

## Flavor Release from $\iota$ -Carrageenan Matrices: A Kinetic Approach

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Release of aroma compounds in selected  $\iota$ -carrageenan systems was studied by static headspace analysis. By varying the sodium chloride content, different rheological behaviors were obtained ranging from solution to gel. From the release curves, mass transfer ( $h_D$ ) and partition coefficients ( $K_{ga}$ ) of ethyl butanoate, ethyl hexanoate, and linalool were extracted using a mathematical model based on the penetration theory. This model, previously developed for flavor release from stirred solutions, was found to fit well the data obtained from structured systems (nonstirred conditions) at the beginning and at the end of the release curves: this allowed the determination of  $h_D$  and  $K_{ga}$ . Matrix effects appeared to be dependent on the chemical class of the compounds. For the alcohol, the main effect on both equilibrium partitioning and mass transfer across the interface was ascribed to a salting effect. In the opposite, for esters,  $\iota$ -carrageenan addition induced an increase of aroma retention and also a slower transfer across the interface. The respective effects of an increasing viscosity of the medium and of the formation of a tridimensional network are discussed.

**KEYWORDS:**  $\iota$ -Carrageenan; gels; rheology; aroma release; interfacial mass transfer; diffusivity; partitioning; headspace

### INTRODUCTION

Sensory attributes are critical for the acceptance of food by consumers. Among them, aroma and textural properties are of interest and may determine whether a product will be preferred or not. Added thickening or gelling agents often induce a significant decrease in aroma perception and may also produce off-odor. This observation naturally points out the relationships between textural and aroma perceptions. These relationships contain both a theoretical interest and an obvious practical importance: in order to control aroma perception, we need a better understanding of matrix influences on the overall odor intensities and odor equilibrium between the different aromatic notes of foodstuffs.

Polysaccharides are often used as texture agents for their thickening or gelling properties. These properties are the result of high solvation of polysaccharide macromolecules. Indeed, three types of systems can be generated in increasing order of structuration of the medium: macromolecular solutions, weak gels, and strong gels (1). In the first case, the solvated chains move freely and are highly entangled giving rise to macromolecular solutions that exhibit thickening properties. Examples of thickening agents are galactomannans (guar, locust bean

gum), cellulose derivatives (CMC, HEC, . . .) or xanthan gum. In the two remaining cases, physical cross-linking through polymer–polymer interactions yields a three-dimensional network giving rise to solidlike properties. Carrageenans ( $\kappa$ ,  $\iota$ ), alginates, and pectins are examples of such gelling agents that are widely used in the food industry.

When textural agents are added to food systems, a decrease in both flavor release and perception is often encountered (2, 3). Reversible and nonreversible interactions between biopolymers and flavor compounds have been widely studied and discussed (4).

In the present work, we aimed at a better understanding of aroma release from an aqueous gelled matrix.  $\iota$ -Carrageenan systems have been chosen as model matrices. It is well-known that gelation of  $\iota$ -carrageenan takes place through a conformational transition from a disordered state (coil) to an ordered conformation (helix). This transition is controlled by the ionic content of the medium. Sodium, potassium, or calcium ions are the most common cations that are employed to induce the transition.  $\iota$ -Carrageenan gels are known as fully thermoreversible, the melting temperature being identical to the gelling temperature, unlike  $\kappa$ -carrageenan gels, which exhibit large thermal hysteresis (5). Furthermore, they do not display any syneresis, unlike  $\kappa$ -carrageenans as well. Therefore, the gelation and melting temperatures can be monitored by choosing the cation and varying the salt content in the medium. Moreover, the absence of syneresis makes these systems quite easy to

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handle. By changing only the cations contents of the medium, different degrees of organization will be obtained for each *t*-carrageenan concentration.

The aim of the present paper is, therefore, to combine a mechanical characterization of gelled/nongelled systems with headspace analysis in order to develop a more comprehensive understanding of the influence of macromolecular network formation on flavor release. To have a more extensive interpretation of the obtained data, mathematical models were developed, describing aroma release in the gas phase as a function of physicochemical parameters. These models were based either on gas phase dilution of equilibrium headspace (6) or on following up the return to equilibrium from initial condition with no volatile compound in the gas phase (7). We chose to apply to our data the models developed by Hills' team (7), because they cover a wide variety of food materials and were developed to take into account release into the gas phase in the mouth.

In this model, partition coefficients, binding parameters, and resistance to mass transfer were used to describe the overall release curve in a quite simple exponential form. The model assumes that transport of a volatile compound across the gas–liquid interface can be described by the penetration theory of interfacial mass transfer. It was thus assumed that phases were homogeneous and that no concentration gradients were formed within the sample or the air.

In the present study, we tried to apply a mathematical model proposed by Harrison and Hills (9) on headspace analysis data obtained from nonstirred structured systems. By limiting the number of constituents in the matrices, one flavor compound and one polymer type in saltwater, we have chosen to focus on the flavor/polymer network relationship and to avoid multiple interactions between ingredients.

## MATERIALS AND METHODS

**Materials.** *t*-Carrageenans were kindly supplied by Rhodia Food (Aubervilliers, France). Ethyl butanoate and ethyl hexanoate were supplied by Degussa (Grasse, France). Linalool was obtained from Sigma-Aldrich (Steinheim, Germany). Purity of aroma compounds was evaluated by GC-MS (>99, 92, and 88%, respectively, for ethyl butanoate, ethyl hexanoate, and linalool). Aroma solutions were prepared in pure water. The three aroma compounds were separately studied.

The main physicochemical characteristics of these compounds are given in **Table 1**. The two esters were chosen because their solubility and their polarity are very different to each other, while having the same chemical function. As shown in **Table 1**, ethyl butanoate has a higher solubility and a lower log P value than ethyl hexanoate. Linalool belongs to another chemical class and presents a solubility close to that of ethyl butanoate but a high log P value like ethyl hexanoate.

**Polysaccharide Matrices. Equilibrium Measurements: in Nongelling Conditions.** These experiments were performed on dispersed systems of *t*-carrageenan without salt. The polysaccharide matrices were prepared by mixing *t*-carrageenan in water. The mixture was stirred at 90 °C for 30 min for a complete solvation of all macromolecular chains. Each sample was prepared by mixing 21 g of the polysaccharide solution and 3 mL of the aroma solution at 20 °C. The *t*-carrageenan final concentrations were 0, 0.5, or 1% w/w. For ethyl butanoate and ethyl hexanoate, the final concentration was set to 10  $\mu\text{L L}^{-1}$ ; for linalool, it was 200  $\mu\text{L L}^{-1}$ .

**Kinetic Measurements and Rheological Characterization: in Gelling Conditions.** Time-dependent experiments were performed on systems of *t*-carrageenan containing salt. The polysaccharide matrices were prepared by mixing *t*-carrageenan in the salt aqueous solution (NaCl). Three NaCl concentrations (0.1, 0.3, and 0.5%) were chosen to cover a large range of melting temperatures and of gel rigidity. The mixtures were stirred at 90 °C for 30 min.

**Table 1.** Physicochemical Characteristics of Aroma Compounds

	ethyl butanoate	ethyl hexanoate	linalool
formula	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	C <sub>10</sub> H <sub>18</sub> O
CAS number	105-54-4	123-66-0	78-70-6
molecular weight (g mole <sup>-1</sup> )	116.16	144.22	154.25
boiling point (°C) at 10 <sup>5</sup> Pa	121 <sup>b</sup>	165 <sup>b</sup>	198 <sup>b</sup>
Log P calculated with the method of Rekker <sup>a</sup>	1.70	2.83	3.54
activity coefficient at infinite dilution $\gamma_{\infty}$ in water at 25 °C	803 <sup>c</sup>	16 195 <sup>c</sup> 13 300 <sup>d</sup>	14 000 <sup>e</sup>
saturated vapor pressure (Pa) at 25 °C	2306.5 <sup>c</sup>	224 <sup>c</sup> 346.5 <sup>e</sup>	51.6 <sup>e</sup>
partition coefficient vapor–water at 25 °C	18.11 $\times 10^{-3j}$ 13.5 $\times 10^{-3g}$ 9.3 $\times 10^{-3f}$	3.4 $\times 10^{-2g}$ 2.3 $\times 10^{-2h}$ 1.8 $\times 10^{-2f}$	3.6 $\times 10^{-3i}$
solubility in water (g L <sup>-1</sup> ) at 25 °C	5.6 <sup>c</sup> 5.75 <sup>k</sup>	0.52 <sup>c</sup> 0.46 <sup>k</sup>	2.6 <sup>kl</sup>

<sup>a</sup> Ref 8. <sup>b</sup> Ref 9. <sup>c</sup> Ref 10. <sup>d</sup> Ref 11. <sup>e</sup> Ref 12. <sup>f</sup> Calculated from the activity coefficient at infinite dilution and saturated vapor pressure obtained by footnote c. <sup>g</sup> Ref 13. <sup>h</sup> Calculated from the activity coefficient at infinite dilution obtained by footnote d and saturated vapor pressure obtained by footnote e. <sup>i</sup> Calculated from the activity coefficient at infinite dilution and saturated vapor pressure obtained by footnote e. <sup>j</sup> Ref 14. <sup>k</sup> Ref 15. <sup>l</sup> Ref 16.

Each sample was prepared by mixing 21 g of the polysaccharide solution and 3 mL of the aroma solution at 60 °C. The *t*-carrageenan final concentration was 1% w/w. For ethyl butanoate and ethyl hexanoate, the final concentration was set to 10  $\mu\text{L L}^{-1}$  and to 200  $\mu\text{L L}^{-1}$  for linalool. The same procedure was applied to prepare reference solutions for headspace analysis, in which the hydrocolloid was replaced by an equal mass of pure water. For the rheological characterization, matrices with or without aroma addition were prepared.

**Rheological Characterization.** Dynamic viscoelastic measurements were performed on *t*-carrageenan systems with a stress-controlled rheometer SR5 (Rheometric Scientific Rheometric Scientific, NJ) equipped with coaxial cylinders (cup diameter, 32.54 mm; bob diameter, 30.0 mm; bob length, 59.5 mm) or with a strain-controlled rheometer (RFSII, Rheometric Scientific) also equipped with a coaxial cylinders device (cup diameter, 34.0 mm; bob diameter, 32.0 mm; bob length, 33.0 mm). This latter rheometer was more sensitive and was used when dealing with “fluid” matrices (at low salt concentration).

All samples were prepared as previously described and transferred at 60 °C into the cylinder (set at 60 °C, too). Then, the temperature was progressively decreased down to 30 °C. It was checked that measurements were performed in the linear viscoelastic domain, whether the sample was in the sol or in the gel state. Frequency sweep tests were performed at 30 °C (5% strain) in order to precisely describe the degree of organization of the matrices at the headspace measurements temperature (30 °C). Similar measurements were carried out at temperatures between 30 and 50 °C at 5 °C intervals in order to determine the gelling/melting temperature.

**Static Headspace Analysis. Determination of the Initial Concentrations of Aroma Compounds in the Matrix.** To model aroma release curves, it is important to know the initial concentration in the matrix. To determine the aroma concentrations in the matrix at the beginning of the release experiments, the losses during the sample preparation were estimated.

We calculated the remaining amount of aroma by CH<sub>2</sub>Cl<sub>2</sub> extraction (1 g of sample mixed with 3 mL of CH<sub>2</sub>Cl<sub>2</sub> containing dodecane as external standard) in the following samples. Processed sample: samples used for kinetic measurements and prepared as described above (including the gas phase renewal procedure). Nonprocessed samples: in this latter case, aroma addition was done at 60 °C and the flasks were immediately put at 0 °C (without equilibration at 30 °C and without any gas phase renewal).

The remaining amounts of aroma compounds in the processed sample were deduced by comparing the obtained chromatographic peak areas for the processed samples to that of the nonprocessed ones. The results

**Table 2.** Description of Symbols with Corresponding Default Values Used in the Calculation

symbol	description	value
$A_{ga}$	gas–liquid surface area (cm <sup>2</sup> )	17.9
$c_a(t)$	volatile concn in aqueous phase (mg/cm <sup>3</sup> )	
$c_g(t)$	volatile concn in gaseous phase (mg/cm <sup>3</sup> )	
$c_{if}(0)$	initial volatile concn in aqueous phase (mg/cm <sup>3</sup> )	
$h_D$	gas–liquid mass transfer coefficient (cm/s)	
$K_{ga}$	gas–liquid partition coefficient	
$K_{ga}^{eff}$	effective vapor–liquid partition coefficient	
$K_b$	volatile macromolecule global binding coefficient (M <sup>-1</sup> )	
$C_b$	concn of macromolecule in aqueous phase (M)	
$V_g$	volume of gas phase (cm <sup>3</sup> )	111.63
$V_a$	volume of aqueous phase (cm <sup>3</sup> )	24
$t$	time (s)	

were used for the mathematical modeling. The losses during sample preparation were calculated and are presented in the Results section of the present paper because they give information on the behavior of the aroma compounds in the different studied systems.

**Equilibrium Measurements.** Samples were equilibrated at 30 °C until thermodynamic equilibrium was reached. Vapor phase samples (1 mL) were taken with a gastight syringe (1 mL, SGE) and injected onto a HP 6890 gas chromatograph equipped with a DB-Wax column (J&W Science, i.d. 0.32 mm, 30 m, film thickness = 0.5  $\mu$ m). Temperatures of the injector and FID were, respectively, 240 and 250 °C. The H<sub>2</sub> carrier gas velocity was 37 cm s<sup>-1</sup>. The oven temperature was 67 °C for ethyl butanoate, 90 °C for ethyl hexanoate, and 100–200 °C (5 °C/min) for linalool.

**Kinetics of Aroma Release.** The samples (24 mL) were prepared in quadruplicate in 100 mL borosilicated vials (137 mL actual volume). The volume ratio between the gas phase and the matrix was 4.7. As described above, odorants were added at 60 °C, and then, the samples were equilibrated for 2 h at 30 °C without stirring. To begin kinetic measurements with the lowest aroma concentration in the headspace, the gas phase in the samples was renewed with a 500 mL min<sup>-1</sup> airflow for 2 min. Then, analyzed matrices were equilibrated at 30 °C for different times (5–9000 s) without stirring. The time to reach equilibrium in these experimental conditions varied between 7200 and 9000 s, depending on the aroma compound and the composition of the matrix. Only one sampling and one analysis were performed per flask. Vapor phase samples (1 mL) were taken with a gastight syringe (1 mL, SGE) and injected as described for equilibrium measurements.

**Mathematical Model.** *Mathematical Model Used for Aroma Release Description.* A mathematical model previously developed to describe flavor release from aqueous solution containing flavor-binding polymer was used to interpret the data (7). This model (eq 1) assumes that transport of volatile across the gas–liquid interface can be described by the penetration theory of interfacial mass transfer. This model was successfully applied on liquid phases containing gelatine (17).

$$c_g(t) = \frac{C_{if}(0)}{[(1 + K_b C_b)/K_{ga} + (v_g/v_a)]} \left[ 1 - \exp \left\{ - \frac{A_{ga} h_D}{v_g} \left( \frac{1}{K_{ga}} + \frac{v_g}{v_a} \frac{1}{1 + K_b C_b} \right) \times t \right\} \right] \quad (1)$$

A description of the parameters used in eq 1, with default values, can be found in **Table 2**.

Harrison and Hills (7) used two important features of this model in order to interpret the obtained curves, providing valuable information on the mass transfer coefficient,  $h_D$ , and partition coefficient,  $K_{ga}$ . The mass transfer coefficient is given by the initial rate of release:

$$c_g(t \rightarrow 0) = \frac{C_{if}(0)}{1 + K_b C_b} \frac{A_{ga} h_D}{v_g} t \quad (2)$$

and the partition coefficient by the equilibrium headspace concentration:

$$c_g(t \rightarrow +\infty) = \frac{C_{if}(0)}{\left[ \frac{(1 + K_b C_b)}{K_{ga}} + \frac{v_g}{v_a} \right]} t \quad (3)$$

*Statistical Model Used for Regression Optimization.* Nonlinear regressions were conducted using SAS/STAT. Typically, error variability ( $\epsilon$ ) increases with the mean values, and variation coefficients appear to be nearly constant. Estimation of the mass transfer coefficient was obtained using eq 3, which can be written as:

$$c_g(t) = \alpha t + \epsilon \quad (4)$$

with

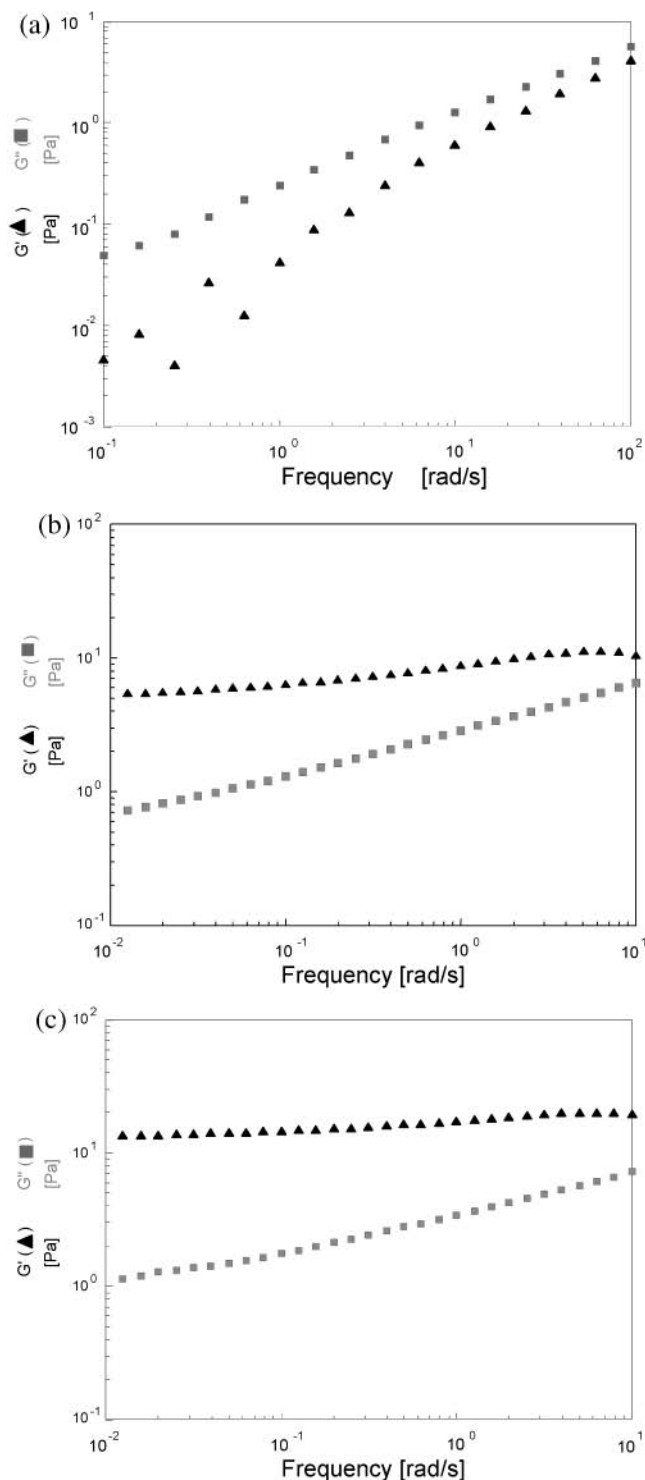
$$\text{Var}(\epsilon) = \sigma^2 [c_g(t)]^\delta$$

The homoscedasticity hypothesis ( $\delta = 0$ ) was tested and rejected.  $\alpha$  and  $\delta$  were estimated using SAS Mixed procedure. Taking into account variance heterogeneity led to a more accurate estimation of the parameter standard error.

## RESULTS AND DISCUSSION

**Rheological Characterization.** The viscoelastic properties of the systems were assessed by means of dynamic oscillatory shear measurements. **Figure 1a–c** shows the variations of the storage modulus ( $G'$ ) and of the loss modulus ( $G''$ ) as a function of frequency (viscoelastic spectra) at 30 °C for the three ionic contents considered, that is, 0.1, 0.3, and 0.5%, respectively. In 0.1% NaCl (**Figure 1a**),  $G''$  and  $G'$  varied strongly with frequency and  $G'' > G'$  all over the accessed frequency range. This is the typical behavior of an entangled macromolecular solution as it is displayed by polysaccharides (1, 18). The results obtained in 0.3 and 0.5% NaCl dramatically contrast with those in 0.1% NaCl:  $G'$  was much higher than  $G''$  and did not vary with frequency. This is evidence that both systems exhibit the typical behavior of a gelled system (19). The values of the  $G'$  modulus,  $\sim 5$  Pa in 0.3% and  $\sim 15$  Pa in 0.5%, are relatively low. This means that the gels are soft while the flat frequency dependence suggests that both systems are true gels. It is clear however that in 0.5% NaCl the gel was more rigid than in 0.3% NaCl. Moreover, from the comparison of  $\tan \delta (= G''/G')$ , which was 0.14 in 0.3% NaCl and 0.067 in 0.5% NaCl as measured at 0.01 rad/s, it could be inferred that the structure of the gel in 0.5% NaCl is slightly denser than in 0.3% NaCl.

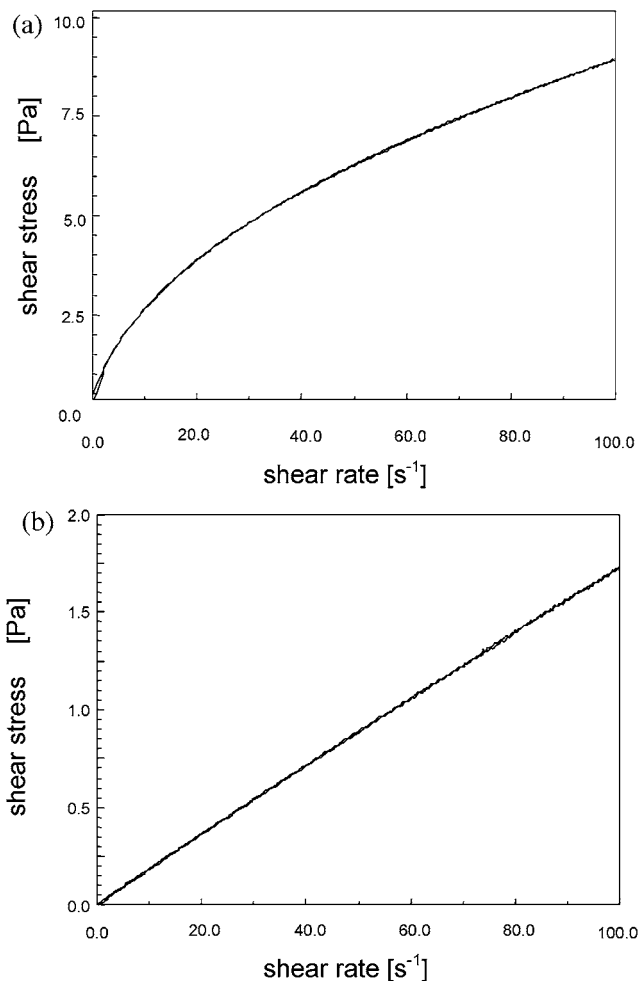
From the same viscoelastic measurements within the temperature range of 15–60 °C, it was possible to determine the melting/gelling temperature of the gels. This was obtained by applying the so-called “ $\tan \delta$  procedure” (20). In this method, the  $\tan \delta (= G''/G')$  variations at different frequencies are plotted as a function of temperature, the melting/gelling temperature being obtained from the common crossing of the curves. This technique initially proposed in the case of synthetic polymers (20) has been successfully applied to biopolymers (21, 22). In the present case (curves not shown), it was confirmed that the gels were entirely thermoreversible, the melting/gelling temperatures being 27.5, 35.5, and 42 °C, respectively, in 0.1, 0.3, and 0.5% NaCl. This is consistent with the fact that at 30 °C, the system was fluid in 0.1% NaCl while it was gelled in the other two conditions. **Figure 2a,b** shows the flow behavior of the carrageenan solution in 0.1% NaCl, respectively, at 30 and 42 °C. A Newtonian behavior was clearly exhibited at 42 °C (viscosity, 0.0175 Pa s) while a shear-thinning behavior was seen at 30 °C with a limiting zero shear Newtonian viscosity ( $\eta_0$ ) of the order of 0.40 Pa s. There is therefore a dramatic difference in the rheology of  $\iota$ -carrageenan solutions from the



**Figure 1.** Mechanical spectra (5% strain; measurement temperature, 30 °C) of 1%  $\iota$ -carrageenan systems in 0.1 (a), 0.3 (b), and 0.5% (c) NaCl.  $G'$  (storage modulus) and  $G''$  (loss modulus).

vicinity of the melting temperature (30 °C) to higher temperatures (42 °C).

In structural terms, it is clear that different structures can be obtained depending upon the ionic content and the temperature (Table 3). The conditions that have been chosen in the present work (30 °C; three NaCl concentrations) correspond to (i) a shear-thinning solution close to the gel point, which could be defined by its limiting Newtonian viscosity ( $\eta_0$ ); (ii) a soft gel whose melting point (35.5 °C) was slightly beyond the experi-



**Figure 2.** Flow curves of 1%  $\iota$ -carrageenan systems in 0.1% NaCl. Measurements at 30 °C (curve a) and at 42 °C (curve b).

**Table 3.** Characteristic Parameters of the Different 1%  $\iota$ -Carrageenan Systems Investigated

	0.1% NaCl	0.3% NaCl	0.5% NaCl
melting/gelling temp (°C)	27.5	35.5	42
structure at 30 °C	macromolecular solution $\eta_0 = 0.4$ Pa s	gel $G' = 5$ Pa; $\tan \delta = 0.14^a$	gel $G' = 15$ Pa; $\tan \delta = 0.067^a$

<sup>a</sup> As estimated at 0.01 rad/s.

ment temperature; and (iii) a slightly more rigid gel with a higher melting temperature (42 °C).

For the three aroma compounds, no significant difference was observed in the viscoelastic properties of  $\iota$ -carrageenan gels. In the case of starched-based food systems, addition of aroma compounds led to slightly weaker gel networks, which was mostly related to the formation of inclusion complexes with amylose (23).

**Losses of Aroma while Preparing the Samples.** Losses of aroma during the preparation of the samples have been estimated. The results (Figure 3) give information on the behavior of aroma compounds in water and polysaccharide matrices. For ethyl hexanoate, the loss was significantly more important ( $\alpha = 0.05$ ) in water (29.8%) than in gels (6.2%). The

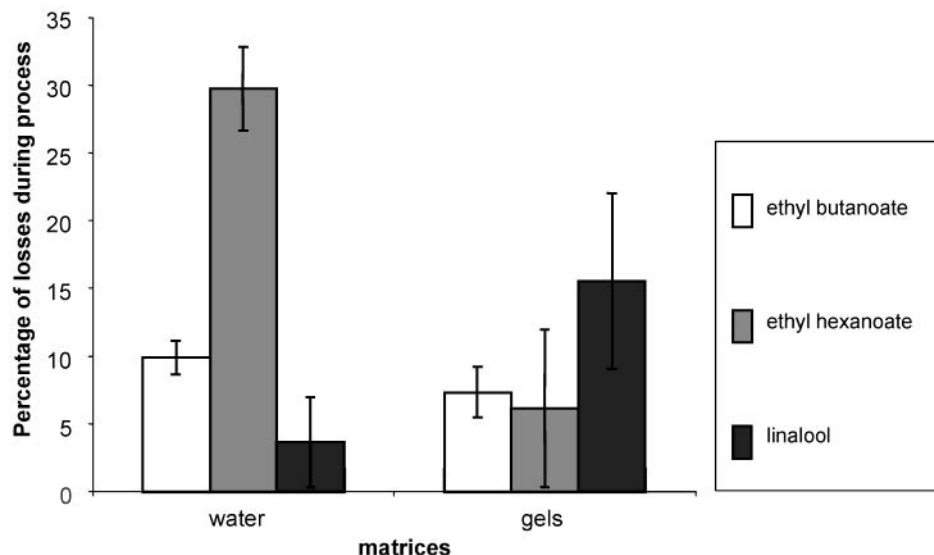


Figure 3. Losses of volatiles during process in water and 1%  $\iota$ -carrageenan systems (gels), both with 0.3% NaCl.

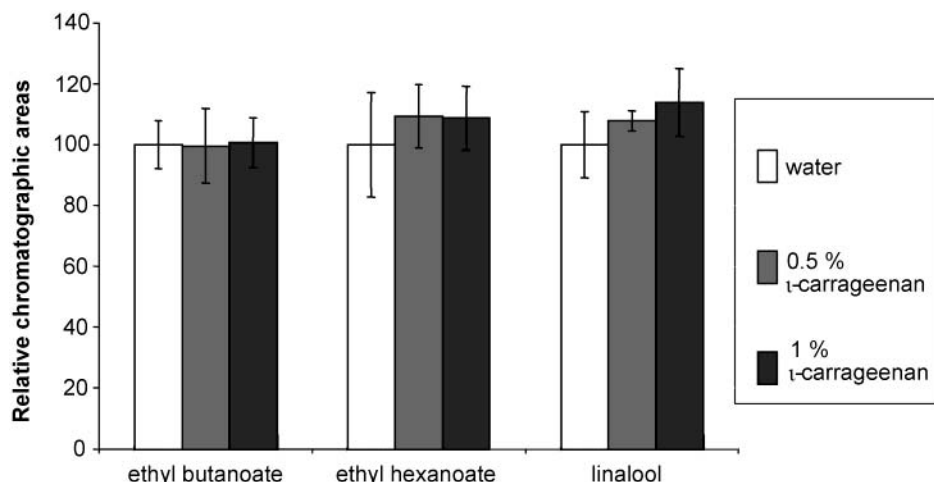


Figure 4. Effect of  $\iota$ -carrageenan concentration on flavor concentration (peak area) in the headspace at equilibrium (without NaCl addition). Each chromatographic area was divided by the mean value obtained with water for the same compound.

same tendency, but non significant, was observed with ethyl butanoate (9.9% in water and 7.3% in gels). The differences between ethyl hexanoate and butanoate can easily be explained by a higher hydrophobicity and a lower solubility of the former (Table 1). For linalool, the loss in water was significantly less important than for esters. Despite a higher log P value, this difference can be explained by the water solubility of linalool, which is five times higher than that of ethyl hexanoate (Table 1). Contrarily to esters, the loss of linalool in gels was found to be three times higher (15.5%) than that estimated in water (3.7%).

#### Equilibrium Measurements: in Nongelling Conditions.

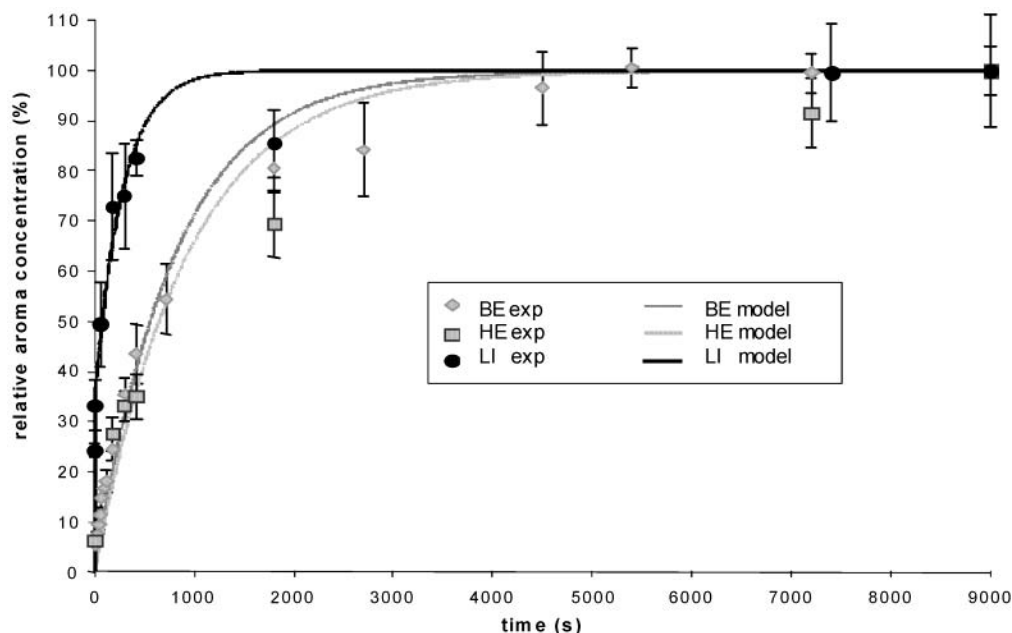
These experiments were performed on dispersed systems of  $\iota$ -carrageenan without salt, to evidence molecular interactions between  $\iota$ -carrageenan and flavor compounds. As shown in Figure 4, no significant retention was observed in the carrageenan matrices. In these macromolecular solutions, where chains are under coil conformation and move freely, no molecular interaction can be evidenced for the concentrations studied. Thus, for our experiments, the general model (eq 1) can be simplified, considering that  $K_b = 0$ .

**Kinetic Measurements: in Gelling Conditions.** Time-dependent experiments were performed on  $\iota$ -carrageenan systems containing sodium chloride.

**Time-Dependent Release Curves.** Figure 5 shows the time-dependent release curves of ethyl butanoate, ethyl hexanoate, and linalool from salted water (0.1% NaCl). For each compound, 100% of release corresponds to the concentration in the gas phase measured at equilibrium:  $4.52 \times 10^{-2}$ ,  $9.77 \times 10^{-2}$ , and  $16 \times 10^{-3} \mu\text{L L}^{-1}$  for, respectively, ethyl butanoate, ethyl hexanoate, and linalool. Three parts of the curves can be distinguished.

The initial part (between 0 and 300 s for esters and 0 and 180 s for linalool) is almost linear. This part of the curve can be described by eq 2 of the mathematical model. The final part of the curves is horizontal ( $t > 5000$  s). It corresponds to the thermodynamic equilibrium between the two phases and depends essentially on the aroma compound partition coefficient  $K_{ga}$  (as described by eq 3). The lines displayed in Figure 5 correspond to the fit of experimental points by eq 1. Clearly, the fit was satisfying in the initial and final parts of the curves.

In the middle part of the curves, a deviation between theoretical and experimental points can be observed. Such a deviation has already been reported (17, 24). When experimental points lied above the theoretical fit, this was explained by an increasing area of exchange due to an increasing stirring rate. In the reverse case, the fact that experimental data were lower than theoretical ones was explained by an inefficient stirring



**Figure 5.** Flavor release of ethyl butanoate (BE), ethyl hexanoate (HE), and linalool (LI) in water with 0.1% NaCl at 30 °C. For each aroma compound, experimental points (BE exp, HE exp, and LI exp) are fitted using the mathematical model (eq 1), (model BE, model HE, and model LI).

rate (24). Indeed, mass transfer across the liquid–gas interface depends on the respective concentrations of solute into the thin layer on both sides of the interface. Generally unknown, these concentrations are assumed to be equal to that in the bulk of the phases. These phases are consequently assumed to be perfectly stirred. The mass transfer coefficient is related by the penetration theory to the solute diffusion coefficient ( $D$ ) and to the contact time of an element of solution with the gas phase ( $T_e$ ):

$$h_D = 2 \left( \frac{D}{\pi T_e} \right)^{1/2} \quad (5)$$

This mean contact time  $T_e$  is assumed to be proportional to the stirring rate (25). Data obtained on liquid stirred phases containing gelatin (17) confirmed this assumption. Additionally, in agreement with the Stokes–Einstein relation between  $D$  and viscosity, the mass transfer coefficient was found to be inversely proportional to the square root of viscosity.

However, in our experiment performed on structured systems, the phases were not stirred. Bakker et al. (17) used this model with several experimental conditions and in particular a wide range of stirring rates in order to determine the applicability of the model. In aqueous gelatine solution (15% w/v), mass transfer coefficients of diacetyl were found to be linearly dependent on the square root of the stirring rate. Consequently, mass transfer cannot be considered as absolute values and should be only compared for similar experimental conditions. In our previous study (26), we were interested in the use of this mathematical model for the treatment of aroma release curves with very different systems from a structural point of view. The questions were as follows: do solutions and gelled systems exhibit the same mass transfer mechanisms in nonstirred conditions, and is it possible to compare mass transfer coefficients obtained with the same mathematical model? In this study, the calculation showed that apparent kinetic orders of the release, at the beginning of the release, were the same for water (the most typical solution) and for hard gels, indicating that the same mechanisms occurred in the two systems. This observation allows one to estimate and to compare  $h_D$  values obtained in

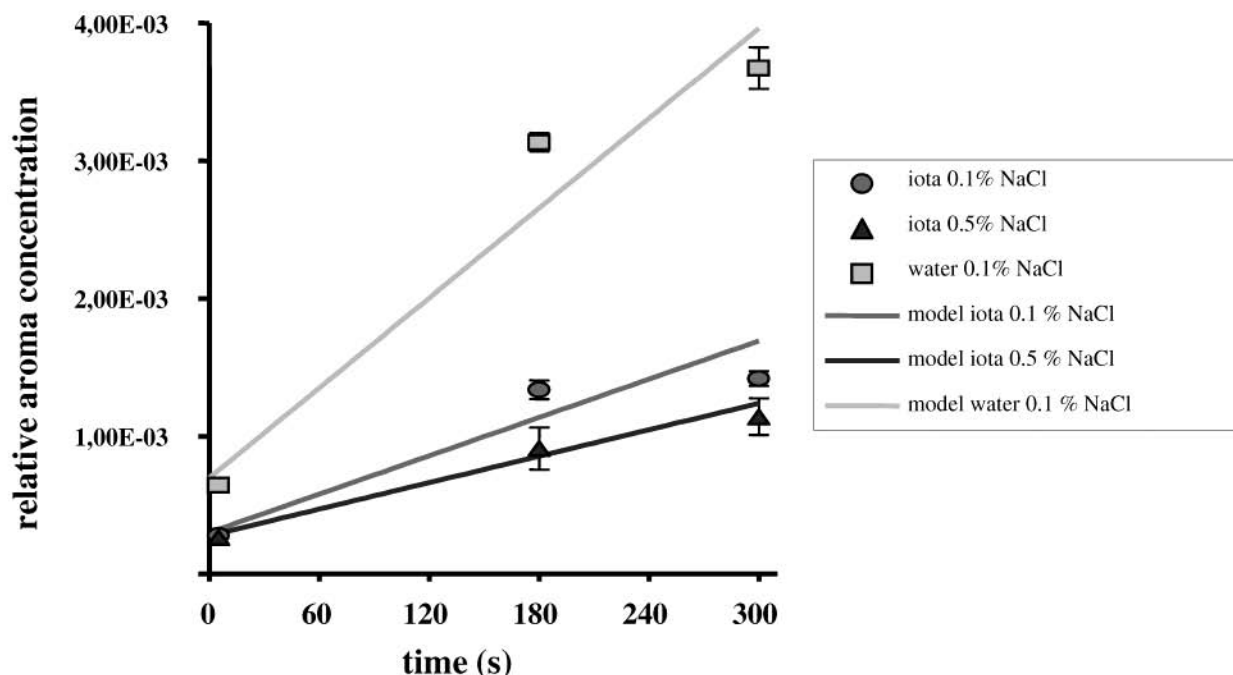
nonstirred conditions. Nevertheless, a supplementary time-dependent phenomenon takes place during aroma release, for instance, the establishment of a concentration gradient between the surface layer and the bulk of the matrices. For this reason, our values cannot be compared with others obtained with different experimental conditions and  $h_D$  should be called the “apparent” mass transfer coefficient.

Similar curves than those presented in **Figure 5** for a water solution are obtained in  $\iota$ -carrageenan matrices. As an example, initial parts of the release curves of ethyl hexanoate are shown for the different systems (**Figure 6**). Values obtained at the beginning of the release (0–300 s) were modeled using eq 4. Values obtained at equilibrium are given in **Table 4**.

With regard to the difference between aroma compounds, linalool has a faster relative rate of release than esters. Consequently, the intercept values at time = 0 were higher than that found for esters. This point shows the difficulties linked with this methodology. Therefore, to obtain the best fit of the data and thus a good estimation for  $h_D$ , eq 2 was modified, including an intercept parameter to be estimated.

**Estimated Parameters.** The two main coefficients obtained from the release experiments are the partition coefficient ( $K_{ga}$ ) and the mass transfer coefficient ( $h_D$ ):  $K_{ga}$  is given by the plateau in the final part while  $h_D$  is obtained from the slope of the initial part of the curve. All of these coefficients in water and in the presence of  $\iota$ -carrageenan in the three ionic conditions are given in **Table 4**.

(a) **Partition Coefficients.** Partition coefficients ( $K_{ga}$ ) in water for the three aroma compounds are lower but in the same range than those found in the literature (**Table 1**). Differences also exist between authors in relation to the method employed. For example, the data obtained by van Ruth and co-workers (14) by static headspace analysis on ethyl butanoate are twice those calculated from activity coefficients at infinite dilution and saturated vapor pressure found by Le Than and co-workers (10). However, relative values obtained for flavor compounds follow the same tendency for all of the authors. Partition coefficients obtained for ethyl butanoate are half of those estimated for ethyl hexanoate. The two additional carbons of the aliphatic chain of



**Figure 6.** Initial part of the release curves of ethyl hexanoate (concentration in the vapor phase/total initial concentration in the matrices) in water with 0.1% NaCl and in 1%  $\iota$ -carrageenan systems with 0.1 and 0.5% NaCl at 30 °C. Experimental points are fitted using the mathematical model (eq 4).

**Table 4.** Mass Transfer and Vapor/Medium Partition Coefficient for Ethyl Butanoate, Ethyl Hexanoate, and Linalool in Water and 1%  $\iota$ -Carrageenan Matrices with Several Amounts of NaCl<sup>a</sup>

	ethyl butanoate			ethyl hexanoate			linalool		
	$K_{ga} \times 10^3$	$h_D \times 10^6$ cm s <sup>-1</sup>	95% interval confidence $\times 10^6$	$K_{ga} \times 10^3$	$h_D \times 10^6$ cm s <sup>-1</sup>	95% interval confidence $\times 10^6$	$K_{ga} \times 10^5$	$h_D \times 10^6$ cm s <sup>-1</sup>	95% interval confidence $\times 10^6$
water	4.52 B,b	27.3 A,b	$\pm 3.0$	10.62 B,a	68.0 A,a	$\pm 9.6$	9.41 C,c	1.19 A,c	$\pm 0.32$
0.1% NaCl	4.93 A,b	29.9 A,b	$\pm 2.0$	13.75 A,a	76.4 A,a	$\pm 6.1$	11.17 B,c	1.23 A,c	$\pm 0.37$
0.5% NaCl	3.85 C,b	17.9 B,b	$\pm 1.2$	6.72 C,a	29.9 B,a	$\pm 4.7$	10.68 B,c	1.13 A,c	$\pm 0.32$
$\iota$ -carrageenan 1%	3.86 C,b	15.1 C,b	$\pm 1.3$	5.31 D,a	25.7 BC,a	$\pm 2.9$	10.83 B,c	0.74 A,c	$\pm 0.55$
0.1% NaCl	3.69 C,b	15.0 C,b	$\pm 1.3$	5.62 CD,a	20.0 C,a	$\pm 2.9$	12.99 A,c	1.32 A,c	$\pm 0.57$
0.3% NaCl									
$\iota$ -carrageenan 1%									
0.5% NaCl									

<sup>a</sup> For each column, the same capital letters mean that the results are not significantly different (based on 95% interval confidence). For each line, the same small letters mean that the results (respectively, for  $K_{ga}$  and  $h_D$ ) are not significantly different (based on 95% interval confidence).

ethyl hexanoate explain a reduced solubility, an increased Log P value, and reduced partition coefficients. Between ethyl hexanoate and linalool, the higher solubility of the alcohol explains its lower affinity for the gas phase and thus a lower partition coefficient.

For linalool, comparing partition coefficients in water with 0.1 and 0.5% NaCl, a significant increase can be observed (+18%) due to a salting out effect. This effect is also found in  $\iota$ -carrageenan systems (+21% between 0.1 and 0.5% NaCl). Moreover, if we compare water to carrageenan systems with the same amount of salt, a slight increase (+13.5–16%) in partition coefficients is noticed by addition of carrageenans. This could be partly explained by the Na<sup>+</sup>/K<sup>+</sup> counterions of the polysaccharide powder (of the order of 0.01% w/w), but it could also be due to a salting out effect of carrageenan itself. These results confirm the previous observation (Figure 4) on dispersed systems without salt that no interaction occurs between linalool and  $\iota$ -carrageenan. Previous studies on other polysaccharides showed that high methoxylated pectin (HMP) does not bind

linalool (27) whereas complexes are found between amylose and linalool (28).

In the case of esters, a significant decrease of partition coefficients is observed with  $\iota$ -carrageenan addition ( $\alpha = 0.05$ ) (Table 4) contrary to our previous experiments in dispersed systems without salt (Figure 4). In experiments performed on HMP (27), a retention of esters by model jam systems (with sucrose as the gelling agent) was evidenced whereas no binding effect was observed by the exponential dilution method in systems containing only esters and HMP (without sucrose). In our case, a possible reason might be a conformational specificity for esters/ $\iota$ -carrageenan molecular interactions. Indeed, in our first experiments (without salt), polysaccharide chains were only solvated and in a statistical coil form. In processed samples (with salt), a coil–helix conformational transition occurs during gelation (29). For a given temperature, structural information on  $\iota$ -carrageenan in our experimental conditions would be necessary to go further in the interpretation of our results. For these two esters, a salting out effect was evidenced in water

but not in polysaccharide matrices. The salting out effect is probably less important than the reverse effect due to changes in the matrix organization.

Indeed, as previously shown (**Figure 2**), the higher the NaCl concentration, the more linked are the  $\iota$ -carrageenan helices. For ethyl hexanoate, significant differences are observed only between the 1%  $\iota$ -carrageenan system in 0.1% NaCl and those in 0.3% NaCl. The first one is characterized as an entangled macromolecular solution whereas the second exhibits the behavior of a soft gel (**Figure 2**). An explanation could be that the more important effect is the three-dimensional network formation (0.1 and 0.3% NaCl) and that the increase in hardness of gelled matrices (0.3 and 0.5% NaCl) may be balanced by the opposite salting out effect.

(b) *Initial Rates of Release*. During the short time period of the eating process, flavor release will depend essentially on the breakdown processes and on initial rates of release. Moreover, in model gels differing by their gelatin concentration, the rate of release showed a good correlation with perception (30). By modeling the initial part of the curves using mass transfer coefficient as the fitting parameter, information on the flavor transfer through the matrix–gas interface can be obtained.

**Table 4** gives the mass transfer coefficients ( $h_D$ ) of the three aroma compounds in the studied matrices. Previous studies calculated mass transfer coefficients under stirring conditions (17). These authors showed that mass transfer coefficients decrease with the square root of the stirring rate (rps). Our values are lower than those by working in nonstirring conditions. Moreover, the systems and flavor compounds are not the same.

In water, no significant effect of salt addition was detected for any of the three compounds whereas an effect was observed at equilibrium. Indeed, it is logical to assume that mass transfer coefficients do not depend on the affinity of aroma compounds for the two phases contrary to partitioning. With regard to differences between compounds in water, the higher  $h_D$  values for esters than for linalool are in agreement with previous studies on diffusion (27).

Moreover, polysaccharides induced a significant decrease in mass transfer values of the two esters. This can be easily explained by an increasing viscosity as predicted by the Stokes–Einstein equation. Previously, Bakker et al. (17) validated this theory, showing a negative correlation between viscosity of gelatine solution and diacetyl  $h_D$  values. However, Roberts et al. (31) compared the effects of equiviscous sucrose, guar gum, and carboxymethylcellulose solutions on the release rates of seven aroma compounds. They concluded to a combined effect of viscosity, steric hindrance, water activity, and also molecular interactions. In our case, the results point out different behaviors of aroma compounds according to chemical classes. With such a low amount of polymer (1% w/w), the effect of steric hindrance and water activity can be considered negligible. However, weak interactions between the polymer chains and the esters may induce a decrease in aroma diffusion rate through macromolecule entanglement. Even if no information can be found on aroma diffusion in carrageenan matrices, several drug molecules with different hydrophobicity but the same shape and same chemical functions were differently affected by carrageenan addition in agarose gels (32). These differences were explained by hydrophobic interactions between drugs and carrageenan chains. In our case, this may explain differences between the two esters (**Table 1**). For linalool, no effect of either polysaccharide addition or network formation was evidenced. This could be explained by its low mass transfer coefficient and large 95% confidence intervals and higher concentration

at time = 0, whereas a better precision was obtained for esters. Another explanation could be that polysaccharide addition induces two opposite effects, hydrophobic interactions and a salting out effect due to the counterions of carrageenan itself. In the case of linalool, the second would be the most important. Thus, viscosity, hydrophobic interactions, and salting out effects seem to occur but the respective importance of each still has to be determined and understood.

In the case of ethyl butanoate, the decrease in mass transfer coefficients is more pronounced between 0.1 and 0.3% NaCl polysaccharidic systems than between 0.3 and 0.5% NaCl. This difference can be explained by the fact that the 0.1% salt system is not gelled. Indeed, formation of a three-dimensional network may influence  $T_e$  and/or  $D$  (eq 5) and therefore values of mass transfer coefficients.

To conclude about the effects of both carrageenan addition and sol–gel transition on  $h_D$  (i.e., diffusion coefficients and/or  $T_e$ ), diffusion measurements in the studied systems are needed. For the pectin systems previously discussed (17), apparent diffusion coefficients were evaluated using the concentration profile method (33). Nevertheless, this method gives a great variability of the results and the obtained coefficients may also contain the effect of free convection and molecular interaction. Other techniques using measurements on very short distances such as fluorescence recovery after photobleaching (34) allow determination of more realistic diffusion coefficients. However, these techniques can only be applied with specific probes and not with aroma compounds. The development of new high precision methods applicable for the measurement of aroma diffusion is therefore required.

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