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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

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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).

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

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