Journal of Food Engineering 100 (2010) 557–566

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Determination of aroma compound diffusion in model food systems: Comparison of macroscopic and microscopic methodologies

Isabelle Déléris [a,*], Isabelle Andriot [b], Mallory Gobet [b], Céline Moreau [b], Isabelle Souchon [a], Elisabeth Guichard [b]

[a] UMR 782 INRA-AgroParisTech Génie et Microbiologie des Procédés Alimentaires, 1 avenue Lucien Brétigniéres, F-78850 Thiverval-Grignon, France
[b] INRA, UMR 1324 CSGA, 17 Rue Sully, F-21000 Dijon, France

ARTICLE INFO

Article history:
Received 12 March 2010
Received in revised form 8 May 2010
Accepted 12 May 2010
Available online 16 May 2010

Keywords:
Self-diffusion
Apparent diffusion
Gel structure
Aroma compounds

ABSTRACT

Diffusion properties at macroscopic and microscopic scales for three aroma compounds (in solution and gel systems) were characterized using three different methodologies: the diffusion cell and the Volatile Air Stripping Kinetic methods for the determination of apparent diffusion coefficients and the pulsed-field-gradient Nuclear Magnetic Resonance method for the determination of self-diffusion coefficients. The accuracy of the methods was established by comparing ethyl hexanoate diffusion coefficient in water or D_2O solution and in 1%-agar gel system at 25 and 30 °C. The robustness of the three methodologies was also investigated in 1%-*iota*-carrageenan system with different NaCl content leading to gel strengthening.

In 1%-agar gel as well as in 1%-*iota*-carrageenan systems, the apparent or self-diffusion coefficients of aroma compounds had the same order of magnitude regardless of the approach, ranging between 2.3×10^{-10} and 10.4×10^{-10} m^2 s^{-1}. Diffusion properties were discussed in terms of the different observation scales (diffusion scales) and of the nature of gel network.

1. Introduction

Food organoleptic properties are largely dependent on the way aroma compounds are released and perceived during food eating. These two phenomena involve multi-factorial and complex processes that depend on both physiological and physico-chemical parameters.

In food science, a better control of food flavouring needs a better understanding of aroma compound mobility/diffusion within food products. Concerning the study of food products, the choice of a diffusion measurement method is often a critical step to obtain exploitable data (Westrin et al., 1994), notably because of the complexity in terms of composition and/or structure of the studied media.

The determination of relevant thermodynamic and kinetic parameters such as air/product partition coefficient, and diffusion or mass-transfer coefficients is a way to characterize the impact of product composition and structure on aroma mobility and release.

The air/product partition coefficient $K_{H/P}$ of a molecule (i) from a product is defined as the ratio of mass concentrations at equilibrium in the gaseous phase (C_{iH}, kg m^{-3}) and in the food product (C_{iP}, kg m^{-3}) (Eq. (1)).

$$K_{H/P} = C_{iH}/C_{iP} \quad (1)$$

It can provide quantitative information on the retention effect of food matrix on aroma compounds (de Roos, 2000; Jouquand et al., 2004; Seuvre et al., 2004). However, aroma release and perception are time-dependent phenomena and the knowledge of kinetic parameters is necessary to better understand the behaviour of volatiles in food matrices (de Roos, 2003; Boland et al., 2006).

Molecular diffusion is defined as the net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion and results in a gradual mixing of material (Cussler, 1997). In a phase with uniform temperature and with no external forces on the particles, the diffusion process can result in complete mixing or in a state of equilibrium. Molecular movements can be either translational (due to the gradient concentration of the diffusing species) or rotational (corresponding to the frequency of molecular reorientation). Molecular diffusion can be mathematically described using Fick's First law (Eq. (2)), in which the diffusion coefficient D can be defined as the rate of transfer of the diffusing molecule across the diffusion section divided by the space gradient concentration in this specific section (validity in steady state conditions).

* Corresponding author. Tel.: +33 (0)1 30 81 54 86; fax: +33 (0)1 30 81 55 97.
E-mail address: isabelle.deleris@grignon.inra.fr (I. Déléris).

0260-8774/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2010.05.006

$$J = -D \times \frac{\partial C}{\partial x} \quad (2)$$

where J is the flux (kg s^{-1} m^{-2}), D the diffusion coefficient (m^2 s^{-1}), C the concentration (kg m^{-3}) and x the distance (m). When transient flow is considered, Fick's second law gives:

$$\frac{\partial C}{\partial t} = D \times \frac{\partial C}{\partial x^2} \quad (3)$$

where t is the time (s).

For the experimental determination of diffusion coefficients, lots of methods are described in the literature (Westrin et al., 1994; Cussler, 1997; Cayot et al., 2008) each one having its advantages and limits depending on the application fields. Mobility characterization at macroscopic scale can be assessed by experimental methods based on the presence of a concentration gradient. The concentration profile technique (axial diffusion between two pieces of product or between a piece of product and another phase with different initial concentrations) appears as one of the reference methods for food (Gros and Ruegg, 1987; Gerla and Rubiolo, 2003; Sebti et al., 2004). However, its application from an experimental point of view is reduced to materials that can be sliced, and the large set of samples that is required limits its use (Voilley and Bettenfeld, 1985). The diaphragm cell technique has also been largely applied, notably for dispersed systems (Landy et al., 1998) or for gels and foods (Djelveh et al., 1989). These last methods are relatively inexpensive, easy to set up and are accurate to as much as 0.2% (Cussler, 1997). However, they are often invasive and not adapted to non-solid products.

Instrumental techniques such as Fluorescence Recovery After Photobleaching (FRAP) (López-Esparzaa et al., 2006), Fluorescence Correlation Spectroscopy (FCS) (Masuda et al., 2006) or Nuclear Magnetic Resonance (NMR) (Simoneau et al., 1993; Gostan et al., 2004; Rondeau-Mouro et al., 2004; Savary et al., 2006b) have also been widely used to characterize mobility of molecules within matrices or through films at microscopic scale. More specific instrumental technologies can also be applied, such as ultrasonic velocity profiling to access sucrose diffusion in oil-in-water emulsions (Basaran and McClements, 1999) or dynamic light scattering in micro-emulsions (Michel et al., 2002). But, in the case of food characterization, sample opacity, product complexity (composition or structure) as well as the high costs or the high technical character of equipments largely contribute to limit their application.

Facing the few data available in the literature concerning diffusion properties of aroma compounds within food products, the comparison of results obtained with different methods is a tempting solution. But one can wonder about the reliability of such an approach as observation scales (microscopic versus macroscopic) are different.

The aim of this study was to compare diffusion properties of aroma compounds in model food products determined by three methodologies. The diffusion cell (Déléris et al., 2008) and the Volatile Air Stripping Kinetic (VASK) (Lauverjat et al., 2009) methods use a global approach and enable the determination of apparent or effective diffusion, D_{app}, at macroscopic scale. Pulsed Field Gradient (PFG-) NMR spectroscopy is a high resolution technique for measuring local diffusion at a microscopic scale in a non invasive way (Antalek, 2002; Cohen et al., 2005; Price, 2000; Stallmach and Galvosas, 2007). PFG-NMR allows the investigation of the translational movements of molecules commonly referred as the self-diffusion process and defined by self-diffusion coefficients, D_{self}.

In a first step, the accuracy and the reliability of the three methodologies were compared for the determination of the diffusion properties of ethyl hexanoate at 25 and 30 °C in water or D_2O and 1%-agar gel. Then, by varying NaCl content, 1%-*iota* carrageenan systems of different rheological structures were considered. Investigating the influence of gel structure on aroma compound diffusion enables to discuss results in relation with the observed diffusion scale for each methodology.

2. Experimental sections

2.1. Materials

Aroma compounds (ethyl hexanoate, 2-heptanone, 1-octen-3-ol), D_2O (99.9% purity) with 0.05% TSP (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt) and NaCl were purchased from Sigma Aldrich (France). Aroma compounds purity was checked by GC–MS (>95%). *Iota*-carrageenan was supplied free of charge by Rhodia Food (France). Agar was purchased from Merck (Germany). Physico-chemical parameters of aroma compounds are given in Table 1.

2.2. Preparation of diffusive media

Agar gel and *iota*-carrageenan systems were prepared at 1% (w/w) in water (for diffusion cell and VASK methods) or in D_2O (for NMR measurements).

Agar gel was prepared by mixing 1%-agar (w/w) in boiling water or D_2O, and by stirring for 1 h at 85 °C (gelling temperature 35 °C) (Millàn et al., 2002).

Carrageenan matrices were prepared by mixing *iota*-carrageenan powder (1% w/w) in water or D_2O with different salt content (0%, 0.6% or 1.5% w/w of added NaCl). Each matrix was stirred for 30 min at 90 °C to obtain the total solubilization of carrageenans (gelling temperature 32.5 °C) (Millàn et al., 2002).

Regardless of the method, products were poured into the appropriate containers while still warm so that gelling occurred *in situ* (40 g in 1.7 L diffusion cell (0.1 m diameter), 25 g in 0.25 L flask (Schott, France, 65×10^{-3} m diameter) for the VASK method or 0.5 g in sealed NMR tube (5×10^{-3} m diameter, $V_{observation}$ = 0.5 mL). The use of gelling material and of a constant temperature during measurements, made it possible to avoid convection linked to uncontrolled local movements without changing diffusivity properties in the entrapped solution (Menting et al., 1970).

The diffusion of aroma compounds was studied in H_2O or D_2O at 25 and 30 °C and in gelling materials at 25 °C for 1%-agar gel (w/w) and 30 °C for 1%-*iota*-carrageenan matrices (w/w). Table 2 summarizes the studied diffusive media and molecules, and the three methodologies: diffusion cell, VASK method and PFG-NMR spectroscopy detailed in the next sections.

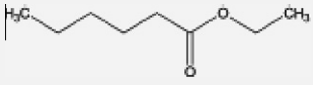
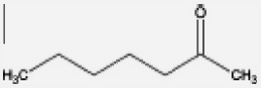
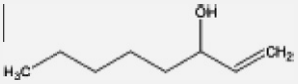
For cell diffusion, pure aroma compounds were placed at the bottom of the diffusion cell and non-flavoured agar or carrageenan matrices were used.

Aroma stock solutions (ethyl hexanoate, 2-heptanone and 1-octen-3-ol) were previously prepared in H_2O for VASK method, and in D_2O for NMR spectroscopy. Flavoured products were prepared by adding and mixing aroma solutions. This was done to obtain a given final concentration (Table 2) in the appropriate container at a temperature higher than the gelling temperature (35 °C for agar and 32.5 °C for *iota*-carrageenan).

2.3. Rheological characterization of 1%-agar gel

Dynamic oscillatory measurements were performed on agar gel using a stress-controlled rheometer Physica MCR301 (Anton Paar, Germany) equipped with coaxial cylinders (ISO3912, cup diameter 28.92 mm; bob diameter 26.66 mm; gap length 39.99 mm). The hot sample was poured and covered with a layer of paraffin oil to minimize evaporation during measurements, and left to stabilize

Table 1
Physico-chemical parameters of aroma compounds and their apparent air/product partition coefficients $K_{H/P}$ from water at 25 °C, from 1%-agar gel at 25 and 30 °C and from 1% *iota*-carrageenan systems at 30 °C, and associated standard deviations.

		Ethyl hexanoate	2-Heptanone	1-Octen-3-ol
Structure				
Molecular weight ($g\ mol^{-1}$)		144.21	114.19	128.21
logP[a]		2.83	1.73	2.60
$K_{H/P}$ (10^{-3}) literature	Water, 25 °C	29.5[b], 34.0[c]	5.7[g]	–
	Water, 30 °C	30.2[d]	–	3.1[h]
	1%-Agar gel, 25 °C	46.2[e], 55.0[f]	–	–
$K_{H/P}$ (10^{-3}) experimental values[i]	Water, 25 °C	33.5 ± 1.6	–	–
	1%-Agar gel, 25 °C	38.1 ± 3.5	–	–
	1%-Agar gel, 30 °C	62.1 ± 5.6	12.0 ± 0.8	2.73 ± 0.6
	1%-ι-carrageenan, 0% NaCl, 30 °C	77.1 ± 9.1	20.7 ± 1.1	3.27 ± 0.2
	1%-ι-carrageenan, 0.6% NaCl, 30 °C	58.5 ± 8.0	23.6 ± 1.6	2.72 ± 0.3
	1%-ι-carrageenan, 1.5% NaCl, 30 °C	41.1 ± 5.4	6.72 ± 2.6	2.66 ± 0.3

[a] Estimation with EPISuite™ program.
[b] Experimental data (Athès et al., 2004).
[c] Experimental data (Landy et al., 1996).
[d] Experimental data (Savary et al., 2006a).
[e] Experimental data (Déléris et al., 2008).
[f] Experimental data (Lauverjat et al., 2009).
[g] Experimental data (Jouquand et al., 2004).
[h] Experimental data (Yven et al., 1998).
[i] Experimental determination using the Phase Ratio Variation method.

Table 2
Summary of the studied systems and of the applied methodologies to characterize aroma compound diffusion.

	Diffusing media			
	Studied property	H_2O or D_2O	Agar gel (1% w/w) in H_2O or D_2O	*Iota*-carrageenan systems (1% w/w) in H_2O or D_2O with 0%, 0.6% or 1.5% w/w NaCl
Methods for diffusion measurement		T = 25 or 30 °C	T = 25 or 30 °C	T = 30 °C
Diffusion cell	Apparent diffusion	Pure aroma compound in the bottom of the diffusion cell. Non-flavoured media		
VASK	Apparent diffusion	Flavoured with: 1.3 μM ethyl hexanoate	Flavoured with: 1.3 μM ethyl hexanoate +1.0 μM 2-heptanone +4.1 μM 1-octen-3-ol	Flavoured with: 1.3 μM ethyl hexanoate +1.0 μM 2-heptanone +4.1 μM 1-octen-3-ol
PFG-NMR	Self-diffusion	Flavoured with: 1 mM ethyl hexanoate or 0.3 mM 2-heptanone or 0.3 mM 1-octen-3-ol	Flavoured with: 1 mM ethyl hexanoate	Flavoured with: 0.3 mM ethyl hexanoate or 0.3 mM 2-heptanone or 0.3 mM 1-octen-3-ol

at 20 °C. Small deformation oscillatory shear measurements were performed at strain amplitude of 1% (within linear viscoelastic range). The protocol used was a frequency sweep with a mechanical spectrum from 100 to 0.01 Hz in log mode. Measurements were done once a day over 4 days. The reproducibility of G′ and G″ values was within 5%.

2.4. Determination of apparent diffusion coefficients with the diffusion cell and the VASK method

The determination of apparent diffusion coefficients with the diffusion cell or the VASK method is based on the fitting of a mechanistic model, which results from mass transfer analysis in the systems, to experimental release kinetics. An accurate determination of apparent diffusion properties requires the preliminary measurement of air/product partition coefficients $K_{H/P}$ of aroma compounds.

2.4.1. Experimental determination of the air/product partition property $K_{H/P}$ of aroma compounds

The Phase Ratio Variation method (PRV) (Ettre et al., 1993) was used to access the air/product partition coefficient. For this purpose, water was flavoured with ethyl hexanoate at 0.2 mM and 1%-agar gel and 1%-*iota*-carrageenan matrices with a mixture of ethyl hexanoate, 2-heptanone and 1-octen-3-ol (0.2 mM each, final concentrations in the product). Vials (22.4 mL, Chromacol, France) were prepared once products were gelled. They were incubated at the studied temperature over night (25 and 30 °C for agar gel and 30 °C for carrageenan matrices). Two mL of the headspace above the product were sampled and injected with an automatic HS CombiPal sampler (CTC Analytics, Switzerland) into a gas

chromatograph (GC-FID HP6890, Germany) equipped with an HP-INNOWax polyethylene glycol semi-capillary column (30 m × 0.53 mm, with a 1 μm-thick film) and a flame ionization detector. The temperatures of the gas chromatograph injector and detector (GC-FID HP6890, Germany) were set at 250 and 240 °C, respectively. The oven program was 15.4 min long, starting at 50 °C, for 8 °C min^{-1} up to 85 °C, for 5 °C min^{-1} up to 100 °C, for 10 °C min^{-1} up to 170 °C and 1 min at 170 °C. The carrier gas was helium (flow rate 8.4 mL min^{-1} corresponding to a 57 cm s^{-1} average velocity at 50 °C). Peak areas were measured using Hewlett–Packard Chemstation integration software. A non-linear regression was applied in order to accurately determine the air/product partition coefficients (Atlan et al., 2006). All experiments were performed in triplicate to validate the repeatability of the measurements.

2.4.2. Determination of experimental release kinetics of aroma compounds using the diffusion cell

The system, as schematised in Fig. 1A, was composed of two main gaseous compartments (V_G and V_H), separated by the studied product supported by a thin hydrophobic porous membrane (polypropylene, porosity: 55%; thickness: 25 μm) (Déléris et al., 2008). The diffusion cell was closed after 40 g of product was deposited on the membrane (product height $h_{gel} = 2 \times 10^{-2}$ m) and placed in a temperature-controlled vessel (25 or 30 °C) during several hours for temperature equilibration. The experiment started with the introduction of pure aroma compounds in the bottom part of the apparatus with a 50 mL syringe and lasted 6 days. Aroma compounds moved from the gaseous phase of the lower compartment, diffused through the food product and were finally released in the gaseous phase of the sampling compartment. This release was measured by regularly sampling the headspace above the product with a gastight syringe as described by Déléris et al. (2007). Each measurement was performed in duplicate for each product.

2.4.3. Experimental release kinetics using the VASK method

The Volatile Air Stripping Kinetic method (VASK) is based on the measurement of the variation in aroma compound gaseous concentration above a layer of product when a gaseous flow rate is applied (Fig. 1B). An aliquot of 25 g of flavoured product (product height $h_{gel} = 7.5 \times 10^{-3}$ m) was gelled in 0.25 L flasks (Schott, France) closed with gastight caps (Omnifit 00945Q-2V) and placed in a thermostated vault (25 or 30 °C) during 12 h to let the thermodynamic equilibrium between the product and the headspace set up before measurement, as already described by Lauverjat et al. (2009). Flasks were then connected to a high sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS) (Ionicon Analytik, Innsbruck, Austria). The PTR-MS technique was used as described by Hansel et al. (1995). The PTR-MS instrument drift tube was thermally controlled (60 °C) and operated at 1.8 (±7.5 10^{-3}) mbar with a voltage set at 600.1 (±0.4) V. The ratio E/N (E is the electric field and N is the number density of the gas in the drift tube) was 168.7 (±0.2) Td (Townsend 1 Td = 10^{-17} cm^2 V^{-1} s^{-1}). Valves on vial caps made it possible to purge the flask headspace for 12 min with a constant air flow (fixed between 20 and 40 mL min^{-1}). Measurements were performed using the Multiple Ion Detection mode with a dwell time per mass of 0.1 s. From the fragmentation patterns of the individual compounds, the studied compounds were monitored with m/z 69 (1-octen-3-ol), m/z 115 (2-heptanone) and m/z 145 (ethyl hexanoate). No fragment overlapping and no ionization competition were noticed. The signal-to-noise ratio varied from 70 to 700 depending on the measured m/z, meaning that the responses for the studied compounds sufficiently exceeded the baseline. Mass/charge ratios m/z 21 (signal for $H_3{}^{18}O^+$) and m/z 37 (signal for water clusters H_2O–H_3O^+) were monitored to check instrument performances and cluster ion formation. The count rate of H_2O–H_3O^+ was 0.99–1.99% of the count rate of $H_3{}^{16}O^+$ ions, which was (8.4–10.2) 10^6 count s^{-1}. Three replicates were performed for each product.

2.4.4. Determination of apparent diffusion properties from release kinetics

For both methods, the apparent diffusion coefficient D_{app} (m^2 s^{-1}) was determined by numerically fitting a mechanistic model to the experimental release data using the Levenberg–Marquardt algorithm (least squares curve fitting). The mechanistic model is composed of a set of differential equations describing the main mass transfer phenomena occurring within the compartments of the diffusion cell (headspace, gaseous phase and product, Déléris et al., 2008) or within the 0.25 L flask (Lauverjat et al., 2009). Transport was considered as one-dimensional along the vertical axis and uniform on the cross section. Assumptions on local thermodynamic equilibrium at the interfaces and mass flux conservation through the interfaces at all times and mass balances for each phase led to a mathematical description of the systems. The main assumption was a limiting diffusive mass transfer of aroma compounds within the product layer, characterized by an apparent diffusion coefficient of the aroma compound in the product (D_{app}) on the basis of Fick's second law (Eq.(4)).

$$\frac{\partial C_P(x,t)}{\partial t} = D_{app} \times \frac{\partial^2 C_P(x,t)}{\partial x^2} \tag{4}$$

where C_P is the aroma compound concentration in the gel (kg m^{-3}), t the time (s) and x the vertical position (m). The gaseous phases

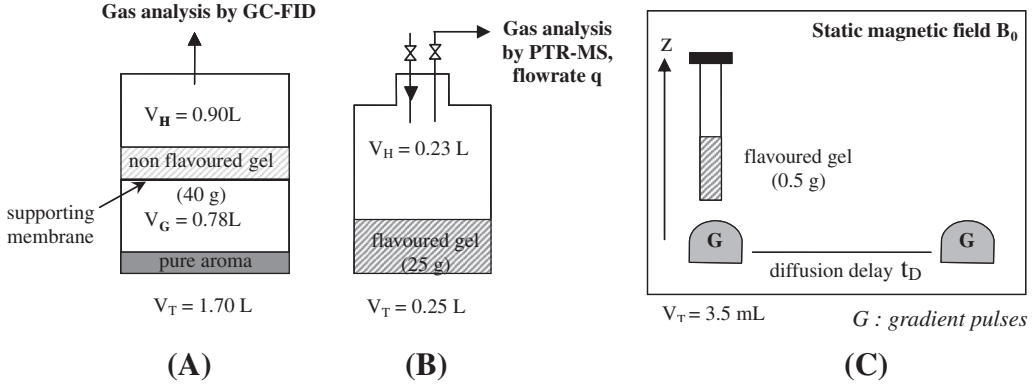


Fig. 1. Principles of the three methodologies: (A) the diffusion cell (V_T = 1.70 L with V_G = 0.78 L and V_H = 0.90 L, ϕ = 0.1 m, $h_{gel} = 2 \times 10^{-2}$ m, m_{gel} = 40 g); (B) the VASK method (V_T = 0.25 L, $\phi = 65 \times 10^{-3}$ m, $h_{gel} = 7.5 \times 10^{-3}$ m, m_{gel} = 25 g) and (C) the NMR tube (V_T = 3.5 mL, $V_{observation}$ = 0.5 mL, $\phi = 5 \times 10^{-3}$ m, $h_{gel} = 35 \times 10^{-3}$ m, m_{gel} = 0.5 g).

were considered as uniform, and a convective mass transfer was assumed, characterized by a mass-transfer coefficient k_H (Eq. (5)).

$$V_H \times \frac{dC_H(t)}{dt} = A \times k_H \times [C_{iH}(t) - C_H(t)] - Q \times C_H(t) \quad (5)$$

where A is the cross section of the system (m^2), C_H the aroma compound concentration in the gas above the product ($kg\ m^{-3}$), C_{iH} the aroma compound concentration in the gaseous phase at the interface gas/product ($kg\ m^{-3}$), Q the stripping flow rate ($m^3\ s^{-1}$) and V_H the volume of the gaseous phase above the product (m^3). For the diffusion cell (closed space), the flow rate value is zero.

The interfacial balance was characterized by the air/product partition coefficient $K_{H/P}$, defined as the ratio between the aroma concentrations on either side of the interface (Eq (1)). At the product/headspace interface, mass flux conservation was written as:

$$A \times D_{app} \times \frac{\partial C_P(x,t)}{\partial x} = A \times k_H \times [C_{iH}(t) - C_H(t)] \quad (6)$$

Numeric calculations were performed using Matlab 7 software (The Mathworks, Natick, MA) and the associated statistical toolbox. Confidence intervals were determined to evaluate the accuracy of the estimated apparent diffusion coefficients.

2.5. Determination of self-diffusion coefficients using PFG-NMR spectroscopy

In PFG-NMR experiment, the molecular displacement of a molecule is probed by applying an external linear magnetic field gradient along one sample axis, the *z*-axis, as schematised in Fig. 1C. The gradient pulses (G) applied before (gradient encoding period) and after (gradient decoding period) the experimental diffusion time (t_D) allow the positions of the nuclei to be tracked. With no concentration gradient, NMR is thus capable of monitoring the random motion or translational motion in the millisecond-second time range.

Over the course of the diffusion experiment, the '*I*' signal intensity of the diffusive molecule decays exponentially with the square of the gradient area according to:

$$I = I_0 \exp\left(-D_{self} \times q^2 \times t_D\right) \quad (7)$$

where I_0 is the signal intensity in the absence of an applied magnetic field gradient, D_{self} is the self-diffusion coefficient ($m^2\ s^{-1}$), q^2 is the gradient amplitude with $q = \gamma \times g \times \delta$ where γ is the gyromagnetic ratio of the observed nucleus ($G^{-1}\ s^{-1}$), and g and δ are the gradient strength ($G\ m^{-1}$) and length (s) respectively, t_D is the experimental diffusion time (s).

The decay rates of the exponential curves for the molecules are thus proportional to their respective self-diffusion coefficients (D_{self}). In isotropic solutions, under well-defined *in vitro* conditions, diffusion is closely related to the size of molecules, according to the Stokes–Einstein equation:

$$D_{self} = \frac{k_B \times T}{6 \times \pi \times \eta \times R_H} \quad (8)$$

where k_B is the Boltzmann constant ($J\ K^{-1}$), T the temperature (K), η the viscosity of the medium (Pa s), and R_H the hydrodynamic radius of the sphere (m).

In general, for unrestricted Gaussian diffusion, the self-diffusion coefficient (D_{self}) is related to the Einstein relation from the mean square displacement in space ($\langle r^2 \rangle$) during the observation time (t_D):

$$\langle r^2 \rangle = 6 \times D_{self} \times t_D \quad (9)$$

All diffusion ^1H NMR spectra were recorded at either 25 or 30 °C using a 500 or 600 MHz Bruker spectrometer equipped with a 5 mm *z*-gradient Bruker inverse probe. Temperature was calibrated using a Bruker sample temperature calibration tube (80% glycol-DMSO).

The gradient system was calibrated at 5450 $G\ m^{-1}$ (maximum intensity). The pulse gradient spin echo (PGSE) NMR was performed with the STE sequences, modified with bipolar pulses (STE-BPP), and longitudinal eddy current delay (STE-BPP-LED). The 90° flip angle pulse length was 8.5 μs. The duration between the two pulsed gradients (t_D) was put to 150 ms. A recovery gradient delay of 1000 μs was applied after each pulsed gradient of 1000 μs pulse length (δ).

All sequence parameters were adapted for each sample, so as to observe the aroma NMR signal intensity which disappears completely at 95% of the full gradient strength. Sixteen experiments were recorded with the gradient intensity sampled linearly from 5% to 95%. The number of scans was 64 for aroma solutions, 256 for carrageenan systems, and 512 for agar gel.

All data were processed using Gifa 5.2 software with the ILT method using the Maximum Entropy algorithm (MaxEnt) as previously described by Gostan et al. (2004).

For one molecule, the calculated self-diffusion coefficient D_{self} ($m^2\ s^{-1}$) is an average value from diffusion coefficients which are calculated for each proton peak. The NMR experiment was performed twice. Each sample was prepared in duplicate, except for agar gel prepared in four replicates.

After preparation, the NMR tube was stored at 25 or 30 °C until measurements were done (24 h before measurement). Measurements were performed both 1 and 6 days after product fabrication for D_2O solutions and agar gel to reproduce/mimic the measurement duration of the cell diffusion method.

3. Results and discussion

3.1. Rheological characterization of agar and iota-carrageenan systems

For 1%-agar gel, the median value of storage modulus (G′) ranged between 255.0 (250.3; 260.3) Pa at 0.1 Hz and 413.4 (405.9; 425.3) Pa at 10 Hz and the median value of loss modulus (G″) between 103.5 (98.5; 110.5) Pa at 0.1 Hz and 186.9 (181.3; 192.3) Pa at 10 Hz at 20 °C. The evolution of G′ and G″ illustrated the classical behaviour of a gel as evidenced by G′ > G″ and the limited variation of G′ and G″ values with frequency.

The rheological characterization (measurements performed between 0.1 and 10 Hz) of 1%-*iota*-carrageenan systems prepared in H_2O and D_2O with different NaCl contents was already performed and published (Juteau et al., 2004; Gobet et al., 2009). *Iota*-carrageenan solutions containing small NaCl concentrations (0–0.3% w/w) are considered as macromolecular solutions. For the 1%-*iota*-carrageenan system with 0.1% NaCl, the median value of storage modulus (G′) ranged between 3.5×10^{-3} Pa at 0.1 Hz and 5.0×10^{-3} Pa at 10 Hz and the median value of loss modulus (G″) between 3.5×10^{-2} Pa at 0.1 Hz and 0.5 Pa at 10 Hz.

At higher salt contents (from 0.3% w/w NaCl), a more structured gel was progressively formed, illustrated by a firmness increase with an increase in added NaCl content from 0.3% to 1.5% (w/w). Although the strength of each gel was higher in D_2O than in H_2O probably because of a viscosity difference (67% and 38% increases for G′ and G″, respectively), the rheological properties of *iota*-carrageenan systems in both media evolved similarly with NaCl addition (Gobet, 2008).

Agar and carrageenan systems present the ability to form strong thermoreversible gels at low concentrations in aqueous solutions. In both cases, the construction and the behaviour of such 3-dimensional (3D) networks are based on the self-associativity of the regular primary structures of these polysaccharides (association of molecular chains to form helices, which then aggregate to form a network) (Lahaye, 2001) and have thus similar structure.

Both modulus presented higher values for 1%-agar gel than for 1%-*iota*-carrageenan systems, even in presence of 1.5% of NaCl and D_2O, indicating that 1%-agar gel is a stronger and more structured gel than carrageenan systems from a rheological point of view. This is in agreement with literature data: the main difference between agar and *iota*-carrageenan monomers is the presence of two negative charges (sulphate groups) for *iota*-carrageenan, which increases electrostatic repulsion between chains and could thus explain that junction zones between chains are weaker for carrageenan than for agar (Stephen, 1995).

3.2. Determination of air/product partition coefficients of aroma compounds

The apparent air/product partition coefficients $K_{H/P}$ of the aroma compounds measured from water, from 1%-agar gel and from 1%-*iota*-carrageenan matrices are given in Table 1.

Concerning ethyl hexanoate, the air/water partition coefficient at 25 °C and the air/product partition coefficient in 1%-agar gel at 25 and 30 °C were in agreement with literature data (water, Athès et al., 2004; agar, Déléris et al., 2008; Lauverjat et al., 2009). No significant difference was observed between partition coefficients in water and in 1%-agar gel at 25 °C, suggesting that the presence of agar chains did not modify the release of ethyl hexanoate. As expected, the temperature increase from 25 to 30 °C induced a higher amount of ethyl hexanoate released from agar gel. In 1%-*iota*-carrageenan systems at 30 °C, data were similar to those obtained by Juteau et al. (2004) and Chana et al. (2006).

No data was available in the literature for the two other aroma compounds, 2-heptanone and 1-octen-3-ol, in *iota*-carrageenan systems. Nevertheless, our results were in agreement with those obtained by Bylaite et al. (2004) (43 aroma compounds in 0.5%-*lambda*-carrageenan solutions).

Significantly more ethyl hexanoate was released from 1%-*iota*-carrageenan without any NaCl than from agar gel (+24%) at 30 °C whereas the air/product partition coefficient of ethyl hexanoate in 1%-*iota*-carrageenan gel with 0.6% NaCl was similar to the one in agar gel at 30 °C. The fact that 1%-*iota*-carrageenan without NaCl is still a macromolecular solution while 1%-agar and 1%-*iota*-carrageenan system with 0.6% NaCl have a gel structure could explain this result (entrapment in the formed network).

Regarding the effect of salt content on aroma compound partition properties in *iota*-carrageenan systems, the air/product partition coefficients of ethyl hexanoate and of 2-heptanone significantly decreased (46% and 67%, respectively, Kruskall and Wallis test, $p < 0.05$) when salt content increased from 0% to 1.5%. The aroma release could be hindered by obstruction and entrapment effects caused by the formation of the three-dimensional network (physical cross-linking through polymer–polymer interactions) in presence of salt, giving 'solid-like' properties to the system, as already described by Juteau et al. (2004). Concerning 1-octen-3-ol, the same tendency can be observed but at a lesser extent (no significant difference), probably because the air/water partition coefficient of this molecule was already low.

3.3. Diffusion coefficient of ethyl hexanoate in water/D_2O and in 1%-agar gel at 25 and 30 °C

In order to compare the three diffusion methodologies, ethyl hexanoate diffusion coefficient in water or D_2O solution and in 1%-agar gel was measured at 25 and 30 °C. Results are summarized in Table 3.

The accuracy of the three methods was good, with variation coefficients below 5%, except for NMR measurements (10%) and cell diffusion (7%) with agar gel at 25 °C. Variations can be explained in the first case by the difficulty to prepare NMR tube when gelled media are studied (size and geometry of the measurement cell) and in the latter case by the low number of experimental points performed during one experiment.

The self-diffusion coefficient D_{self} of ethyl hexanoate in D_2O (measured by NMR) was in agreement with Wilke and Chang calculation (7.2×10^{-10} m^2 s^{-1} at 25 °C) (Wilke and Chang, 1955) and with literature data (8.5×10^{-10} m^2 s^{-1} at 30 °C) (Savary et al., 2006b). The duration of the storage period (1 or 6 days after product fabrication) before measurements were performed in D_2O did not show any significant effect on self-diffusion properties. The apparent diffusion coefficient D_{app} of ethyl hexanoate in water obtained with the diffusion cell method was 1.3-fold higher than the one measured by NMR after a 6 day storage period (which corresponds to the duration of an experiment with the diffusion cell). A part of this 30%-overestimation with the diffusion cell method could be explained by convection phenomena that can occur during the measurement duration and highlighted that this method was not well-adapted for liquid media. The problem of convection in liquid media can also occur with the VASK method and can partly explain the 22%-overestimation (in comparison with NMR results) even if in this case, the experiment duration (only few minutes), the high number of experimental points (two measurements per second) and the sensitivity of the analytical instrument led to a more reliable determination of apparent diffusion properties than with the diffusion cell.

In agar gel, apparent and self-diffusion coefficients of ethyl hexanoate obtained with the three methods showed only small differences as they ranged from 5.57×10^{-10} to 6.97×10^{-10} m^2 s^{-1} (median value 5.57 (5.54–5.92) 10^{-10} m^2 s^{-1}) at 25 °C and were in good agreement with literature data. As an example, Rega et al. (2002) measured an effective diffusion coefficient of 7.9

Table 3
Diffusion coefficients of ethyl hexanoate in water/D_2O solution and 1%-agar gel at 25 and 30 °C determined with the diffusion cell method, the VASK method or by NMR measurements and associated standard deviations. NMR measurements were performed both 1 and 6 days after product fabrication.

D (10^{-10} m^2 s^{-1}) ethyl hexanoate	Methods					
	Diffusion cell[a]		VASK method[b]		NMR[c]	
	25 °C	30 °C	25 °C	30 °C	25 °C	30 °C
Water/D_2O	9.01 ± 0.45	–	8.37 ± 0.29	–	6.84 ± 0.15[b] 6.92 ± 0.16[d]	8.21 ± 0.21[b] 8.19 ± 0.4[d]
1%-Agar gel	6.97 ± 0.49	6.59 ± 0.63	5.57 ± 0.14	7.90 ± 0.69	5.57 ± 0.63[b] 5.46 ± 0.56[d]	7.03 ± 0.39[b] 6.93 ± 0.68[d]

[a] The experiment lasted 6 days (see materials and methods section).
[b] The measurement was performed after a 1-day storage period.
[c] In presence of D_2O instead of H_2O.
[d] The measurement was performed after a 6-day storage period.

$\times 10^{-10}$ m^2 s^{-1} with a relative standard deviation of 15.2% for ethyl hexanoate at 24 °C using the concentration-profile method.

No significant difference was observed on self-diffusion coefficients of ethyl hexanoate in 1 day-aged or 6 day-aged agar gels determined by NMR regardless of the temperature, meaning that aroma compound interaction that could exist with product components or/and gel structure did not evolve during the 6 days storage period (Mann and Whitney test, $U = 7$, $n_1 = n_2 = 4$, $p > 0.05$). We could thus assume that during this period, the chains of agar remained in a rather immobile arrangement as soon as gelation took place. This result was quite important as the three methodologies used in this study do not refer to the same time scales as measurement/experiment duration range from several minutes for VASK method, to several hours for NMR technique or to several days for the diffusion cell method.

Furthermore, convection phenomena (or product evolution) seemed to be limited in the diffusion cell when measurements were done with a gelled material since the overestimation of diffusion coefficient (in comparison with the two other methods) was smaller than when measurements were performed in liquid media. The observation scales of the three methods must also be taken into account for the interpretation of the measured diffusion process. With the diffusion cell or the VASK methods, the distance covered by molecules during diffusion process can be considered as the macroscopic dimension of the corresponding product layer in the containers (20×10^{-3} m in diffusion cell or 7.5×10^{-3} m in flasks). The distance covered by the molecule during the NMR diffusion delay can be estimated at 26 μm (Eq. (9), $t_D = 150$ ms). Nevertheless, as VASK method gave similar diffusion coefficient than NMR, it can be strongly supported that the measured diffusion of the aroma compound in agar gel is close to the self-diffusion. This would mean that the size of the diffusing spaces is much larger than the length of the observed diffusion path so that aroma molecules did not undergo any obstruction effect due to the presence of large macromolecule chains. Likewise, no specific interaction occurs between aroma compound and agar molecules. This would confirm that agar chains keep quite immobile after gel formation and that large spaces completely filled by water molecules exist between agar chains as already mentioned in literature (Stephen, 1995).

With this gelling material, a small viscosity effect on diffusion process is mostly expected since obstruction effects due to network formation remain limited, as suggested by partition coefficient measurements and as already highlighted in previous studies (Voilley and Bettenfeld, 1985; Menting et al., 1970; Labille et al., 2007). These observations were supported by the fact that a slight but not significant decrease (24%) in ethyl hexanoate diffusion in agar gel compared to water was noticed (calculations performed on the whole set of data, Mann and Whitney test, $U = 2$, $n_1 = 4$, $n_2 = 4$, $p > 0.05$). This would mean that the diffusive space is mainly composed of pure water molecules and that only viscosity effect impacts on diffusion coefficient (according to the Stokes–Einstein equation). The diffusion of ethyl hexanoate in agar gel could be assimilated to the diffusion process in pure water. Thus, agar gel was used as the diffusive medium reference for macroscopic methods for further experiments.

Measurement of diffusion coefficients of ethyl hexanoate have also been done at 30 °C in D_2O and 1%-agar gel. As expected by the Stokes–Einstein equation, an increase in the self-diffusion coefficient of ethyl hexanoate in D_2O (1.2-fold) and in 1%-agar gel (1.3-fold) can be noticed with a temperature increase from 25 to 30 °C (Table 3). The same trend (1.4-fold increase) was observed with data obtained with the VASK method in 1%-agar gel. No significant difference was noticed in apparent diffusion properties obtained with the diffusion cell method with a temperature increase.

If we compare the diffusion properties of ethyl hexanoate at 30 °C in 1%-agar gel obtained with the three methodologies (Table 3), NMR and VASK methods gave similar values, ranging between 7.03×10^{-10} and 7.90×10^{-10} m^2 s^{-1}. In comparison, the value obtained with the diffusion cell method was slightly but not significantly underestimated.

In order to better investigate the effect of the diffusive medium on diffusion properties, the diffusion of three aroma compounds was measured in 1%-*iota*-carrageenan without NaCl (macromolecular solution) and with 0.6% and 1.5% NaCl (gels with increasing firmness).

3.4. Application of the three methodologies for the determination of aroma compound diffusion in 1%-iota-carrageenan systems differing in gel structure at 30 °C

The diffusion coefficients of three aroma compounds were measured using the three methodologies in 1%-*iota*-carrageenan system with different NaCl content. Increasing NaCl content for a fixed concentration of *iota*-carrageenan favours the aggregation of helices and leads to the formation of more structured system. This is thus a way to obtain information on diffusion process in systems with different rheological characteristics.

Fig. 2 displays apparent and self-diffusion coefficients obtained at 30 °C for (a) ethyl hexanoate, (b) 2-heptanone and (c) 1-octen-3-ol in 1%-*iota*-carrageenan matrices without NaCl (macromolecular solution) and with 0.6% and 1.5% w/w NaCl (gels). Data obtained for reference media (D_2O for NMR measurements and 1%-agar gel for macroscopic methods) are also presented.

The apparent diffusion coefficients D_{app} of aroma compounds in carrageenan systems obtained with macroscopic methods ranged between 3.42×10^{-10} ($\pm 0.30 \times 10^{-10}$) m^2 s^{-1} and 10.4×10^{-10} ($\pm 0.23 \times 10^{-10}$) m^2 s^{-1} (Fig. 2). The self-diffusion coefficient D_{self} of the three aroma compounds in carrageenan systems varied from 6.54×10^{-10} ($\pm 0.22 \times 10^{-10}$) m^2 s^{-1} to 8.36×10^{-10} ($\pm 0.34 \times 10^{-10}$) m^2 s^{-1} (Fig. 2). As expected, a 19% to 27%-decrease in self-diffusion coefficients was noticed between aroma compounds in D_2O and in carrageenan solution/gels, as already observed (Juteau et al., 2007). The self-diffusion properties of ethyl hexanoate and 1-octen-3-ol were the most impacted by the presence of the polysaccharide. For a given system (one matrix and one aroma compound), self-diffusion coefficients D_{self} and apparent diffusion coefficients D_{app} had the same order of magnitude. We can yet notice that the few numbers of experimental points for one release kinetic as well as the few numbers of replicates can lead to a less reliable determination of diffusion properties with the diffusion cell than with the VASK method, even if standard deviation is low.

With macroscopic methods, the apparent diffusion properties of ethyl hexanoate seemed to be 0.7-fold lower in 1%-*iota*-carrageenan than in 1%-agar gels at 30 °C (Fig. 2a). These results highlighted the impact of the diffusive medium and gel arrangement on molecule mobilities. Yet, for 2-heptanone, no significant difference was observed and for 1-octen-3-ol, results seemed to depend on the applied method (60%-increase between agar and carrageenan systems with the diffusion cell method versus 32% decrease with the VASK method). Moreover, no difference between 1%-agar and 1%-*iota*-carrageenan in ethyl hexanoate self-diffusion properties was noticed with NMR measurements (Fig. 2a). Even if gelation mechanisms are similar between agar and *iota*-carrageenan system (conversion of fluctuating helices in solutions to rigid and ordered helical structures and aggregation of these helical structures), the aggregation step for *iota*-carrageenan depends on the salt and temperature conditions (Lahaye, 2001). With 1%-*iota*-carrageenan without NaCl, gelation is incomplete (macromolecular solution), leading to partial network formed by chain segments intertwined in double helices dispersed in water. For agar,

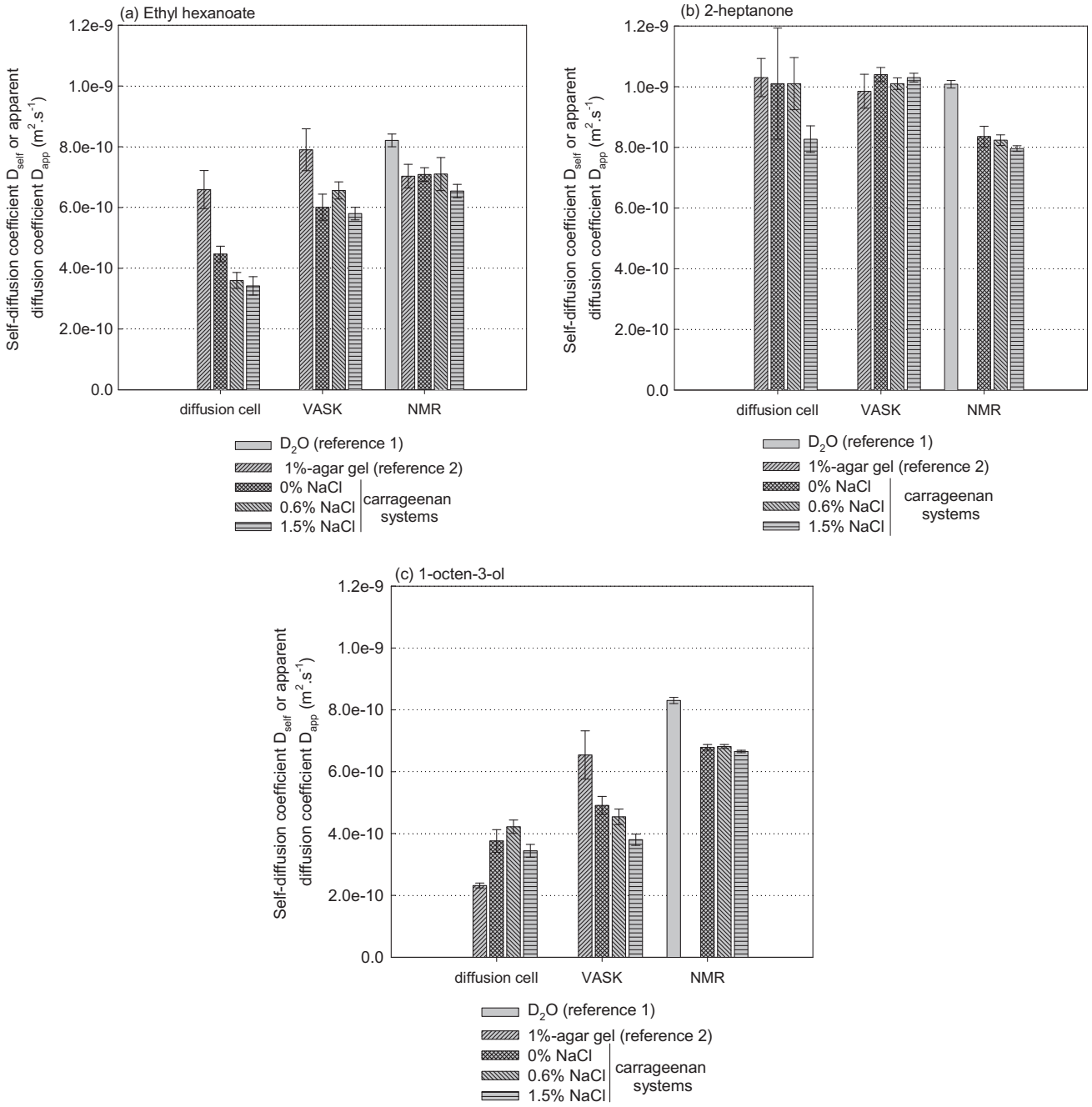


Fig. 2. Means and associated standard deviations of diffusion coefficients of (a) ethyl hexanoate, (b) 2-heptanone and (c) 1-octen-3-ol in reference systems (1%-agar gel for diffusion cell or VASK methods and D_2O for NMR measurements) and in 1%-*iota*-carrageenan systems with different NaCl content at 30 °C obtained using the diffusion cell method (2 replicates), the VASK method (3 replicates) or by NMR measurements (2 replicates).

an extended and stronger network is formed. Depending on the measurement scale, the observed diffusion is not influenced in the same way by the structure.

In carrageenan systems, a slight but not significant overestimation (15–25%) of the apparent diffusion coefficients of 2-heptanone was noticed compared to self-diffusion coefficients (except for 1%-*iota*-carrageenan gel with 1.5% NaCl) (Kruskall and Wallis test, $p > 0.05$) (Fig. 2b). Once again, this can be attributed to the observation level: more phenomena than only diffusion can be considered with macroscopic methods than with NMR, leading to diffusion overestimation. By contrast, the apparent diffusion properties of ethyl hexanoate (Fig. 2a) and 1-octen-3-ol (Fig. 2c) were significantly underestimated (from 11% to 46%) in comparison with self-diffusion properties (Kruskall and Wallis tests, $p < 0.05$).

Whatever the diffusive medium (D_2O, agar or carrageenan systems), when comparing aroma compounds mobilities, the diffusion coefficient of 2-heptanone was always higher than the one of ethyl hexanoate, itself higher than the one of 1-octen-3-ol, regardless of the method and of the NaCl content of matrices. By considering their hydrophobic parameter (log*P*) and their molecular weight (Table 1), 2-heptanone was the smallest and the less hydrophobic molecule, which can explain its fastest diffusion. However, the physico-chemical parameters of the two other aroma compounds

did not undergo this trend as the alcohol is smaller (although somewhat less hydrophobic) than the ester.

All these observations suggested that diffusion coefficients depend on: (i) the method used and in particular on the detection mode and/or (ii) the diffusion processes which seemed to be aroma compound specific in these systems.

Each diffusion method has its specific set-up and its detection mode that can lead to "deviations" on the determination of diffusion coefficient. First, as previously discussed, NMR tube is a very small container compared to macroscopic method, requiring special attention for gel insertion (bubbles, etc.). We can also assume that the difference in the containers used for each method probably impact the rate of temperature decrease when the products are poured, and thus the gel structure. From the three methodologies, the highest standard deviations were obtained with the diffusion cell method, probably because of the experimental operating mode (manual sampling, experiment duration) which limits the number of replicates.

As previously suggested, differences in diffusion coefficient values could also be attributed to the observation scales. Even if the orders of magnitude of self or apparent diffusion properties remained similar, a pure diffusion process is not 'systematically' measured with macroscopic method and transfer phenomena can be considered with macroscopic methods, leading to diffusion overestimation as observed for the ketone. On the other hand, for the ester and the alcohol, macroscopic methods probably highlighted the slowdown effect of product structure (obstruction), which can not be considered with NMR measurements (local diffusion). We could also wonder if container geometry could not impact on gel structure. In other words, although carrageenan is in its gelling state with 0.6% NaCl, no evidence enabled to conclude that the polysaccharide 3D-network was exactly the same in a 5 mm NMR tube than in a 0.25 L flask.

Two main parameters can be underlined: (i) the existence of a viscosity effect, i.e. aroma compound mobility appeared to be affected by frictional effects between polysaccharide molecules (based on the hydrodynamic theory (Masaro and Zhu, 1999) but did not seem to be limited by the gel network and (ii) the impact of structural chains arrangement.

It is possible that for the strongest gel (agar), the self-association of polysaccharide chains to an ordered 3D-network promotes the presence of free and large spaces available for molecular movements of aroma compounds, which could explain highest diffusion properties. Previous results of Gostan et al. (2004) and Rondeau-Mouro et al. (2004) support this hypothesis as a slight but significant increase in aroma diffusion of ethyl butanoate was observed in 1%-*iota*-carrageenan gelling system by adding NaCl (0.1–0.5% w/w). In our study, regardless of the method, no significant effect of NaCl content on diffusion properties was highlighted between 0%, 0.6% and 1.5% w/w NaCl (Kruskal and Wallis test, $p > 0.05$). Despite the progressive setting-up of the carrageenan gel with NaCl content, no hindering/obstruction effect on the displacement of small molecules was evidenced, suggesting strongly that the increase in gel strength promotes the formation of large diffusion spaces.

4. Conclusions

Results highlighted that self or apparent diffusion coefficients, determined respectively with microscopic and macroscopic methods, were in the same order of magnitude, even if observation scales were different and did not include exactly the same mechanisms.

Differences between methods mainly concerned the way of operating. The easiness, the reliability and the robustness of the diffusion cell method make it particularly adapted for complex food systems (in terms of composition and structure). However, the main drawback remains the experiment duration, which can constitute a problem for product with limited shelf life. Based on the same approach, the VASK method suppresses this drawback as diffusion properties can be reliably determined in a few minutes. But for these two macroscopic methods (diffusion cell and VASK method), an accurate determination of apparent diffusion property needs the knowledge of initial concentration in products and of air/product partition coefficients for the studied aroma compounds, which can be an additional source of errors.

NMR method is a direct method, reproducible, not destructive and relatively quick but needs the use of expensive equipment (as for VASK method). NMR tube preparation in the case of gelled media and data treatment when real food products are concerned, are drawbacks that can limit its application. Overall, the VASK and NMR methods gave the same results.

Thus, the methods described in this study for the determination of diffusion properties appeared to be complementary and to give comparable results. The choice of the best suitable methodology will depend on the objectives of the study (macroscopic or microscopic) but also the feasibility in function of the medium.

Acknowledgements

We gratefully acknowledge Rhodia Foods for providing carrageenan. The authors kindly acknowledge the Analytical Platform Lipid-Aroma (UMR CSGA, INRA, Dijon, France) and D. Forest for its technical contribution.

References

Antalek, B., 2002. Using pulsed gradient spin echo NMR for chemical mixture analysis: how to obtain optimum results. Concepts in Magnetic Resonance 14, 225–258.

Athès, V., Lillo, M.P., Bernard, C., Perez-Correa, R., Souchon, I., 2004. Comparison of experimental methods for measuring infinite dilution volatilities of aroma compounds in water/ethanol mixtures. Journal of Agricultural and Food Chemistry 52, 2021–2027.

Atlan, S., Trelea, I.C., Saint-Eve, A., Souchon, I., Latrille, E., 2006. Processing gas chromatographic data and confidence interval calculation for partition coefficients determined by the phase ratio variation method. Journal of Chromatography A 1110, 146–155.

Basaran, T.K., McClements, D.J., 1999. Non destructive monitoring of sucrose diffusion in oil-in-water emulsions by ultrasonic velocity profiling. Journal of Colloid and Interface Science 220, 429–435.

Boland, A.B., Delahunty, C.M., Van Ruth, S.M., 2006. Influence of the texture of gelatin gels and pectin gels on strawberry flavour release and perception. Food Chemistry 96, 452–460.

Bylaite, E., Ilgunaite, Z., Meyer, A.S., Adler-Nissen, J., 2004. Influence of *lambda*-carrageenan on the release of systematic series of volatile flavor compounds from viscous food model systems. Journal of Agricultural and Food Chemistry 52, 3542–3549.

Cayot, N., Dury-Brun, C., Karbowiak, T., Savary, G., Voilley, A., 2008. Measurement of transport phenomena of volatile compounds: a review. Food Research International 41, 349–362.

Chana, A., Tromelin, A., Andriot, I., Guichard, E., 2006. Flavor release from *iota*-carrageenan matrix: a quantitative structure–property relationships approach. Journal of Agricultural and Food Chemistry 54, 3679–3685.

Cohen, Y., Avram, L., Frish, L., 2005. Diffusion NMR spectroscopy in supramolecular and combinatorial chemistry: an old parameter – new insights. Angewandte Chemie International Edition 44, 520–554.

Cussler, E.L., 1997. Diffusion. Mass Transfer in Fluid Systems, second ed. University Press, Cambridge.

de Roos, K.B., 2000. Physicochemical Models of Flavor Release from Foods. Flavor Release, ACS Symposium Series 763, Roberts and Taylor, pp. 126–141.

de Roos, K.B., 2003. Effect of texture and microstructure on flavour retention and release. International Dairy Journal 13, 593–605.

Déléris, I., Atlan, S., Souchon, I., Marin, M., Tréléa, I.C., 2008. An experimental device to determine the apparent diffusivities of aroma compounds. Journal of Food Engineering 85, 232–242.

Déléris, I., Lauverjat, C., Tréléa, I.C., Souchon, I., 2007. Diffusion of aroma compounds in stirred yogurts with different complex viscosities. Journal of Agricultural and Food Chemistry 55, 8681–8687.

Djelveh, G., Gros, J.B., Bories, B., 1989. An improvement of the cell diffusion method for the rapid determination of diffusion constants in gels or foods. Journal of Food Science 54, 166–169.

Ettre, L.S., Welter, C., Kolb, B., 1993. Determination of gas-liquid partition coefficients by automatic equilibrium headspace-gas chromatography utilizing the phase ratio variation method. Chromatographia 35, 73–84.

Gerla, P.E., Rubiolo, A.C., 2003. A model for determination of multicomponent diffusion coefficients in foods. Journal of Food Engineering 56, 401–410.

Gobet, M., 2008. Etude par spectroscopies de RMN 23Na, 31P et 1H effets de la teneur en sel (NaCl) dans des matrices alimentaires. Thèse de doctorat Université de Bourgogne.

Gobet, M., Mouaddab, M., Cayot, N., Bonny, J.M., Guichard, E., Le Quere, J.L., Moreau, C., Foucat, L., 2009. The effect of salt content on the structure of *iota*-carrageenan systems: ^{23}Na DQF NMR and rheological studies. Magnetic Resonance in Chemistry 47, 307–312.

Gostan, T., Moreau, C., Juteau, A., Guichard, E., Delsuc, M.A., 2004. Measurement of aroma compound self-diffusion in food models by DOSY. Magnetic Resonance in Chemistry 42, 496–499.

Gros, J.B., Ruegg, M., 1987. Physical Properties of Foods – 2. Elsevier Applied Science, London.

Hansel, C.L., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., Lindinger, W., 1995. Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level. International Journal of Mass Spectrometry and Ion Processes 149–150, 609–619.

Jouquand, C., Ducruet, V., Giampaoli, P., 2004. Partition coefficients of aroma compounds in polysaccharide solutions by the phase ratio variation method. Food Chemistry 85, 467–474.

Juteau, A., Atlan, S., Déléris, I., Guichard, E., Souchon, I., Trelea, I.C., 2007. Ethyl hexanoate transfer modeling in carrageenan matrices for determination of diffusion and partition properties. Journal of Agricultural and Food Chemistry 55, 3577–3584.

Juteau, A., Doublier, J.L., Guichard, E., 2004. Flavor release from *iota*-carrageenan matrices: a kinetic approach. Journal of Agricultural and Food Chemistry 52, 1621–1629.

Labille, J., Fatin-Rouge, N., Buffle, J., 2007. Local and average diffusion of nanosolutes in agarose gel: the effect of the gel/solution interface structure. Langmuir 23, 2083–2090.

Lahaye, M., 2001. Developments on gelling algal galatans, their structure and physico-chemistry. Journal of Applied Phycology 13, 173–184.

Landy, P., Courthaudon, J.L., Dubois, C., Voilley, A., 1996. Effect of interface in model food emulsions on the volatility of aroma compounds. Journal of the Agricultural and Food Chemistry 44, 526–530.

Landy, P., Rogacheva, S., Lorient, D., Voilley, A., 1998. Thermodynamic and kinetic aspects of the transport of small molecules in dispersed systems. Colloids and Surfaces B: Biointerfaces 12, 57–65.

Lauverjat, C., de Loubens, C., Déléris, I., Tréléa, I.C., Souchon, I., 2009. Rapid determination of partition and diffusion properties for salt and aroma compounds in complex food matrices. Journal of Food Engineering 93, 407–415.

López-Esparzaa, R., Guedeau-Boudeville, M.A., Gambin, Y., Rodríguez-Beas, C., Maldonado, A., Urbach, W., 2006. Interaction between poly(ethylene glycol) and two surfactants investigated by diffusion coefficient measurements. Journal of Colloid and Interface Science 300, 105–110.

Masaro, L., Zhu, X.X., 1999. Physical models of diffusion for polymer solutions, gels and solids. Progress in Polymer Science 24, 731–775.

Masuda, A., Ushida, K., Okamoto, T., 2006. New fluorescence spectroscopy (FCS) suitable for the observation of anomalous diffusion in polymer solution: time and space dependences of diffusion coefficients. Journal of Photochemistry and Photobiology A: Chemistry 183, 304–308.

Menting, L.C., Hoogstad, B., Thilssen, H.A.G., 1970. Diffusion coefficients of water and organic volatiles in carbohydrate-water systems. Journal of Food Technology 5, 111–126.

Michel, E., Cipelletti, L., d'Humieres, E., Gambin, Y., Urbach, W., Porte, G., Appell, J., 2002. Self-diffusion and collective diffusion in a model viscoelastic system. Physical Review E 66 (Art. No. 031402 Part 1).

Millàn, A.J., Moreno, R., Nieto, M.I., 2002. Thermogelling polysaccharides for aqueous gelcasting – part I: a comparative study of gelling additives. Journal of the European Ceramic Society 22, 2209–2215.

Price, W.S., 2000. NMR gradient methods in the study of proteins. Annual Reports on the Progress of Chemistry Section C 96, 3–53.

Rega, B., Guichard, E., Voilley, A., 2002. Flavour release from pectin gels: effects of texture, molecular interactions and aroma compounds diffusion. Sciences Des Aliments 22, 235–248.

Rondeau-Mouro, C., Zykwinska, A., Durand, S., Doublier, J.L., Buléon, A., 2004. NMR investigations of the 4-ethyl guaicol self-diffusion in *iota* (*iota*)-carrageenan gels. Carbohydrate Polymers 57, 459–468.

Savary, G., Guichard, E., Doublier, J.L., Cayot, N., 2006a. Mixture of aroma compounds: determination of partition coefficients in complex semi-solid matrices. Food Research International 39, 372–379.

Savary, G., Guichard, E., Doublier, J.L., Cayot, N., Moreau, C., 2006b. Influence of ingredients on the self-diffusion of aroma compounds in a model fruit preparation: a nuclear magnetic resonance-diffusion-ordered spectroscopy investigation. Journal of Agricultural and Food Chemistry 54, 665–671.

Sebti, I., Blanc, D., Carnet-Ripoche, A., Saurel, R., Coma, V., 2004. Experimental study and modeling of nisin diffusion in agarose gels. Journal of Food Engineering 63, 185–190.

Seuvre, A.M., Diaz, M.A.E., Cayot, P., Voilley, A., 2004. Influence of the composition and the structure of different media on the release of aroma compounds. Lait 84, 305–316.

Simoneau, C., McCarthy, M.J., German, J.B., 1993. Magnetic resonance imaging and spectroscopy for food systems. Food Research International 26, 387–398.

Stallmach, F., Galvosas, P., 2007. Spin echo NMR diffusion studies. Annual Reports on NMR Spectroscopy 61, 51–131.

Stephen, A.M., 1995. Food Polysaccharides and Their Applications. Marcel Dekker Inc., New York, Basel, Hong Kong.

Voilley, A., Bettenfeld, M.L., 1985. Diffusion coefficients of volatiles in concentrated solutions. Journal of Food Engineering 4, 313–323.

Westrin, B.A., Axelsson, A., Zacchi, G., 1994. Diffusion measurement in gel. Journal of Controlled Release 30, 189–199.

Wilke, C.R., Chang, P., 1955. Correlation of diffusion coefficients in dilute solutions. AIChE Journal 1, 264–270.

Yven, C., Guichard, E., Giboreau, A., Roberts, D.D., 1998. Assessment of interactions between hydrocolloids and flavor compounds by sensory, headspace, and binding methodologies. Journal of Agricultural and Food Chemistry 46, 1510–1514.