusion coefficients in food matrices. Measuring unidirectional diffusion from a semi-infinite food cylinder geometry with different boundary conditions is the most frequently applied method to determine the effective diffusion coefficient of a solute in cheese. If the semi-infinite cylinder, containing an initial concentration C_0 of the solute, is in contact

Table I. Principles, advantages and drawbacks of existing methods for the determination of effective diffusion properties in cheese-like matrices.

Technique	Principle	Model	Advantages	Drawbacks	Refs.
Infinite cylinder in contact with a perfectly mixed solution	A semi-infinite cylinder of the matrix, initially free from the diffusing solute, is in contact: <ul style="list-style-type: none"> – either with a well-stirred solution containing a constant concentration C_s of the solute at the interface 	<ul style="list-style-type: none"> – One-dimensional diffusion – macroscopic scale – measurement of the concentration profiles of the migrating solutes along the x axis as a function of time – effective diffusion coefficient 	<ul style="list-style-type: none"> – Can be adapted for various small molecules – easy to implement 	<ul style="list-style-type: none"> – Destructive and low resolution: thin slicing of the sample gives spatial resolution of 1 mm – slow: several days of diffusion – a lot of analyses are required to obtain concentration profiles as a function of the distance and the time – a large number of assumptions are required when using the Maxwell-Stefan multicomponent approach – lack of physical interpretation of the Maxwell-Stefan diffusivities 	[29] [61] [85] [23]
Touching semi-infinite cylinders	– or with another semi-infinite cylinder of matrix containing a concentration C_s of the solute	<ul style="list-style-type: none"> – Fick's second law of diffusion – Maxwell-Stefan diffusivities with the Maxwell-Stefan multicomponent approach 			
Diffusion cell	A slab of matrix is placed in between two compartments of perfectly mixed solutions A and B of different solute concentrations	<ul style="list-style-type: none"> – One-dimensional diffusion – macroscopic scale – evaluation of the solute quantity having migrated through the product slab in a given time – effective diffusion coefficient with Fick's second law of diffusion 	<ul style="list-style-type: none"> – Quite inexpensive – can be adapted to a large range of products – can be adapted to a multicomponent system (simultaneous diffusion of several components) 	<ul style="list-style-type: none"> – Slow: several days of diffusion – accurate determination of solute concentrations is required in both compartments 	[20] [89] [90] [88]

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Table I. Continued.

Technique	Principle	Model	Advantages	Drawbacks	Refs.
SL-NVRK	<ul style="list-style-type: none"> Based on the on-line monitoring of release kinetics of NaCl from a matrix containing a salt concentration C_s into water a conductivity probe, immersed in the well-stirred aqueous solution, continuously measured the electrolytes released until thermodynamic equilibrium 	<ul style="list-style-type: none"> One-dimensional diffusion macroscopic scale effective diffusion coefficient with Fick's second law of diffusion 	<ul style="list-style-type: none"> Non-destructive non-invasive easy and fast (no analytical technique to quantify concentrations) 	<ul style="list-style-type: none"> Lack of specificity of the measure with the conductivity probe modelling difficulties because of the two unknown parameters: the effective diffusion coefficients of salt and of the other electrolytes of the product can be applied to ionic solutes only 	<ul style="list-style-type: none"> [46] [47]
PFG-NMR	<ul style="list-style-type: none"> Based on the attenuation of individual proton resonances under the influence of linear field gradients the amplitude of the signal is directly related to the self-diffusion coefficient of the molecule 	<ul style="list-style-type: none"> Microscopic scale measurement of the self-diffusion coefficient of small molecules (random translational motion of molecules driven by internal kinetic energy) 	<ul style="list-style-type: none"> No initial gradient of concentration non-destructive non-invasive promising approach for characterizing the structural modifications during the coagulation process 	<ul style="list-style-type: none"> High cost difficulty to sample the product in the thin NMR tubes high complexity of the spectral data obtained with real food products difficulty to establish the physical link between the self-diffusion coefficient and the effective diffusivity estimated with classical methods 	<ul style="list-style-type: none"> [13] [55] [56] [16] [22]
NMR imaging	<ul style="list-style-type: none"> Imaging technique used primarily in medical settings to produce high-quality images of the inside of the human body MRI is based on the principles of NMR MRI primarily images the NMR signal from the hydrogen nuclei ^23Na-MRI is based on the paramagnetic properties of the naturally occurring ^23Na isotope 	<ul style="list-style-type: none"> Microscopic scale measurement of the self-diffusion coefficient of water or Na or visualization of water or Na distribution 	<ul style="list-style-type: none"> No initial gradient of concentration non-destructive non-invasive 	<ul style="list-style-type: none"> High cost complex calibration and data handling work insensitive technique to molecules with low mobility difficulty to establish the physical link between self-diffusion coefficient and effective diffusivity 	<ul style="list-style-type: none"> [79] [78] [45]

continued on next page

Table I. Continued.

Technique	Principle	Model	Advantages	Drawbacks	Refs.
FRAP technique	<ul style="list-style-type: none"> – A certain region within a fluorescently labelled sample is irreversibly photobleached with a short intense light pulse – measurement of the fluorescence recovery inside the bleached area as a result of diffusional exchange of bleached fluorophores by unbleached molecules 	<ul style="list-style-type: none"> – Microscopic scale – analysis of the fluorescence recovery inside the bleached area with Fick's law of diffusion – effective diffusion coefficient and fraction of mobile species 	<ul style="list-style-type: none"> – No initial gradient of concentration – simple – non-destructive and slightly invasive 	<ul style="list-style-type: none"> – High cost: a CLSM is necessary – the migrating molecule has to be fluorescent or it must be marked by a fluorescent probe – not adapted to complex and opaque media like cheese 	<ul style="list-style-type: none"> [57] [14] [43]

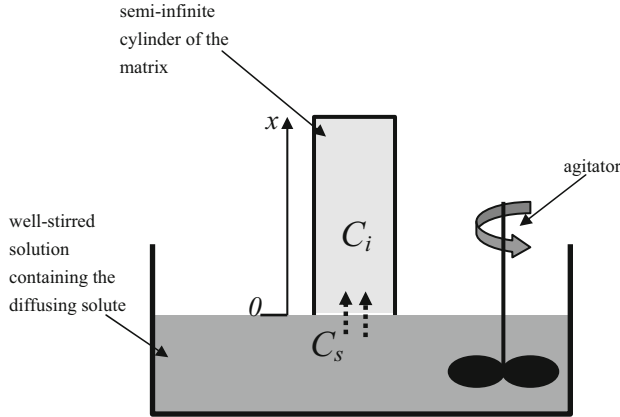


Figure 1. Diagram of the semi-infinite cylinder experimental device.

with a well-stirred solution containing a constant concentration C_s of the solute at the interface ($C_s > C_0$) (Fig. 1), the external mass transfer resistance can be neglected [71] and the boundary conditions are as follows:

$$t = 0 \quad C_i = C_0 \quad (10)$$

$$x = 0 \quad C_i = C_s \quad \text{for } t > 0, \quad (11)$$

$$x \rightarrow \infty \quad C_i = C_0 \quad \text{for } t > 0, \quad (12)$$

where t is the time (s), x is the position (m), C_i is the concentration of solute i in the matrix (kg or $\text{mol}\cdot\text{m}^{-3}$), C_0 is the initial concentration of the solute i in the matrix (kg or $\text{mol}\cdot\text{m}^{-3}$) and C_s is the concentration of the same solute at the interface (kg or $\text{mol}\cdot\text{m}^{-3}$).

The duration of experiments is assumed to be such as the solute does not reach the extremity of the matrix. The matrix is thus considered as a semi-infinite medium. This boundary condition is only valid for Fourier number ($F_0 = \frac{D_{\text{eff}}t}{L^2}$) under 0.05, where L is

the length of the semi-infinite cylinder along the x axis (m).

The solution of equation (8) is then

$$\frac{C(x, t) - C_0}{C_s - C_0} = \text{erfc}\left(\frac{x}{2\sqrt{D_{\text{eff}}t}}\right), \quad (13)$$

where erfc is the complementary error function.

The value of D_{eff} is then determined from concentration profiles by minimizing the sum of squares of the deviations between the experimental (C_{exp}) and model values (C_{model})

$$\text{Crit} = \sum_{i=1}^N (C_{\text{exp}} - C_{\text{model}})^2. \quad (14)$$

If $F_0 > 0.05$, then the assumption of a semi-infinite medium no longer applies and the last boundary condition must be changed. The solution of equation (8) and its boundary conditions can be found in Crank [17] or in Gros and Rügge [29].

An alternative method, called the “touching semi-infinite cylinders technique”, is based on a similar approach [29, 85].

This method consists in bringing into contact two cylinders of the same matrix, each of them having a different initial concentration of the migrating solutes. The concentration profiles are measured from their distance to the interface, as a function of time, along a one-dimensional axis. Crank [17], Gros and Rüegg [29] or Wilde et al. [85] gave the solution of equation (8) and boundary conditions for this unidirectional diffusion from a semi-infinite matrix cylinder, containing an initially uniform concentration of the diffusing substance into a contiguous semi-infinite cylinder initially free of solute or containing lower concentration.

The main drawback of these types of experiments is that they are generally destructive. Thin slicing of the sample gives spatial resolution of about 1 mm. Some studies are less precise with a slice thickness up to 1 cm [74]. Moreover, the measurement in each slice of the solute concentration at different given times of the diffusion process is very time-consuming. This explains why such operations are not extensively repeated. In addition, the thinner the slices, the longer the operation and the higher the number of measurements have to be further performed. Reducing the slice thickness also increases uncertainty on the slice position along the direction of transfer and possibly on concentration measurement (due to less matter) [50]. However, these Fickian approaches based on the concentration profiles of the diffusing solute can be adapted for various small molecules, ionized or not, easy to detect and quantify (water, solutes, colourants and aroma compounds) [15].

Lauverjat et al. [47] recently developed a method, also based on the Fickian approach, for easier and faster determination of diffusion properties of salt in complex matrices. This method, called the solid liquid non-volatile release kinetic method (SL-NVRK), is based on the on-line monitoring of release kinetics of NaCl from a product containing a salt concentration C_s into water. A

conductivity probe, immersed in the well-stirred aqueous solution, continuously measured the electrolytes released until thermodynamic equilibrium. The adjustment of a mechanistic model, ensuing from the analysis of mass transfer to the experimental kinetics, led to the determination of the effective diffusion coefficient of NaCl. However, the main limit is the lack of measurement specificity. Indeed, besides NaCl, the cheese-like model matrices contained other solutes such as KCl, calcium, phosphates, citrates and lactates. Because all these species contribute to the conductivity signal and it was not possible to dissociate the respective contribution of each one, two independent diffusion equations for NaCl and for other electrolytes were necessary. The main difficulty was that the model had to be adjusted to experimental conductivity data using two unknown parameters, the effective diffusion coefficients of NaCl and of the other electrolytes. The other drawback is that this method is specific to measuring diffusion properties of ionic species only.

Vestergaard et al. [78] were the first to develop a ^{22}Na -radioisotope non-destructive method for studying NaCl diffusion in meat. Reliable sodium diffusion profiles in meat were obtained by scanning a cylindrical geometry of meat where diffusion of sodium took place from one end to the other end of the cylinder. The use of radioisotopes in the biological and medical sciences is well established. By administering a suitable compound marked with a radioactive tracer it is, for example, possible to locate abnormalities in specific organs. Since the technique was first applied in cancer diagnostics, it has been extensively developed and it is presently known as Single Photon Emission Computerized Tomography.

Despite the disadvantage of the tracer being radioactive and requiring precautions in its handling, Vestergaard et al. [78] concluded that ^{22}Na measurements are a promising methodology for studying salt diffusion

in meat. This method may be transposed to cheese in order to study the diffusion of salt or other solutes where an atom can be radioactively marked.

2.2.3. Drawbacks of the Fickian approach

The classical Fickian approach of transport phenomena is difficult to apply to food matrices because of their specific characteristics, structure, properties, etc. In fact, even considering cheese as a food matrix with saline solution occluded in the pores, parameters such as porosity, tortuosity and phase ratios are not sufficient to describe the mass transfer process accurately. Some typical pitfalls with the Fickian approach in foods were reported by Doulia et al. [21]:

- The dependence of D_{eff} on the concentration of the component being transferred. In this case, the driving force for mass transfer is the difference in chemical potential and not the difference in concentration.
- The dependence of D_{eff} on temperature. The application of an Arrhenius-type relation is questionable, in case of sudden changes in the matrix microstructure.
- The dependence of D_{eff} on volume changes occurring during dehydration (shrinkage) or rehydration (swelling). In most cases, the influence of volume changes is ignored and implicitly included in D_{eff} value.
- The evaluation of D_{eff} entails that mass transfer is mainly a molecular diffusion mechanism, whereas several other mechanisms are also often involved, such as capillary or Knudsen diffusion.
- In initial and boundary conditions, the distribution coefficient between the two phases should be taken into account. The latter coefficient is the quotient of the concentrations resulting from the equilibrium experiments and reflects the allegation that the driving

force is not the concentration difference. In equilibrium conditions, the distribution coefficient in terms of chemical potential should be equal to 1.

The perverse effect of calculating a D_{eff} (which may be correctly defined as a mass transfer coefficient) from experimental data is then that no effort is made to understand the actual mechanism for mass transfer [1]. In fact, some researchers have correctly noted that it is worthless to calculate diffusion coefficients unless the structure is resolved [26]. It is very probable that the quantification of food microstructure using image analysis will assist in finding the mechanisms and their relative contributions to the transport phenomena, and better modelling [1].

In order to improve modelling of mass transfer phenomena in cheese, several other methods were proposed in the literature, which are reviewed thereafter.

3. MULTICOMPONENT DIFFUSION

3.1. Generalized Fick's model

Zorrilla and Rubiolo [88–90] were the first to develop a model for a multicomponent system (where many components diffuse simultaneously), using the diffusion cell, for determining apparent diffusion coefficients of both NaCl and KCl in cheese during salting and ripening processes.

From a theoretical point of view, mass transport phenomena for a multicomponent system can be physically modelled using three different approaches: (i) the generalization of Fick's law, (ii) the use of irreversible thermodynamics and (iii) the use of Stefan-Maxwell equation. These three approaches are based on kinetic, thermodynamic and hydrodynamic considerations, respectively [12].

The generalized Fick's law is, as indicated by its name, a generalization of Fick's

law initially formulated for binary diffusion [73]. For example, in the case of a ternary mixture, the mass diffusion fluxes J_i^* ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) can be calculated from mass fractions of each species ω_i and mass content of the mixture ρ ($\text{kg}\cdot\text{m}^{-3}$) using

$$\begin{bmatrix} \vec{J}_1^* \\ \vec{J}_2^* \end{bmatrix} = \rho \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \begin{bmatrix} \vec{\nabla}\omega_1 \\ \vec{\nabla}\omega_2 \end{bmatrix}. \quad (15)$$

Note that for the third component (arbitrarily chosen as a reference species)

$$\vec{J}_3^* = \vec{J}_1^* - \vec{J}_2^*. \quad (16)$$

The values of the multicomponent diffusion coefficients D_{ii} (main diffusion coefficients, $\text{m}^2\cdot\text{s}^{-1}$) and D_{ij} (cross diffusion coefficients, $\text{m}^2\cdot\text{s}^{-1}$) depend on (i) the reference velocity chosen to express the diffusion velocity of each species with respect to the bulk flow of the mixture (molar, mass or volume average velocity), (ii) the state variable chosen to describe the composition of the system (molar, mass or volume fraction) and (iii) the arbitrary choice made when designing a reference species. This point considerably restricts the use of multicomponent diffusion coefficients found in the literature since these precisions are often lacking. Note that relationships between these coefficients and the binary values are not known a priori [12].

In Zorrilla and Rubiolo [88–90], the generalized Fick's law form was used as a constitutive equation for the diffusive molar flux of NaCl and KCl during brining and ripening in the cheese. From a physical point of view, using Fick's model is not ideal in that case, but it was used because of its simplicity in the experimental and mathematical works [19]. Generally, for highly dissociable solutes such as NaCl and KCl, the cross diffusion coefficients are smaller than the main ones [25].

Consequently, the main effective diffusion coefficients of NaCl and KCl were much larger ($\sim 4 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$) than the cross diffusion coefficients between NaCl and KCl ($\sim 0.1 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$) in the semi-hard cheese type. Zorrilla and Rubiolo [88–90] observed that main diffusion coefficients of both NaCl and KCl were very similar because of their chemical similarities.

Gerla and Rubiolo [25] also studied multicomponent mass transport of lactic acid and NaCl in a solid-liquid system through the brining process of Pategras cheese. This was done to predict changes in acid concentration during the salting process. The NaCl diffusion rate was independent from the lactic acid concentration gradient, while the lactic acid diffusion rate increased 12 times due to NaCl concentration changes in the cheese. Therefore, in processes involving the simultaneous diffusion of several solutes, the largest solute gradient can cause the modifications of the diffusion properties of minor solutes. If these solutes are important for ripening, the modifications of their diffusion properties can have consequences on the sensorial properties of the cheese. These results established the importance of using multicomponent mass transport models. However, interactions between protons, Na^+ and Cl^- ions within cheese matrices can be explained by other arguments than the magnitude of their gradients since they can all interact with the proteinic network. In that case, Na^+ and Cl^- probably modify electrical charges of proteins and thus their buffering capacity, which in turn affect lactic acid diffusion properties.

Simal et al. [70] and Bona et al. [9, 10] described a mathematical procedure to obtain the diffusion coefficients of different species (salt and water) that simultaneously diffuse in cheese in such a situation that each mass flux is affected by the existence of the others. The correspondent local mass balances combined with Fick's law were simultaneously solved in one dimension [70] or in three dimensions using a numerical finite

difference method [9, 10]. Indeed, with the development of high-performance computers, it is possible to simulate a process close to reality using three-dimensional geometries and numerical techniques such as the finite element method (FEM) [9, 10]. Water losses and salt gain during brining could be adequately simulated using the proposed model. Although the experimental data of water and salt contents were in good agreement with calculated values, the main drawback of the proposed model was the high number of unknown parameters that had to be numerically identified.

The multicomponent analysis of mass transfer phenomena is an alternative to the classical modelling method presented in the Section 4.2.3. However, it was previously reported that from a physical point of view, the use of Fick's model may give misleading results when the Fickian analysis is applied in a complex system like food products. Indeed, the simplifications imposed on the model may affect its accuracy. Alternative methods described by irreversible thermodynamics and the Stefan-Maxwell theory have then come into force. In these approaches, the driving force is the chemical potential.

3.2. Stefan-Maxwell approach

Payne and Morison [61] developed a Stefan-Maxwell multicomponent approach to model salt and water diffusion in cheese. Stefan-Maxwell's model expresses the chemical gradient of potential like a linear function of the matter flux. A full description of this equation is given by [73]:

$$\frac{x_i}{RT} \left(\frac{\partial \mu_i}{\partial x} \right) = \sum_{j=1}^n \frac{x_i x_j}{D_{ij}^{SM}} (v_j - v_i), \quad (17)$$

where D_{ij}^{SM} are the Stefan-Maxwell diffusion coefficients between components i and j ($\text{m}^2 \cdot \text{s}^{-1}$), R is the ideal gas constant, $8.31414 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, T is the temperature

(K), x_i , μ_i and v_i are respectively the molar fraction, the molar chemical potential ($\text{J} \cdot \text{mol}^{-1}$) and velocity relative to stationary coordinates ($\text{m} \cdot \text{s}^{-1}$), of the component i .

Payne and Morison [61] considered cheese as a three-component system consisting of NaCl (component 1), water (component 2) and a matrix of protein and fat (component 3).

In regard to the Fickian approach, the main advantage of Stefan-Maxwell equation is that no reference species is needed. Secondly, as corrections for thermodynamic non-ideality are included in this analysis, the concentration dependence of Stefan-Maxwell diffusion coefficients is not as strong as that of Fickian diffusion coefficients. In the case of dilute gases, the Stefan-Maxwell diffusion coefficients correspond to the binary values (Fickian diffusion coefficients). However, when applied to concentrated aqueous solutions or food matrices like cheese, the Stefan-Maxwell diffusion coefficients are no longer equal to the binary values.

For Payne and Morison [61], the main difficulties encountered with this model were the determination of water activity and the activity coefficient of salt in cheese. The value of cheese matrix activity was not required because it could be assumed that the diffusional flux of the matrix was insignificant. To solve the model, values for the Stefan-Maxwell diffusion coefficients between salt, water and the cheese matrix were required. However, there are very little data available in the literature for the Stefan-Maxwell diffusion coefficients, and none were found for cheese, salt and water. This does present a number of problems, the most significant being that the accuracy of the model is limited by the accuracy of these values [61]. Stefan-Maxwell diffusion coefficients are mainly determined empirically by doing a large number of assumptions. Payne and Morison [61] fitted experimental data from Geurts et al. [27] and Wesselingh et al. [84] to model

Table II. Literature review of effective diffusion coefficients found for small solutes in different cheese types.

Cheese	Composition dry matter (DM) (g·kg ⁻¹), fat/DM (g·100 g ⁻¹) and pH	Brining and/or ripening conditions			Geometry	Model	Effective diffusion coefficient (D_{eff}) ($\times 10^{-10}$ m ² ·s ⁻¹)	Refs.
		Process considered	Temperature (°C)	Brine composition				
<i>Solute: NaCl</i>								
Camembert (soft-type cheese)	DM 410 fat/DM 45	Brining and ripening	14	300 g·kg ⁻¹ NaCl pH 4.6	Slab	Fick (1D)	~ 2.54	[41]
Cuartirollo Argentino (soft-type cheese)	DM 480 fat/DM 51.7	Brining and ripening	7.5	205 g·kg ⁻¹ NaCl agitated or brine at rest	Finite rigid slab	Fick (1D)	3.6	[51, 52]
Feta	DM 440 fat/DM 43	Dry-salted	13	–	Semi-finite geometry	Fick (1D)	2.3	[87]
White cheese (semi-hard, Turkey)	DM 450 fat/DM 42 pH 5.3	Brining	4, 12.5 and 20	150–200 g·kg ⁻¹ NaCl	Finite slab	Fick (1D)	2.1, 3 and 4 (no effect of brine concentration)	[74]
White cheese (semi-hard, Turkey)	DM 450 fat/DM 42 pH 5.3	Brining	4–20	150–200 g·kg ⁻¹ NaCl	Finite slab	Fick (1D)	2.2–4.2	[75]
Prato cheese (semi-hard, Brazil)	DM 517 fat/DM 53 pH 5.2	Brining	10	150, 200 and 250 g·kg ⁻¹ NaCl	Parallelepiped	Fick (3D) and neural network	1.64, 4.25 and 3	[7]
Romano (hard-type cheese)	DM 535 fat/DM 38	Brining	20	160 g·kg ⁻¹ NaCl	Slab	Fick (1D)	2.54–3.35	[35]

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Table II. Continued.

Cheese	Composition dry matter (DM) (g·kg ⁻¹), fat/DM (g·100 g ⁻¹) and pH	Brining and/or ripening conditions			Geometry	Model	Effective diffusion coefficient (D_{eff}) ($\times 10^{-10}$ m ² ·s ⁻¹)	Refs.
		Process considered	Temperature (°C)	Brine composition				
Sbrinz (hard-type cheese)	DM 650 fat/DM 48	Brining and ripening	Brining at 12 °C (4 days) and diffusion at 7, 11, 15 and 20 °C	200 g·kg ⁻¹ NaCl	Touching semi-infinite cylinders (after the brining step)	Fick (1D)	1.06 (± 0.15) to 1.88 (± 0.27) (temp. coef.: 0.063 $\times 10^{-10}$ m ² ·s ⁻¹ ·°C ⁻¹)	[29]
Cheddar (hard-type cheese)	DM 650	Ripening	10	–	Slab	Fick (1D)	1.16	[86]
Emmental (hard-type cheese)	DM 600 fat/DM 48	Brining	4–18	250 g·kg ⁻¹ NaCl; 0.3 g·kg ⁻¹ CaCl ₂ pH 5.4	Infinite cylinder	Fick (1D)	0.62–2.22	[60]
Model cheese (Gouda style)	DM 580–630 fat/DM ~ 50	Ripening RH 87%	13	–	Slab	Fick (1D)	2.3	[28]
Model cheese (Gouda style)	DM 533, 566 and 638 fat/DM 62, 50, 22 and 12 pH 4.9–5.6	Brining	12.6	130–310 g·kg ⁻¹ NaCl; 15 g·kg ⁻¹ CaCl ₂	Flat cylindrical shape	Fick (1D)	~ 2.3 1.16–3.24 (temp. coef.: 0.12 $\times 10^{-10}$ m ² ·s ⁻¹ ·°C ⁻¹)	[26]
Model cheese	DM 370 and 440 fat/DM 20 and 40 pH 6.2 and 6.5 0.5 and 1.5 g·100 g ⁻¹ NaCl	Release of NaCl from the cheese into water	13	Water	Infinite cylinder	Fick (1D)	2.74–5.1 (± 0.01)	[46]
			15	Artificial saliva	Fick (1D)	2.81–3.43	[23]	

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Table II. Continued.

Cheese	Composition dry matter (DM) (g·kg ⁻¹), fat/DM (g·100 g ⁻¹) and pH	Brining and/or ripening conditions			Geometry	Model	Effective diffusion coefficient (D_{eff}) ($\times 10^{-10}$ m ² ·s ⁻¹)	Refs.
		Process considered	Temperature (°C)	Brine composition				
<i>Solute: water</i>								
White cheese (semi-hard, Turkey)	DM 450 fat/DM 42 pH 5.3	Brining	4, 12.5 and 20	150–200 g·kg ⁻¹ NaCl	Finite slab	Fick (1D)	15% brine: 1.96–3.64; 20% brine: 1.69–3.09	[76]
<i>Solutes: NaCl and water</i>								
Fresh cheese Pasteurized cow and goat milk	No data	Brining	5, 15 and 20	280 g·L ⁻¹ NaCl; 15 g·L ⁻¹ CaCl ₂	Cylinder and parallelepiped	Fick (1D)	Water: 5.71, 8.83 and 9.99; NaCl: 3.56, 8.26 and 9.17	[70]
Mahon cheese (soft-type cheese, Spain)	DM 244	Ripening RH 85%	12	280 g·L ⁻¹ NaCl; 15 g·L ⁻¹ CaCl ₂	Parallelepiped	Fick (3D)	Water: 0.078; NaCl: 5.3	[71]
Gouda (semi-hard cheese)	DM 565 fat/DM 53	Brining	20	170 g·kg ⁻¹ NaCl	Slab	Maxwell- Stefan (1D)	$D_{\text{salt-chesse}}^{\text{SM}} =$ 0.0027 – 0.014 from the core to the edge of the cheese	[61]
<i>Solutes: NaCl and KCl</i>								
Fynbo cheese (semi-hard, Turkey)	DM 470 fat/DM 29.6–36.2	Brining	12	100 g·L ⁻¹ NaCl; 100 g·L ⁻¹ KCl; 15 g·L ⁻¹ CaCl ₂	Diffusion cell	Fick (1D)	NaCl: 4.14; KCl: 3.91	[89]
Prato cheese (semi-hard, Brazil)	DM 540 fat/DM 52.8	Brining	10	146 g·L ⁻¹ NaCl; 50.6 g·L ⁻¹ KCl; 5 g·L ⁻¹ CaCl ₂	Parallelepiped	Fick (1D)	NaCl: 2.6; KCl: 2.77	[8]

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Table II. Continued.

Cheese	Composition dry matter (DM) (g·kg ⁻¹), fat/DM (g·100 g ⁻¹) and pH	Brining and/or ripening conditions			Geometry	Model	Effective diffusion coefficient (D_{eff}) ($\times 10^{-10}$ m ² ·s ⁻¹)	Refs.
		Process considered	Temperature (°C)	Brine composition				
Prato cheese (semi-hard, Brazil)	DM 540 fat/DM 52.8	Brining	10	146 g·L ⁻¹ NaCl; 50.6 g·L ⁻¹ KCl; 5 g·L ⁻¹ CaCl ₂	Parallelepiped	Fick (3D)	NaCl: 2.8; KCl: 2.94	[10]
<i>Other solutes</i>								
Lactose in small curd cottage cheese	No available information	Washing	25	Demineralized water pH 4.5 (H ₃ PO ₄)	Sphere	Fick (1D)	3.8	[11]
Lactose in Skimmed Quark cheese (Soft-type cheese, Germany)	No available information	–	4	–	Touching semi-infinite cylinders	Fick (1D)	1.37 (\pm 0.13)	[85]
Sucrose in milk	Fat 15 g·kg ⁻¹	Contact with 15 g·100 g ⁻¹ agar gel	20–24 (room temperature)	–	Touching semi-infinite cylinders	Fick (1D)	<i>Initial gel sucrose concentration</i> C_{s0} 787 g·L ⁻¹ : 1.9, C_{s0} 515 g·L ⁻¹ : 2.6, C_{s0} 279 g·L ⁻¹ : 3.9	[81]
Lactic acid and NaCl in Pategras	DM 544 fat/DM 43 Lactic acid 13 g·kg ⁻¹	Ripening RH 90%	13	200 g·kg ⁻¹ NaCl; 5 g·kg ⁻¹ CaCl ₂	Finite slab	Fick (1D) multicomponent diffusion	NaCl: 3.2 lactic acid: \sim 1	[25]

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Table II. Continued.

Cheese	Composition dry matter (DM) (g·kg ⁻¹), fat/DM (g·100 g ⁻¹) and pH	Brining and/or ripening conditions			Geometry	Model	Effective diffusion coefficient (D_{eff}) ($\times 10^{-10}$ m ² ·s ⁻¹)	Refs.
		Process considered	Temperature (°C)	Brine composition				
Potassium sorbate in American processed cheese	DM 600 fat/DM 45	Brining	Room temperature	250 g·L ⁻¹ potassium sorbate solutions	Cubes (finite slab)	Fick (1D)	1.31	[40]
Potassium sorbate in Mozzarella	DM ~ 500 fat/DM 45						0.674	
Aroma compounds in model cheese: diacetyl, heptan-2-one, and ethyl hexanoate	DM 370 fat/DM 20 and 40 pH 6.2 1.5 g·100 g ⁻¹ NaCl	Release of aroma compounds in the air	13	–	VASK	Fick (1D)	Diacetyl: 0.04; heptan-2-one: 0.2–0.12; ethyl hexanoate: 0.18–0.07	[47]

the Stefan-Maxwell diffusion coefficients. The model successfully predicted independent shrinkage arising from an excess of outgoing diffusion of water over the incoming diffusion of salt. Their model also indicated that there was a large interaction between salt and the cheese matrix, which caused a significant reduction in the diffusion of salt into cheese. Further work is required to interpret the Stefan-Maxwell diffusion coefficients from a physical point of view.

4. CHARACTERISTIC VALUES OF EFFECTIVE DIFFUSION COEFFICIENTS IN CHEESE

Extensive data on diffusion coefficients in cheese are available in the literature, but cover a large range of values. This is undoubtedly due to the complexity and diversity in cheese structure and composition. This variability depends on the cheese type and origin, as well as on various methods of determination which are not always fully explicit, nor justified [50].

4.1. Salt and moisture transfer

Most of the published studies concerning mass transfer phenomena during cheese production deal with the salting and ripening processes. After moulding, cheese is placed in brine and a net movement of Na^+ and Cl^- ions, from the brine into the cheese, results from the osmotic pressure difference between the cheese moisture and the brine. Consequently, moisture diffuses throughout the cheese matrix to restore osmotic pressure equilibrium [34]. The amount of salt retained and water removed from the cheese depend, mostly, on brine concentration and brining time [32]. Salt diffusive migration in cheese usually occurs slowly. For example, salt equilibration times for cheese range from about 1–2 weeks in soft cheese to several months

in semi-hard cheese type. In Parmesan cheese, which represents an extreme case, salt equilibrium is only attained after about 10 months [64]. For the controlled manufacture of these products, it is therefore important to know the factors influencing salt penetration and to be able to predict the diffusion rates. This implies the knowledge of the apparent diffusion coefficient of salt and its dependence on factors such as temperature and brine concentration.

Water and NaCl diffusion transport processes in and out of the cheese matrix during classical brining and ripening are most of the time described using the second Fick's law, considering the diffusion coefficient as constant. This diffusion coefficient represents the NaCl effective diffusion coefficient when considering the cheese matrix and NaCl as the two components of the binary diffusion system [52]. For NaCl, the effective diffusion coefficient D_{eff} varies from $1\text{--}5.5 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ depending on cheese, compared to $1.16 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ for the diffusion coefficient of NaCl in pure water at temperatures around $12.5 \text{ }^\circ\text{C}$ (Tab. II). Temperature has a strong effect on the effective diffusion coefficient of NaCl in some cheese types, which can increase up to $9.2 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ at $20 \text{ }^\circ\text{C}$ during the brining of Fresh cheese [70].

This increase was attributed by Geurts et al. [27] to an increase in true diffusion and to some effect on diffusion-interfering factors. For them, the temperature increase could lead to a possible decrease in the viscosity of the cheese moisture fraction and to a modification of the amount of protein-bound water, which could result in an increase of the relative pore width of the protein matrix. The acceleration of the mass transfer rate with the temperature is not so important in semi-hard and hard-type cheeses, with effective diffusion coefficients up to $2\text{--}4 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ at $20 \text{ }^\circ\text{C}$ in cheese like Romano [35], White cheese [75], Sbrinz [29] or Emmental [60]. Indeed, moisture content is much inferior in

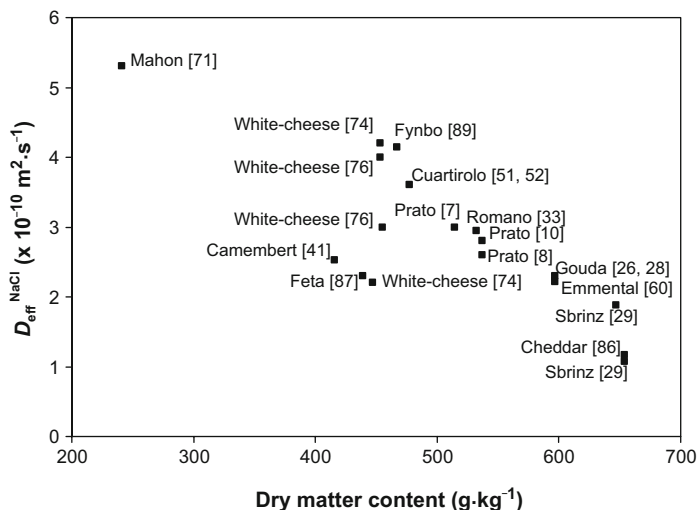


Figure 2. Effective diffusion coefficient of salt versus dry matter content in different cheese types.

semi-hard and hard-type cheeses than in soft- or fresh-type cheeses. Diffusion-interfering effects, which mainly depend on water and protein-bound contents, are then probably much less marked in hard-type cheeses than in soft-type cheeses when the temperature increases.

The factors affecting the rate of salt diffusion in cheese during salting have already been investigated in detail by Geurts et al. [27], Guinee [31, 32] and Guinee and Fox [33–37]. These factors are (i) the concentration gradient across the different zones of cheese, which has a major effect on the level of salt absorption by a cheese during salting, but scarcely affects the rate of salt diffusion; (ii) the ripening temperature and (iii) the cheese composition (fat, protein and moisture). It is difficult to establish the individual effect of each component on the salt diffusion rate because strong interactions exist between them, depending on the cheese microstructure. Data on NaCl effective diffusion coefficients reported on Table II were subjected to statistical analysis by the multiple linear regression (MLR) procedure in Excel[®]. MLR analysis

provides an equation that can be used to predict D_{eff} of salt in cheese matrices, function of parameters such as composition (dry matter (DM) and fat on dry matter ratio (Fat/DM)), temperature (T) and brine composition if available. Each parameter was first centred and reduced to minimize the impact of data order of magnitude. The best equation obtained for D_{eff} of salt was

$$D_{\text{eff}} = 3.39 - 1.25 \times \text{DM} + 0.24 \times \text{fat/DM} - 0.14 \times T. \quad (18)$$

A highly significant ($P < 0.001$) coefficient of multiple determination (R^2) of 0.75 for this model indicated that D_{eff} can be estimated using these parameters. Fat/DM, T and brine composition parameters were not significant ($P < 0.1$). DM was the only significant parameter ($P < 0.001$), meaning that effective diffusion coefficients of salt solutes can be accurately predicted in cheese matrices knowing their dry matter composition (Fig. 2).

Flourey et al. [23] and Lauerjat [46] were first to study the release of salt in the mouth during food chewing according to

the composition of model cheese matrices. The release of salt from the cheese into artificial saliva was mathematically modelled as an effective diffusion process with Fick's second law. The variation in the effective diffusion coefficient of salt according to the cheese matrix compositions was linked to their structural and textural properties. Effective diffusion coefficients were included between 2.7 and $5.1 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ at $13\text{--}15$ °C depending on the matrix composition (Tab. II). These values were of the same order of magnitude as published diffusion coefficients that were measured during the brining of real cheeses of same dry matter and fat content (Fig. 2).

Table II shows that literature on water diffusion in cheese during brining and ripening is not so abundant. Effective moisture diffusion coefficients in cheese have been reported by Luna and Chavez [53] for Gouda cheese, Turhan and Gunasekaran [75] for White cheese and Simal et al. [69, 70] for Mahon and Fresh cheeses. During the salting of cheese in brine, salt and moisture gradients develop from the surface to the core [53]. The ripening process implies water losses due to dehydration of the cheese and salt migration to achieve an almost uniform salt distribution, which is an important factor in cheese ripening [90]. Notice that the values of effective diffusion coefficients of water considerably vary depending on cheese type, and more particularly on the experimental method that was employed to model moisture transfer (Tab. II). It is then difficult to link those values to cheese composition.

During the brining and ripening of cheese, not only is the water content in cheese reduced and the salt concentration increased but, for example, the lactic acid concentration is also modified. Detection of lactic acid in the brine proves that this solute is able to diffuse from the cheese into the brine [48]. Other solutes than salt and water, like lactic acid or small peptides for example, are of crucial importance for the final quality of the cheese and its preservation.

However, diffusion properties of those components were almost not modelled. In the following paragraphs, we give a complete review of the mass transfer properties of these other small solutes in cheese matrices, like lactose, additives and metabolites.

4.2. Transfer of other solutes

Publications concerning the diffusion of small solutes in cheese matrices, except from salt and moisture, are scarce (Tab. II). They deal with the diffusion of whey components such as lactose or sucrose [11, 81, 85], lactic acid [25] and potassium sorbate [40]. One recent study also deals with the diffusion properties of aroma compounds in model cheese matrices of different compositions [47]. Only one research team has published results about mass transfer phenomena of metabolites resulting from biological activities in cheese during brining or ripening [2–4, 72].

4.2.1. Transfer of whey components

Warin et al. [81] modelled the effective diffusion coefficient of sugar in agar gel/milk bilayer system in order to mimic the sucrose and lactose transfer between a dairy product and a fruit layer. The system was modelled with a liquid milk phase on the top of a gel containing agar, citric acid and different concentrations of sucrose. Average disaccharide concentrations at different locations were determined for the system after different diffusion times. Average disaccharide concentrations in each slice of agar gel were deduced from total solids after subtracting agar content and from total solids after subtracting protein and fat contents in the milk phase. Experimental data were fitted to Fick's second law with separate effective diffusion coefficients of sugar in the milk and in the agar gel phases. As sucrose and lactose have the same molecular weight and a similar structure, the authors made the hypothesis that their diffusion properties

were identical. Experimental values of effective diffusion coefficients in milk and agar gel obtained at room temperature (22 °C) were compared to a correlation reported by Hallström et al. [39] for sucrose diffusivity concentration dependence in aqueous solution at the same temperature:

$$\log D_s = -8.271 - 9.2x_s, \quad (19)$$

with D_s the effective diffusion coefficient of lactose and sucrose ($\text{m}^2\cdot\text{s}^{-1}$) and x_s the mole fraction of sucrose. For Warin et al. [81], as the effective diffusivity of sucrose in the agar gel and milk phases could be estimated using a correlation usually employed for the calculation of diffusion coefficients in aqueous solutions, there was neither exclusion effect due to the porosity of the agar phase, nor obstruction effect due to tortuosity of the gel, on the disaccharide diffusion properties. This confirms results showing an effective diffusion coefficient of sucrose in 1.5% agar membranes identical to that in water [49]. With regard to the milk phase, similarly, they concluded that there were no exclusion or obstruction effects of milk proteins on the effective diffusion coefficient of disaccharide solutes.

This study led to interesting results with regard to mass transfer properties of sugar in liquid and low-concentrated matrices. However, it gave no information on effective coefficients of such solutes in structured solid matrices like cheeses.

Bressan et al. [11] modelled the diffusion of whey components (rich in lactose) from small curd cottage cheese particles during their washing process. They considered the diffusion of solutes as isothermal (25 °C) in a porous network with several refinements to account for the whey on curd surfaces. Three geometrical approximations (slab, cube and sphere) for small curd cottage cheese particles were examined using Fick's second law. It was assumed that there was no chemical reaction in the system and no

convective mass transfer in the pores. The term "whey components" was used by the authors to take solutes from low molecular salts to whey proteins into account in the model. One solution to the problem of presenting all solids in a single pseudocomponent was to use a lumped parameter model [6]. The model also included a correction for the whey introduced into the washing system on the surface of the curd or entrained among cheese particles.

Bressan et al. [11] concluded that diffusion from a spherical cheese particle considering whey entrained in curd interstices by capillary forces was an acceptable basis for a mass transfer model. According to them, the model yielded to an effective diffusion coefficient of expected magnitude for lactose, i.e. $3\text{--}4 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ at 25 °C (Tab. II). The diffusion coefficient of lactose at infinite dilution in water at 25 °C is $5.2 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ [54]. The effective lactose diffusion coefficient in the cheese is smaller than the value for infinitely diluted solution, mainly due to the sterical hindrance to the random movement of lactose by the cheese matrix.

Wilde et al. [85] have also studied matrix effects on the diffusion rates of lactose in a soft-type cheese (Quark cheese) and several milk acid gels of different dry matter contents. A two-chamber diffusion tube was used to determine the effective diffusion coefficient of lactose. The product enriched with lactose was introduced into one of the two cylinders and the product with the original lactose content into the other to ensure the concentration difference required for diffusion. The concentration of the diffusing lactose was measured in each slice of 1 mm thickness using both a high pressure liquid chromatography (HPLC) analysis and enzymatic test kits. The model of one-dimensional infinite media with a constant cross-section based on Fick's second law of diffusion for time-dependent diffusion process was verified with regard to the effective diffusion coefficient of lactose

in viscous milk products. The effective diffusion coefficient D_{eff} obtained from lactose concentration profiles at 4 °C in skimmed Quark cheese (dry matter 180 g·kg⁻¹) was $1.37 \pm 0.13 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. In the milk acid gels, D_{eff} showed a linear decline from 1.7 to $0.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ as the dry matter of the product increased from 110 to 210 g·kg⁻¹. The effective lactose diffusion coefficient in skimmed Quark cheese was higher than the value observed in milk acid gels with the same dry matter content (180 g·kg⁻¹). Indeed, Quark cheese is a suspension of coagulated casein particles that are dispersed in a milk whey phase. Lactose diffusion may then mainly take place in the liquid whey phase. Pure diffusion of lactose molecules here is probably slowed down by the dispersed casein particles. Indeed, the structure of milk acid gels gets built up directly in the chamber, resulting in a homogeneous protein network that causes a higher diffusion resistance for lactose molecules. For Wilde et al. [85], the slope of the straight line could characterize the matrix resistance to lactose diffusion.

Although these studies revealed interesting results on the diffusion properties of lactose in dairy matrices, we are still quite far from the microstructure of traditional cheeses from soft- to hard-type cheeses for which dry matter contents are superior to 350 g·kg⁻¹. We could not find any published studies concerning lactose diffusion in such solid matrices.

4.2.2. Transfer of food additives

Potassium sorbate is widely used in processed cheese as a natural preservative. Effective diffusion coefficient of potassium sorbate in American processed and Mozzarella cheeses was determined by Han and Floros [40]. American processed cheese is an emulsion of ingredients such as milk, whey, milk fat, milk protein concentrate, whey protein concentrate and salt, which does not meet the legal definition of

cheese itself. American processed cheese and Mozzarella cheeses had a maximum moisture of 400 and 480–510 g·kg⁻¹ and a minimum milk fat of 270 and 39–42 g·kg⁻¹. To determine the effective diffusion coefficient D_{eff} , the concentration of potassium sorbate in sliced cheese was measured as a function of the distance from the cheese surface. D_{eff} was calculated by non-linear regression with experimental data based on Fick's second law. D_{eff} of potassium sorbate through American processed cheese was $1.31 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ and for Mozzarella cheese $6.74 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$. American processed cheese, because of a higher ratio of moisture-to-fat than the one of Mozzarella cheese (Tab. II), enables the fastest diffusion of water-soluble components. For Han and Floros [40], knowledge of the effective diffusion coefficient of potassium sorbate allows one to accurately estimate the concentration of this preservative agent inside and at the surface, function of time. It will then be possible to predict the preservation time of the product, which corresponds to a residual concentration of potassium sorbate above the critical fungistatic level inside and at the surface of the product [40].

4.2.3. Transfer of aroma compounds

Lauverjat et al. [47] estimated the effective diffusion coefficients of three aroma compounds (diacetyl, heptan-2-one and ethyl hexanoate) in model cheese differing by their composition (Tab. II). They tested two experimental methods: the classical diffusion cell method and the volatile air stripping kinetic (VASK) method. The VASK method is based on the measurement of the aroma compound's gaseous concentration above a layer of product when a gaseous flow rate is applied. Aroma compound's concentration is then measured in-line using a high sensitivity proton transfer reaction-mass spectrometer. This method is much faster than the classical diffusion cell method,

but it is dedicated to the volatile compounds released from the product. Comparing the values obtained for two model cheeses differing by their fat on dry matter ratios, the known effect of fat content on aroma mobility was mainly observed for the two hydrophobic compounds (heptan-2-one and ethyl hexanoate). When the fat on dry matter content increased from 20% to 40%, the effective diffusion coefficients showed a 45% decrease for heptan-2-one and a 60% decrease for ethyl hexanoate (Tab. II).

4.2.4. Transfer of metabolites

Aldarf et al. [2], Stephan et al. [71], Aldarf et al. [3] and Amrane et al. [4] modelled – independently – the diffusion of lactate, glutamate and ammonium in relation either to the growth of *Geotrichum candidum* or to the growth of *Penicillium camembertii* at the surface of model matrix (agarose) simulating Camembert cheese. The main purpose of these papers was to study the mechanisms of diffusion and to propose a theoretical approach that could be subsequently applied to curd during ripening for its monitoring and control. The assimilation of lactic acid by *G. candidum* (and *P. camembertii*) growing at the surface of the curd induced a concentration gradient, which results in the diffusion of this metabolite from the core to the rind. In a similar way, ammonium production at the surface of the curd induced a diffusion of this metabolite from the rind to the core. These diffusion mechanisms appeared therefore as the main factors in soft cheese ripening.

These authors developed a diffusion/reaction model in which the diffusion of lactic acid from the bottom of the gel to the upper surface, or that of glutamate and ammonium from the upper surface to the bottom of the gel, is induced by their respective consumption and production at the surface of the gel due to fungal growth. Growth kinetics were described using the widespread Verlhust model [58], and both substrate consumption

and ammonium production were considered to be linked to growth. The experimental diffusion gradients of substrates (lactate and glutamate) and ammonium recorded during *G. candidum* growth were fitted to the Fick's second law using Crank's solution [17]. Effective diffusion coefficients were deduced from the experimental concentration gradients. Values of $4.63 \pm 0.34 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ for lactate, $6.48 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ for glutamate and $9.26 \pm 0.58 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ for ammonium were found, regardless of the pH of the experiment. For lactate and ammonium components, the effective diffusion coefficients found in 2% agarose were, respectively, 57% and 64% of their value in pure water.

This result clearly showed that agarose gel slowed down the diffusion rates of lactate and ammonium components. The diffusion/reaction model fitted with the experimental data until the end of growth, except with regard to ammonium concentration gradients during *G. candidum* growth on peptone-lactate-based medium. Of course, the diffusion/reaction model has to be considered as a preliminary step, which has to be followed by a similar work on real dairy model media, more precisely a lactic curd, in order to better understand the mechanism of curd neutralization, responsible for the development of texture.

5. ALTERNATIVE METHODS APPLICABLE TO CHEESE

Concentration profiles can also be considered on a microscopic scale using a representative molecule, or probe molecule, which can be easily characterized using a specific technique [15]. Recent advances in non-invasive, continuous techniques of measurement, e.g. magnetic resonance imaging (MRI), NMR or FRAP, now allow the use of higher space and time resolutions (Tab. I). Indeed, using radioactively labelled or fluorescent molecules, it is possible to measure the rate

of diffusion of one component in a multicomponent system. What is involved is an interchange of labelled and unlabelled molecules, while the total amount of that molecule, labelled and unlabelled, is constant throughout the system [15]. The transport of molecules is essentially caused by intermolecular collisions (Brownian motions). As a consequence, no mass flow occurs and a diffusion coefficient called “self-diffusion coefficient” is measured [18].

5.1. Nuclear magnetic resonance

The pulsed field gradient NMR (PFG-NMR) technique is a powerful tool that can be used to measure polymer self-diffusion coefficients in suspensions and gels. It is a non-destructive and non-invasive way to measure the self-diffusion coefficient of small molecules by detecting the proton mobility [16]. In a PFG-NMR experiment, the observation time can vary from few milliseconds up to several seconds. Depending on the observation time, the magnitude of the diffusion coefficients obtained at different observation scales enables one to discriminate the different transport mechanisms. For example, if the self-diffusion is independent of the observation time for a porous system, then the system exhibits no restriction to diffusion.

In 1983, Callaghan et al. [13] compared water self-diffusion in Cheddar and Swiss-type cheeses. Their results have shown that water molecules were not confined in water droplets, but had the freedom to move over distances much longer than the fat droplet sizes. The magnitude of the diffusion coefficients was consistent with a migration along the surface of the protein chains. According to Mariette et al. [55], water diffusion in casein systems can be explained by two diffusion pathways: one around and the other through the casein micelles. The obstruction effect on water diffusion was related to local restrictions at the casein micelle surface and explained the absence of any effect of

casein gelation by rennet. Moreover, Metais et al. [56] showed that the water self-diffusion coefficients in casein matrices could not be simply explained by the water content only. When caseins, fat globules and soluble fractions are mixed in order to obtain cheese models, the effect of each constituent should be determined to accurately explain the water self-diffusion. They also showed that the two obstruction effects, relative to fat globules and casein micelles, seemed to be independent. This result was in agreement with the observation of Geurts et al. [27], despite the fact that the measurement methods and the diffusing molecules considered were different.

Colsenet et al. [16] used PFG-NMR spectroscopy to study the diffusion of molecular probes (polyethylene glycols (PEG)) in casein suspensions and casein gels, in order to determine the effects of probe molecular size, casein concentrations and rennet coagulation. A more complex behaviour was observed for PEG molecules than for water. First of all, a strong dependency of diffusion on probe size was observed, both in casein suspensions and in casein gels: as the PEG size increased, the self-diffusion coefficient was reduced. This effect was more pronounced for high casein concentrations than for low casein concentrations: the larger the PEG size, the greater the obstruction to diffusion. Second, the formation of a rennet gel resulted in an enhanced self-diffusion coefficient for the largest probes.

The main drawback of this technique is the high cost of the material. Its main difficulty for the scientists is to establish the physical link between this self-diffusion coefficient measured by PFG-NMR and the values of the effective diffusion coefficient estimated in complex matrices with more classical methods. Moreover, it is restricted to the study of mass transfer phenomena of solutes which present spectral properties easily discernable from spectral data of the matrix components. The application of this

technique to solutes like small peptides or proteins naturally present in cheese is thus hardly possible.

5.2. Magnetic resonance imaging

Other promising non-destructive approach to measure diffusion properties of salt and water in food products is MRI.

^{23}Na -MRI is based on the paramagnetic properties of the naturally occurring ^{23}Na isotope, which makes it detectable in strong magnetic fields [79]. Within the past decade, ^{23}Na -MRI has proved to be a reliable method for quantitative and qualitative assessment of salt in various foods such as fermented soy paste (Miso), pickled cucumbers and plum seeds [42], snow crab [59] and pork meat [30, 63]. Besides being non-destructive, this method has the advantage of being easily supplemented by other relevant measurements such as sodium profiles and diffusion-weighted imaging, simply by changing the acquisition parameters. Diffusion-weighted imaging allows the visualization of changes in microscopic water molecule motion (Brownian motion) and quantitative measures of diffusion properties of water in food structures like muscle tissues [79]. For Vestergaard et al. [78], the ^{23}Na -MRI methodology is still under intense investigation around the world because the problem of sodium being partly “invisible” (a certain percentage of the Na^+ is not detected) has not been solved yet.

MRI has also been used to visualize water distribution in one, two or three directions during the drying, rehydration, freezing and thawing of various fruits and vegetables [65, 66]. Indeed, loss of proton mobility during phase transitions results in a decrease in signal intensity. Kuo et al. [45] applied this technique to study the formation of ice during freezing of pasta filata and non-pasta filata Mozzarella cheeses, the spatial redistribution of water T_2 relaxation time and the changes of water self-diffusion coefficient within unfrozen and frozen-stored cheese

samples. Images of water spin number density and water T_2 relaxation time were obtained using spin-echo imaging pulse sequence. The water self-diffusion coefficient was measured by PFG spin-echo technique. They measured a significant change in T_2 and D values of water following freezing-thawing. The D values of the frozen-stored pasta filata Mozzarella cheese samples were higher than those for the unfrozen samples. Such a difference was not observed for the non-pasta filata Mozzarella cheese samples. These results were attributed to the microstructure differences between the two cheeses.

Despite the advantage of being a very precise non-destructive analytical technique, MRI presents some inherent difficulties, like a complex calibration and data handling work, errors in the determination of the physical boundaries and possible low signal-to-noise ratios [24]. Moreover, the conventional MRI techniques are typically designed for component with high molecular mobility, for which the water T_2 relaxation times are rather long ($> \text{ms}$). Such techniques are then insensitive to molecules with low mobility, for which the transverse relaxation times are very short ($< \text{ms}$). Therefore, limitations of conventional MRI have hampered its application to a major class of food systems, i.e., where mobility of water is restricted because of its strong association with the matrix [62].

5.3. Fluorescence recovery after photobleaching

Within the last 30 years, FRAP has become an important and versatile technique to study the dynamics in various systems, such as living cells, membranes and other biological environments [14]. In polymer physics, the photobleaching methods are employed to investigate diffusion in macromolecular systems, particularly in networks. Although the technique is relatively old, its application to study endogenous

intracellular proteins in living cells is relatively recent [14]. A review of the fundamentals of FRAP and several examples of its applications is given by Meyvis et al. [57]. Its principle is to irreversibly photobleach a certain region within a fluorescently labelled sample by irradiation with a short intense light pulse. Immediately after bleaching, a highly attenuated light beam is used to measure the recovery of fluorescence inside the bleached area as a result of diffusional exchange of bleached fluorophores by unbleached molecules from the surroundings. The analysis of this process yields information about the diffusion coefficient and the fraction of mobile species.

In a common FRAP experiment, only the rate of recovery of the fluorescence intensity within some preselected area is measured. Performing the experiment in a confocal laser scanning microscope (CLSM) reveals the same information with high spatial resolution [68]. To measure the mobility of a fluorescent molecule such as green fluorescent protein, images of the fluorescently labelled cell are collected over time, while the fluorescent and photobleached molecules redistribute until equilibrium is reached. By plotting the relationship between fluorescence intensity and time, the mobility of the fluorescent proteins can be directly measured [14]. The most commonly used approach to describe the mobility of molecules during FRAP experiments is to assume the spatiotemporal dynamics of these molecules to be diffusive in nature. Under this assumption, the kinetic parameter that measures the rate of movement is the effective diffusion coefficient, determined with Fick's diffusion model. This microscopic, non-destructive and slightly invasive technique, in which the probe concentration remains micromolar, originates from mobility studies in biological membranes [5]. It was then extended to other fields, mostly for liquid or highly hydrated systems, in which diffusion follows the Stokes-Einstein law [44]. It covers a wide

range of apparent diffusion coefficients, from 10^{-20} to $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ [43].

In spite of its interest and its simplicity to be implemented, the FRAP technique has not been used yet for the determination of solute diffusion coefficients in dairy matrices. Indeed, to be able to use this method, the migrating molecule has to be fluorescent or labelled with a fluorescent probe. This is not the case of small solutes such as NaCl or water. For bigger molecules, it is necessary to find a fluorescent probe with a great affinity for the diffusing solute to be labelled or with similar size and physicochemical properties in order to simulate the targeted molecule. Moreover, this method seems difficult to adapt to complex and opaque matrices like cheese.

6. CONCLUSION

Mass transfer of solutes in cheese is essential for the ripening process and the final quality of the cheese. Numerous studies have been reported on the transfer of salt in different cheese types during the brining and ripening processes. Some of them also take the simultaneous counterflow of water into account, even if modelling moisture transfer seemed to be more complicated. Effective diffusion coefficients of salt and moisture in different cheese types and compositions have been reported in this review. Regardless of the cheese origin, its type (soft, semi-hard or hard) and its composition (dry matter, fat and pH), the effective diffusion coefficients of salt ranged between 1 and $5.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ at around 10–15 °C. A significant linear relationship between dry matter content of the matrix and effective diffusion coefficient of salt was statistically observed. However, these values should be considered cautiously because their comparison is difficult. Indeed, there are very large discrepancies of approaches used to determine solute mass transfer properties and of

the experimental conditions employed. For example, if diffusion properties are obtained using the concentration profile method with an invasive method to follow the migrating molecule concentration, spatial resolution is generally quite low and the results are not precise enough.

Very few papers are dealing with the mass transfer properties of other small solutes in cheese. However, modelling the effective diffusion coefficient of cheese minor components, such as lactose and biological metabolites, substrates and products of the enzymatic activity of immobilized colonies, seems essential for the control and the optimization of cheese ripening. Indeed, migration rates of those solutes are probably the limiting step during the ripening stage. The knowledge of the migration rates appears to be essential for the full understanding of cheese ripening.

Alternative methods considered as non-destructive, such as MRI, NMR or FRAP techniques, are currently developed to measure the self-diffusion coefficient of solutes in heterogeneous matrices. Thanks to their high space resolution, these techniques make it possible to obtain concentration profiles of the migrating solute with a good precision and to avoid problems due to sample variability. However, they are still difficult to apply to complex and heterogeneous media like cheese (Tab. I). Further research is necessary to adapt those promising methods to the determination of mass transfer properties of a wide variety of small solutes in complex heterogeneous matrices like cheese or other real food media.

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