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Interfacial activity and emulsifying behaviour of inclusion complexes between helical polysaccharides and flavouring molecules resulting from non-covalent interactions

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ABSTRACT

This study deals with the fabrication of inclusion complexes starting from a cross coupling of seven helical polysaccharides (host) and six flavouring agents (guest). Neither of the substrates is considered as an emulsifier when studied alone. Due to a complexation mechanism, the presence of intermolecular hydrogen bonds between substrates was highlighted by infra-red spectroscopy and ^{13}C NMR. In addition, depending on the polysaccharide used, the guest molecule could be preferentially located either inside or in the interstitial spaces of the helix. In a comparison between raw substrates, the inclusion complexes obtained presented the unique interfacial activity of decreasing surface tension values (γ) and, in some cases, their behaviour in water was similar to that of regular emulsifiers due to the presence of a critical aggregation concentration (CAC). Substrate concentrations and the ratios between them were the main parameters investigated in this study, which focused on the two inclusion complexes: vanillin/amylose and vanillin/ι-carrageenan. The first decreased γ values by as much as 53 mN/m with a double transition, whereas the second could cause γ fall to 36 mN/m with a regular break. In addition, these systems were able to stabilize foams for up to 60 min, which confirmed their unique emulsifying properties.

1. Introduction

Most food products are made from ingredients that are preferably dispersed either in an aqueous phase or in oil and then mixed. From a physicochemical point of view, this whole system is considered as a biphasic system called an emulsion or foam, depending on the physical nature of the phase dispersed in the liquid (i.e. one liquid in a second immiscible liquid in the form of fine droplets in the case of an emulsion, or a gas phase in a liquid for foams (Leal-Calderon, Schmitt, & Bibette, 2007).

In order to stabilize the dispersions, emulsifiers are commonly used. Because of a polar duality within their molecular structure, such molecules preferentially localize at the interface. The polar head – the hydrophilic part - is located in the water whereas the non-polar tail – the lipophilic contribution - is directed into the oil or gas phase (Hasenhuettl & Hartel, 2008). Lecithin, mono- and di-glycerides of fatty acids or even polysorbates are the best known of such molecules in agro food science at present but their number is still limited.

Depending on external factors, emulsions or foams become unstable through several mechanisms, such as Ostwald ripening, coalescence or creaming. Creaming can be attenuated by adding a thickening agent inside the aqueous phase to increase its viscosity. Several thickening agents are mostly polysaccharide molecules (i.e. glucose polymers composed of monosaccharide units within a glycosidic linkage) such as xanthan or amylose (starting from starch). In the case of carrageenan or agar-agar, backbone is composed with galactose units. Although they are generally hydrophilic, in solution, some of these polymers exhibit a helical conformation due to the presence of hydrophobic units on their macromolecular structures. Therefore, the external surface of the helix is hydrophilic, whereas the internal cavity is hydrophobic (Immel & Lichtenthaler, 2000; Rees, 1969, 1972a, 1972b; Rundle & Baldwin, 1943). In the case of amylose, this conformation is noted V-Amylose (Katz, 1937).

Due to the difference of polarity within the helical configuration,

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the tail of an amphiphilic molecule can be included inside the hydrophobic cavity, resulting in the formation of an inclusion complex. This structure is also called “Type I”. The “host-guest” mechanism is widely described in the literature concerning emulsifiers such as fatty acids or monoacylglycerol and amylose (Pareyt, Finnie, Putseys, & Delcour, 2011; Putseys, Lamberts, & Delcour, 2010; Seo, Kim, & Lim, 2015) and explains why such emulsifiers are often used in manufactured cereal products as anti-staling agents to prevent amylose retrogradation and to preserve softness over time (Stampfli & Nersten, 1995). In addition, these emulsifiers have shown the best results as regards complexation index (e.g. a monoglyceride content of at least 90% in amylose). This value was obtained with a UV spectrophotometric method by calculating the relative difference between amylose-lipid and amylose absorbance (Kaur & Singh, 2000; Tang & Copeland, 2007). To a lesser extent, it is possible to use other food emulsifiers as guest molecules, such as lecithin, in an amylose helix but, in this case, the complexation index is only around 30% (Krog, 1971; Liu, Waters, Rose, Bao, & King, 2013).

Guest inclusion inside an amylose helix is possible according to two mechanisms, depending on the chain length and/or the polar head of the emulsifier, as the ligand can be positioned either longitudinally inside the helix cavity or in the interstitial space between helices. Nevertheless, whatever the position, it seems that the complex is stable thanks to the intramolecular bonds of amylose (Van der Waals forces and hydrogen bonds) and also the intermolecular interactions between amylose and ligands (Putseys et al., 2010). These low-energy interactions can be easily broken by heating, which means that inclusion complexes remain stable within a limited temperature range, typically up to 95–105 °C (Galloway, Biliaderis, & Stanley, 1989; Karkalas, Ma, Morisson, & Pethrick, 1995).

To go further in the comprehension of these assemblies, some interesting studies have focused on capric, myristic, oleic and stearic acid or sodium stearate inclusion with amylose and corn starch respectively and determined the complexation index for both systems. Also, the surface tension as a function of the lipid content in the starch has been measured (Marinopoulou, Kalogianni, & Raphaelides, 2016; Wu, Chen, Lv, Du, & Zhu, 2012). In all cases, a dependence was clearly observed with fatty acids, which suggests a possible modulation of surface activity by complexation in comparison to initial substrates.

Since then, other inclusion complexes have emerged that starts from polysaccharides and include either metals, drugs or flavouring molecules (Luo et al., 2016; Yeo, Thomson, & Peterson, 2016; Zhang et al., 2016). In the latter case, an example with an association between vanillin and amylose has been described and widely characterized by several analytical techniques (Rodriguez & Bernik, 2013). In this case, molecular modelling of the complex suggested that vanillin was located inside the amylose helix. During this study, complexes with vanillin were also made by varying the type of amylose (e.g. pure amylose: APT III or amylose extracted from a high amylose starch: Hylon VII). From FT-IR, circular dichroism, X-ray diffraction or differential scanning calorimetry, it was concluded that the complexation was more efficient when amylose extracted from Hylon VII starch was used.

Furthermore, inclusion complexation with flavouring compounds is of growing interest for the retention and release of these molecules, which can be useful in food science. It is sometimes possible to encapsulate two flavouring molecules inside the helix, which can lead to enhanced inclusion abilities (Kasemwong & Itthisoponkul, 2013; Yeo et al., 2016). For example, only 5% of limonene can be encapsulated inside the amylose helix whereas, when it is associated with thymol, up to 70% may be reached. Lastly, a spontaneous association complex has been made starting from methylcellulose and small polyphenols (e.g. tannic acid). Depending on the ratio, it seems that these assemblies have the capacity to stabilize both emulsions and foams, especially when methylcellulose is ten times larger than tannic acid (Patel, Ten-Hoorn, Hazekamp, Blijdenstein, & Velikov, 2013). One might therefore wonder if, as well as the commonly used regular emulsifiers, inclusion complexes starting from non-emulsifying raw materials also have an interfacial activity.

Consequently, we decided to go further and show that a structure like an inclusion complex (starting from non-amphiphilic molecules between flavouring molecules and helical polysaccharides) has a single behaviour in solution, close to that of an emulsifier. Several associations were investigated by varying host and guest. Two systems made from vanillin and amylose, or vanillin and ι-carrageenan showed interesting properties, especially when parameters such as the ratio of concentrations or their respective values were varied, and surface tension measurements were made. Compared to their respective raw substrates, the assemblies were characterized by infra-red spectroscopy (ATR-FTIR). Besides, in particular when ι-carrageenan was used as the guest, ^{13}C NMR was also carried out and show a good match with the previous analytical method. In the latter case, it was possible to determine the preferential location of the guest molecule in the polysaccharide (i.e. inside the helix cavity or in the interstitial spaces of the helix). In order to prove their emulsifying abilities in solution, both inclusion complexes were used to generate foams and their stabilities followed over time.

2. Materials and methods

2.1. Chemicals

Flavours: vanillin (4-Hydroxy-3-methoxybenzaldehyde, purity > 99%), thymol (2-isopropyl-5-methylphenol, > 99%), furaneol (4-Hydroxy-2,5-dimethyl-3-furanone, > 98%), isoamyl acetate (3-Methylbut-1-yl acetate, > 97%), menthol ((1R,2S,5R)-2-Isopropyl-5-methylcyclohexanol, 99%), and menthone ((2S,5R)-2-Isopropyl-5-methylcyclohexanone, > 97%), and reagents: potassium iodide solution (KI, 0.1 mol/L) and iodine solution (I_2, 0.05 mol/L) were all purchased from Sigma Aldrich. High amylose (min 70%) maize starch, Hylon VII, was provided by Ingredion® (France). Gellan gum, ι-carrageenan and κ-carrageenan were supplied by CP Kelco (USA) and Kalys (France). Carob bean gum and xanthan were both purchased from Arlès (France). All these polysaccharides were of analytical degree and were used as received.

2.2. Preparation of Hylon VII solutions

The desired amount of Hylon VII and milli-Q water were introduced into a three-necked round bottom flask. The mixture was heated at 130 °C for 90 min. The suspension was then cooled down to ambient temperature. Prior to use, the suspension was centrifuged at 4000 rpm for 4 min. Then the supernatant was removed and used directly for making the complexes.

2.3. General procedure for making complexes

In a first step, the desired amount of each pure guest (mostly in solid form except for menthone and isoamyl acetate, which were in liquid form) was introduced into a three-necked round bottom flask equipped with a condenser, and heated at 70 °C in order to obtain liquid forms in all cases. Then, polysaccharide solution was added at the desired mass concentration. The solution obtained was mixed at the same temperature (70 °C) for 30 min and then cooled to ambient temperature. In the case of Hylon VII, the inclusion complex solution was centrifuged once more at 4000 rpm for 4 min before analysis. All solutions obtained were used and analysed directly after fabrication.

2.4. Structural characterization of inclusion complexes

2.4.1. ATR-FTIR spectroscopy

Pure compounds and complexes were characterized by ATR-FTIR spectroscopy on germanium crystal using a Nicolet 6700 (Thermo

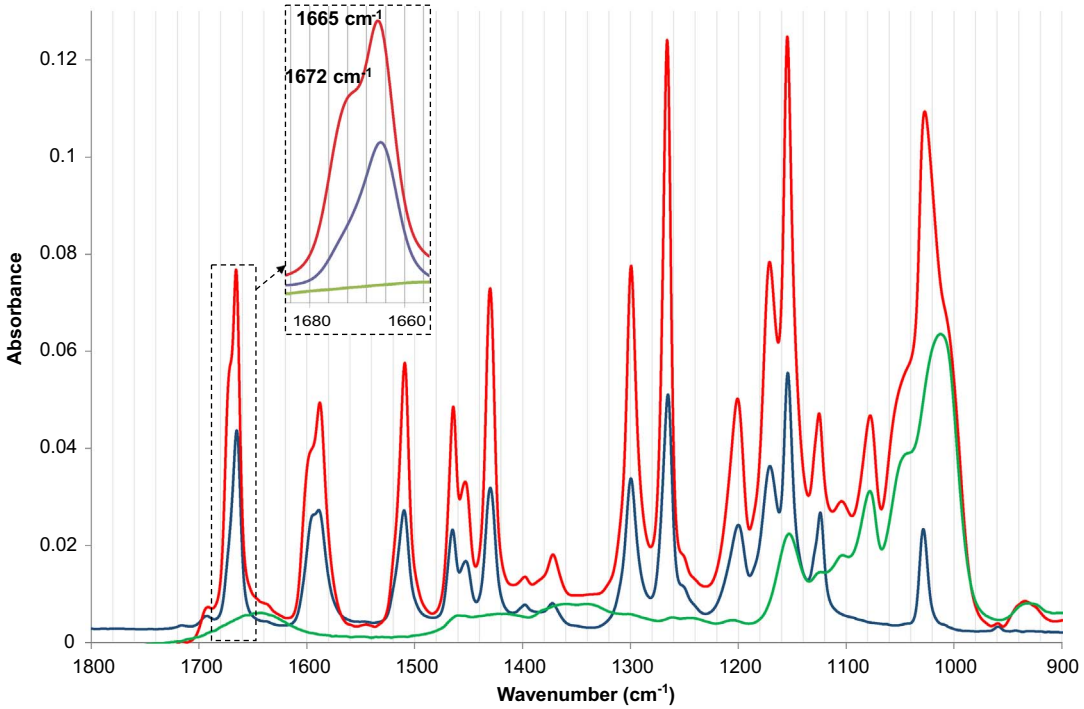

Fig. 1. Infra-red spectra of vanillin (blue solid line), Hylon VII (green solid line) and vanillin/Hylon VII inclusion complex (R = 1/1; red solid line). Insert: Focus on the aldehyde C=O stretching bands between the two systems, revealing an intermolecular hydrogen bond. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Scientific) spectrometer equipped with an MCT detector. Solutions of pure vanillin or pure amylose were prepared at 1% (w/w) in water. The vanillin/amylose mixture was prepared with 1% of both compounds (R = 1/1). 1% vanillin and 0.1% of ι-carrageenan solutions (R = 10/1) were mixed to obtain the vanillin/ι-carrageenan complex. 10 µL of sample were deposited on the ATR crystal and dried. All ATR-FTIR spectra were recorded in the range of 600–4000 cm^{-1} with a resolution of 2 cm^{-1}. Two hundred scans were accumulated for each measurement.

2.4.2. Nuclear Magnetic Resonance (NMR)

The solution NMR measurements were performed on an 800 MHz Bruker Avance III NMR spectrometer SB (Wissembourg, France), working at a ^{1}H frequency of 800.2 MHz and ^{13}C frequency of 201.2 MHz, and equipped with a 5 mm TCI cryo probe ($^{1}H/^{13}C/^{15}N/^{2}H$). For samples prepared in H_2O/D_2O, proton decoupled ^{13}C NMR spectra were recorded with a 90°-pulse sequence of 12 µs, between 64 and 5120 scans, a recycle delay of 5 s and a spectral width of 48 kHz (239 ppm). Processing was performed with a Lorentzian filtering function of 3 Hz. ^{13}C chemical shifts are reported relative to the internal reference of TSP-d_4 (3-(Trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt).

2.5. Viscosity measurements

The viscosities of polysaccharide solutions were measured on a rotational rheometer AR-G2 (TA Instruments, USA) with a coaxial cylinders configuration. The temperature was maintained at 20 °C using the Peltier effect, which allows accurate and rapid temperature control. Viscosity was measured for a concentration at 0.2% wt at a constant shear rate of 0.1 s^{-1} for 5 min.

2.6. Surface tension measurements

Surface tension measurements at the liquid-gas interface were made by a K20 Krüss and a TD1C Lauda tensiometer equipped with either a Wilhelmy plate or a du Nouy ring. Temperature was kept constant at 25 °C with a thermostatically-controlled water bath. Before each sample was taken, the water surface tension was checked. For one trial, surface tension values were recorded until at least three were nearly identical. The result obtained was an average of these values.

2.7. General procedure for foaming tests

Foams were made using two 10 mL syringes connected together by a rubber hose. Typically, 4 mL of a solution was first collected. Then, two more millilitres of air was also drawn. The rubber hose and the second syringe were then connected. Fifty piston strokes back and forth were performed until a foam was created. Stability was then checked as a function of time until complete destabilization.

3. Results and discussion

3.1. Inclusion complex by vanillin/amylose association

3.1.1. Complex preparation and characterization

In a first set of experiments, an amylose/vanillin inclusion complex was made in conditions similar to those described in the literature for the same system (Rodriguez & Bernik, 2013). Hylon VII was preferred as the raw material for this rather than pure amylose (APT III). The authors compared both substrates with vanillin and encapsulation seemed more efficient with Hylon VII. Nevertheless, a preliminary amylose extraction was necessary.

To ensure the presence of amylose in solution, iodine titration was carried out by UV spectrophotometry, (λ = 640 nm). This method revealed the helical structure of amylose through the presence of a typical blue coloration (Gilbert & Spragg, 1964), the absorbance of which was measured in a range of amylose concentrations (from 1.0 to 4.0 mg/mL). Absorbance was plotted versus Hylon VII concentration and a straight line was obtained, with an excellent linear correlation coefficient (R^2 = 0.9971, not shown).

Starting from the amylose solution obtained, an inclusion complex

was made by mixing it with the same weight of vanillin (ratio 1/1 w/w). Fig. 1 shows the ATR-FTIR spectra of vanillin solution (blue solid line), amylose solution (green solid line) and the mixture (red solid line). Full band assignment is reported in Rodriquez and Bernik's publication (Rodriguez & Bernik, 2013). The band observed for the vanillin/amylose mixture is close to an overlapping of the spectra of the two compounds except for the band in the range of 1680–1660 cm^{-1}, which was assigned to the vanillin aldehyde C═O stretching mode (see insert Fig. 1). The C═O stretching mode of free vanillin is observed at 1665 cm^{-1} and a shoulder appears in the ATR-FTIR mixture spectrum at 1672 cm^{-1}, leading to the conclusion that a complex has formed with amylose. Similar shifts were observed for the formation of a vanillin/Hylon-VII inclusion complex (Rodriguez & Bernik, 2013). This shift can be explained by the formation of hydrogen bonding between vanillin's aldehyde C═O and amylose's hydroxyl −OH chemical group. A stable inclusion complex inside the helix is formed but, due to the high intensity of the aldehyde C═O band at 1665 cm^{-1}, free vanillin is still present in the mixture.

3.1.2. Surface tension measurements

Patel et al. focused their study on emulsions and foams with inclusion complexes made from methylcellulose (MC) and tannic acid (TA) and showed that the best stabilization occurred when MC concentration was ten times that of TA ($R_{MC/TA}$ = 10 w/w). According to this observation, it seems that the ratio between raw substrates has a great influence on the surface activity. Therefore, inclusion complexes with vanillin and Hylon VII were prepared by varying the ratio of vanillin (V) to Hylon VII (H) from 5/1 to 1/10 w/w. For this range of solutions, the mass concentration of vanillin was fixed at 1% (corresponding to the theoretical solubility limit in water at ambient temperature) whereas Hylon VII concentration was adjusted so as to maintain the desired V/H ratio.

Surface tension measurements (γ) were first made with the most concentrated solutions of raw substrates (i.e. 1% of vanillin and 10% of Hylon VII). In these most concentrated conditions, γ values measured at 25 °C were 65.8 mN/m for Hylon VII and 65.2 mN/m in the case of vanillin. Vanillin's surface tension value is lower than that of water (65.2 vs 72 mN/m), which could be due to hydrotropic interactions between the aromatic cycles of vanillin (Kabra & Gaikar, 2008; Kunz, Holmberg, & Zemb, 2016). A possible aggregation of amylose chains could also explain the lower γ value in that particular case. Some articles argue that the adsorption at the air-water interface depends on the molecular architecture of the polysaccharides and the presence of hydrophobic moieties of their skeleton (Henni et al., 2005; Wesslen & Wesslen, 2002). Because of the intra- and inter-molecular associations between their hydrophobic segments in aqueous solutions, some polysaccharides may lead to the formation of hydrophobic micro domains. So, solutions of inclusion complex for different ratios were monitored in the present work. Surface tension values are plotted against vanillin/Hylon VII ratio at a fixed concentration of vanillin (1%) in Fig. 2. When there is an excess of vanillin, γ values remain stable (around 65 mN/m) but, from the ratio $R_{V/H}$ = 2/1, surface tension gradually decreases, reaching 53 mN/m at $R_{V/H}$ = 1/6 (i.e. loss of 12 mN/m with respect to raw vanillin or even raw Hylon VII). Beyond this last point, surface tension again becomes stable until the ratio $R_{V/H}$ = 1/10. This result (i) indicates that surface tension can be modulated by a host/guest ratio and (ii) agrees with the observation made by Patel et al. that emulsions are stable because of the presence of a complex within a large excess of polysaccharide. In order to finalize this primary study, dependence on concentration was studied by keeping the V/H ratio constant. In these new conditions, the ratio chosen was that for which the previous γ value was the lowest (here, $R_{V/H}$ = 1/10). The surface tension curve presented in Fig. 3 exhibits a surface-active property shown by the lowering of the water surface tension according to the inclusion complex concentration. It is important to note that, in this range of concentration, vanillin and Hylon VII separately do not show the same

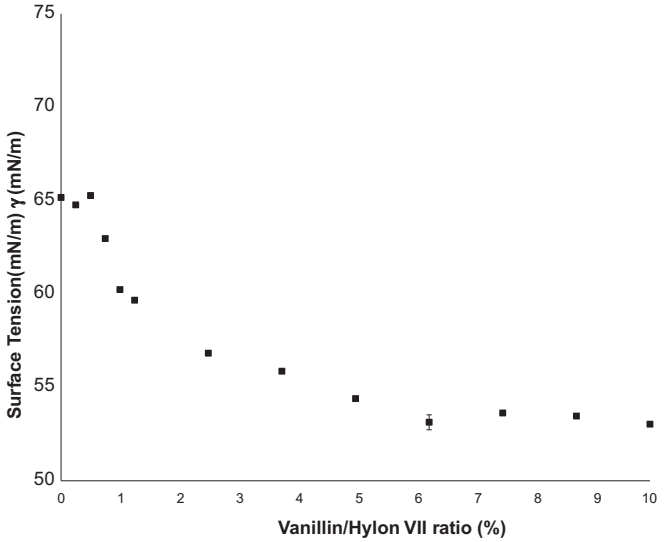

Fig. 2. Surface tension curve as a function of vanillin/Hylon VII ratio at a fixed concentration of vanillin (1%) at 25 °C.

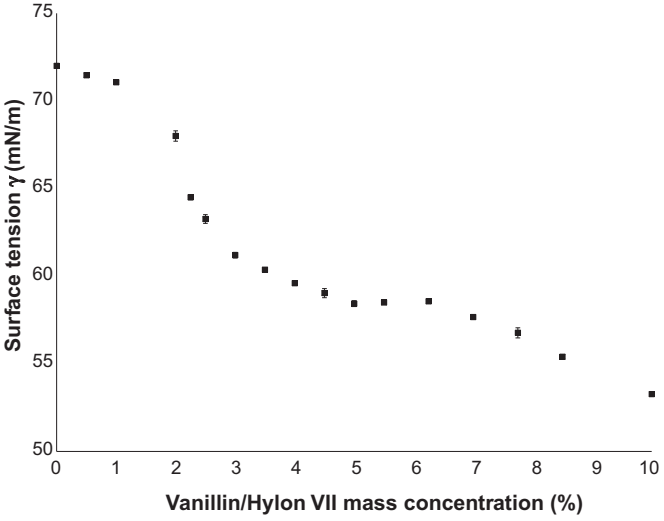

Fig. 3. Surface tension curves as a function of vanillin/Hylon VII inclusion complex concentration at a fixed ratio ($R_{V/H}$ = 1/10) in water at 25 °C.

behaviour than the complex in solution. In the first part of the curve, surface tension decreases rapidly until a break and occurs in the curve at a complex mass concentration of 3.66%. Beyond this point, the surface tension remains stable, and then decreases once again from 6 to 10%. The hypothesis of a second plateau was considered after the last point but was difficult to investigate because of the solubility limit of the vanillin, which prevented further concentration of the complex in these conditions. This kind of behaviour corresponds either to a progressive saturation of the interface or to a possible self-assembly of the inclusion complexes in solution. Nevertheless, this type of behaviour is remarkable and is reminiscent of that obtained by ion-pair surfactants with monomer-micelle-vesicle transitions (Bordes et al., 2007; Rudiuk et al., 2010). Consequently, this observed double transition may correspond to a spontaneous self-assembly of inclusion complexes from a particular concentration. In the case of inclusion complexes with fatty acids or monoglycerides and amylose, these assemblies have been reported to be able to form spontaneous structures where inclusion complexes organize themselves into multi-lamellar layers (Godet, Bouchet, Colonna, Gaillant, & Buléon, 1996; Zobel, French, & Hinkle, 1967). Nevertheless, these kinds of self-assemblies are formed in

solution, either at high temperatures or over time. Thus, it seems difficult for this phenomenon to occur in a spontaneous manner and, furthermore, at ambient temperature. The second hypothesis is that the observed curve could be attributable to the simultaneous presence of aggregates composed of a mixture of different helix lengths. It is thus preferable to mention an average of CAC, as is already the case with a mix of different kinds of surfactants in micellization (Garcia-Rio, Leis, Mejuto, Mosquera, & Rodriguez-Dafonte, 2007; Trawinska, Halmann, & Medrzycka, 2016). Besides, one study focuses on the CAC dependence when starch characteristics are modulated and helps to support this scenario. In the case of amphiphilic starch derivatives, some physicochemical parameters are impacted such as Mw (Molecular Weight) and Rh (Hydrodynamic Radius) mainly. Consequently, depending on the starch size dispersity, the CAC exhibits a wide range of values. (Tizzotti, Sweedman, Schäfer, & Gilbert, 2013). Thus, the latter is the most probable hypothesis in view of the uncontrolled polydispersity of the amylose chain length after extraction from Hylon VII.

3.2. Inclusion complexes with other substrates

On the basis of this promising result, the main goal became to find a more efficient system where surface tension would be lower than that of the system made from vanillin and Hylon VII. Additionally, for better control of concentrations in solution, it would be interesting to use other polysaccharides directly, without a preliminary extraction. To achieve this objective, several polysaccharides and flavouring molecules were used. Among the polysaccharides, only helical structures in water were tested: agar-agar, xanthan, carob bean gum, gellan gum, ι-carrageenan and κ-carrageenan. A wide range of guest flavouring molecules was also tested including menthol, menthone, thymol, furaneol and isoamyl acetate. Physicochemical parameters such as respective solubility log P and molecular volume as well as acceptor/donor bonds are summarized in Table 1. The first three correspond to the best flavours encapsulated in the amylose helix according to Yeo et al.'s study. Furaneol was chosen because of its higher solubility in water than the others (18.5 g/L at 25 °C). Isoamyl acetate, a non-aromatic molecule, was also tested because of its linear molecular structure and the presence of an isopropyl group. In that case, a complexation in the interstitial spaces of the helix was expected, as shown specifically with an amylose/isopropanol association (Buléon, Delage, Brisson, & Chanzy, 1990).

3.2.1. Surface tension measurements on raw polysaccharides

First, inclusion complexes were prepared by mixing the two substrates at room temperature for 90 min. The solutions appeared turbid and heterogeneous. The same procedure was repeated by heating at around 70 °C for 30 min as described in the study on vanillin/amylose complexes (Rodriguez & Bernik, 2013). The solutions obtained this time appeared isotropic even after cooling to room temperature. This observation indicates the need for heat when forming the inclusion complex. To determine the surface activity of these complexes, it was important to measure each polysaccharide separately after this thermal treatment. All measurements were carried out in a similar fashion (i.e. after each fabrication and just after cooling down). With temperature, some polysaccharide chains could become aggregated and consequently decrease surface tension. In one specific example made with corn fibre gum in solution, a reduction of surface tension of around 10 mN/m was obtained by increasing the temperature to 30 °C. The authors argued that an increase in temperature reduced the intermolecular attractive forces, thus decreasing the energy needed for molecular diffusion to the air/water interface (Jin, Cai, Li, Yadav, & Zhang, 2017). Surface tension remained measurable for each polysaccharide up to a mass concentration of 0.2% in solution. Beyond this concentration, gelation occurred, especially when using xanthan, which prevented good repeatability. As shown in Fig. 4, surface tension decreased for all polysaccharides, in agreement with the previous observation in the case of corn fibre gum. The greatest difference was observed for κ-carrageenan (− 17.24 mN/m) whereas the lowest was obtained for gellan gum (− 2.19 mN/m). Even though the gelation mechanisms are not well understood at present (double helix structure followed ether by an extended chain or by an aggregation in a random coil shape), it seems that the presence of ionic charges along the molecular structure could be one explanation for the predisposition to retrogradation (Morris, Rees, & Robinson, 1980; Smidsrod & Grasdalen, 1982). It seems that the presence of charged groups along the chains generate attractive potential between the charge density of polymers and the opposite charges in solution (Borgogna, Bellich, & Cesàro, 2011).

Table 1
Physicochemical parameters of flavours used in the study.

	Flavour molecule	Solubility limit in water at 25 °C (g/L)	1	2	3	4
			Log P	Molecular volume (Å^3)	Acceptor bonds	Donor bonds
a	Vanillin	10.0	1.07	136.59	3	1
b	Furaneol	18.5	0.55	115.15	3	1
c	Menthone	2.1	3.15	171.35	1	0
d	Menthol	0.46	3.33	177.21	1	1
e	Isoamyl acetate	2.0	2.04	140.72	2	0
f	Thymol	1.4	3.34	158.57	1	1

3.2.2. Screening for best "host-guest"

In a first step, the polysaccharide molecules (P) were varied while keeping the same guest, vanillin (V). The conditions were the same as previously (i.e. $R_{V/P}$ = 1/10 w/w). Again, the polysaccharides were dispersed in water at 0.2% wt. in order to make comparisons possible and obtain a fluidity enabling surface tension measurements. For each association, host and guest molecule surface tensions were monitored as well as that of the resulting inclusion complex (columns 1 to 3). Differences were calculated by deducting either the guest ($\Delta_{complex\text{-}guest}$) or host ($\Delta_{complex\text{-}host}$) value from the value for the complex after heat treatment (columns 4 and 5). Starting from these values, a global average has been calculated in order to determine a general effectiveness of each system (column 6). All data are summarized in Table 2. Among all the polysaccharides tested, gellan gum and ι-carrageenan could be considered as good systems because they showed the best negative difference on their respective average. Results were quite similar between these two polysaccharides (− 10.58 and − 10.49 mN/m, column 6). When their intrinsic viscosities were considered, ι-carrageenan exhibited the lower value at the same concentration in water (average viscosity at 20 °C: gellan gum: 0.112 ± 5.10^{-3} Pa·s; ι-carrageenan: 0.070 ± 2.10^{-3} Pa·s). Therefore, more concentrated solutions of inclusion complexes could be reached for ι-carrageenan without considering a strongly viscous medium. Consequently, this host molecule was stored and used in the rest of the study.

In a second step and in a similar way, guest molecules (GM) were tested, keeping ι-carrageenan (ιC) as the host. Conditions were similar to those used in the previous step ($R_{GM/iC}$ = 1/10 w/w; 0.2% in ιC). The results are presented in Table 3. Except for thymol (Entry 6f; + 2.63 mN/m), all surface tension averages showed negative values whatever the guest molecule used. When considering the rest of the flavouring molecules tested, vanillin and furaneol were found to differ from the others and exhibit a high global γ diminution (− 10.49 and − 9.67 mN/m respectively). Thus, using vanillin as the guest seemed to be more effective in both systems than using furaneol. This means that the best association, (i.e. the association exhibiting the lowest surface tension) was made from vanillin/ι-carrageenan.

As shown earlier in the case of the vanillin/Hylon VII inclusion complex, surface activity depended on the ratio between the substrates. In the case of the previous system made from vanillin/Hylon VII,

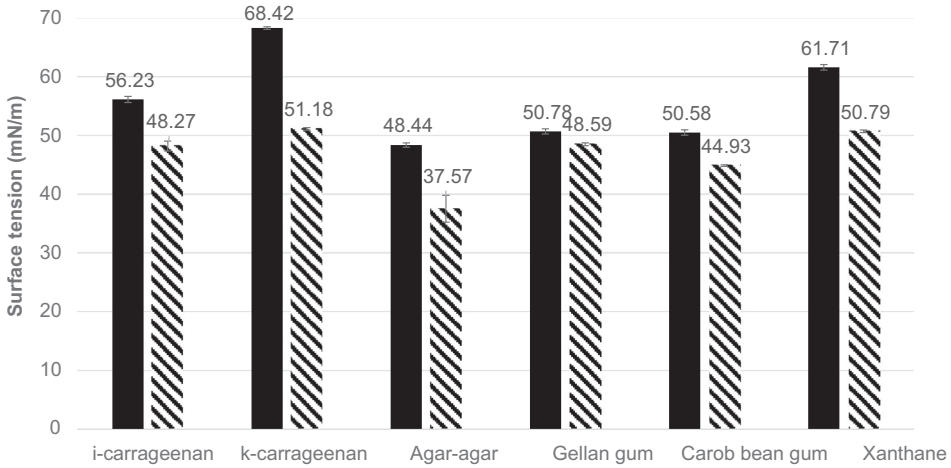

Fig. 4. Surface tension values of polysaccharides 0.2% wt. at 25 °C, before and after heat treatment (70 °C; 30 min) - black and hatched areas respectively.

polysaccharide was in large excess relative to the guest molecule. It was thus interesting to vary the vanillin/ι-carrageenan ratio for this new association. For this purpose, five ratios were tested (V/ιC: 10/1, 5/1, 1/1, 1/5 and 1/10). For the whole set of measurements, the mass concentration of vanillin was fixed at 0.02% whereas that of the ι-carrageenan was modulated to achieve the desired ratio (from 0.002 to 0.2%). Results are shown in Table 4. Once again, surface tension was dependent on the ratio since the lowest surface tension and differences with respect to raw substrates were obtained when vanillin was in large excess over ι-carrageenan, typically by a factor of ten (line a). This observation differs from the findings for the previous system made from vanillin and Hylon VII, where the highest amount of amylose (V/H: 1/10) led to the lowest surface tension. This observation suggests that each association is unique and its surface tension ability is obtained in a restricted range of ratios. For informational purposes, furaneol has also been used with ι-carrageenan in another set of experiments in a similar fashion. By varying ratio between substrates, surface tension has not been modulated as good as vanillin ($F/\iota C_{1/10}$: $\gamma = 41.63 \pm 0.05$ mN/m and $F/\iota C_{10/1}$: $\gamma = 40.43 \pm 0.29$ mN/m). This result indicates the importance of the guest molecule selection inside the helix and also confirms the choice of vanillin for this system.

3.2.3. Structure characterization

Following these significant results with vanillin, all of the samples were first characterized by ATR-FTIR spectroscopy (i.e. V: 1% and ιC: 0.1%, and V/ιC: 10/1 w/w). Fig. 5 presents spectra of both pure compounds and of the mixture. The vanillin C═O stretching mode is affected in the complex; the band is shifted to lower wavenumber at 1663 cm^{-1}. The shift is different from that found with the vanillin/amylose complex, allowing us to conclude that the organization of the vanillin is different in the two mixtures. Among all inclusion complex bands, those corresponding to the C═O stretching mode and the OH phenolic bending mode are shifted compared to raw vanillin (vanillin/complex: 1669/1663 and 1287/1295 cm^{-1} respectively). In comparison with ι-carrageenan, the band corresponding to sulfonyl O═S═O stretching mode is also shifted in the case of inclusion complex (1250 vs 1264 cm^{-1}), (Prado-Fernandez, Rodriguez-Vazquez, Tojo, & Andrade, 2003). Consequently it seems that vanillin's phenolic OH (donor) and ι-carrageenan's sulfonyl (acceptor) groups are engaged in a hydrogen bond leading to the inclusion complex in solution. This particular interaction could not be established in the previous system with amylose due to the absence of acceptor groups on the molecular structure of this polysaccharide.

Focusing now on vanillin's C═O stretching band in the two inclusion complexes made from Hylon VII or ι-carrageenan, it was found that trends differed compared to vanillin. With the Hylon VII, complexation increased the wavenumber (from 1665 to 1672 cm^{-1}) whereas, in the case of ι-carrageenan, the reverse occurred (from 1669 to 1663 cm^{-1}). The most probable hypothesis concerns vanillin's environment within the polysaccharide (Bellamy, 1980). When the substrate establishes hydrogen bonds, band shifting to a lower wavenumber is regularly observed due to an electronic impoverishment of the C═O bond. This means that, in the first case (Hylon VII), vanillin is preferentially located inside the amylose helix as described by Rodriguez and Bernik (2013). The environment is thus mainly hydrophobic, inducing the increase of the wavenumber. In contrast, with ι-carrageenan, the

Table 2
Surface tension monitoring by varying polysaccharide molecules in complexation with vanillin (RV/P = 10; polysaccharides concentration = 0.2% wt) at 25 °C. Differences of surface tension between complexes and either guest or host were obtained by calculation and are printed in italics.

	Polysaccharide molecule	1	2	3	*4*	*5*	*6*
		$\gamma_{Vanillin}$ (mN/m)	$\gamma_{Polysaccharide}$ (mN/m)	$\gamma_{Inclusion\ complex}$ (mN/m)	*$\Delta_{complex\text{-}guest}$ (mN/m)*	*$\Delta_{Complex\text{-}host}$ (mN/m)*	*$Average_{Host\&Guest}$ (5 + 6)/2 (mN/m)*
a	Xanthan	64.90	50.79	56.47	*− 8.43*	*+ 5.68*	*− 1.38*
	Standard deviation	*± 0.12*	*± 0.23*	*± 0.45*			
b	Carob bean gum	64.90	49.37	48.23	*− 16.67*	*− 1.14*	*− 8.91*
	Standard deviation	*± 0.12*	*± 0.27*	*± 0.27*			
c	ι-carrageenan	64.90	48.27	46.10	*− 18.80*	*− 2.17*	*− 10.49*
	Standard deviation	*± 0.12*	*± 0.84*	*± 0.29*			
d	κ-carrageenan	64.90	51.18	53.60	*− 11.30*	*+ 2.42*	*− 8.89*
	Standard deviation	*± 0.12*	*± 0.22*	*± 0.23*			
e	Gellan gum	64.90	48.59	46.17	*− 18.73*	*− 2.42*	*− 10.58*
	Standard deviation	*± 0.12*	*± 0.24*	*± 0.16*			
f	Agar-agar	64.90	37.57	44.80	*− 20.10*	*+ 7.23*	*− 6.44*
	Standard deviation	*± 0.12*	*± 2.31*	*± 0.18*			

Table 3
Surface tension monitoring at 25 °C, by varying guest molecules in complexation with ι-carrageenan ($R_{GM/\iota C}$ = 10; ι-carrageenan concentration = 0.2% wt). Differences of surface tension between complexes and either guest or host were obtained by calculation and are printed in italics.

	Guest molecule	1	2	3	*4*	*5*	*6*
		$\gamma_{Guest\ molecule}$ (mN/m)	$\gamma_{i\text{-}Carrageenan}$ (mN/m)	$\gamma_{Inclusion\ complex}$ (mN/m)	$\Delta_{complex\text{-}guest}$ *(mN/m)*	$\Delta_{Complex\text{-}host}$ *(mN/m)*	$Average_{Host\&Guest}$ *(5 + 6)/2 (mN/m)*
a	Vanillin	64.90	48.27	46.10	*− 18.80*	*− 2.17*	*− 10.49*
	Standard deviation	*± 0.12*	*± 0.84*	*± 0.29*			
b	Furaneol	55.93	48.27	42.43	*− 13.50*	*− 5.84*	*− 9.67*
	Standard deviation	*± 0.19*	*± 0.84*	*± 0.29*			
c	Menthone	41.80	48.27	41.70	*− 0.10*	*− 6.57*	*− 3.34*
	Standard deviation	*± 0.19*	*± 0.84*	*± 0.23*			
d	Menthol	45.03	48.27	42.90	*− 2.13*	*− 5.37*	*− 3.75*
	Standard deviation	*± 0.21*	*± 0.84*	*± 0.11*			
e	Isoamyl acetate	46.23	48.27	44.83	*− 1.40*	*− 3.44*	*− 2.42*
	Standard deviation	*± 0.06*	*± 0.84*	*± 0.19*			
f	Thymol	37.33	48.27	45.43	*+ 8.10*	*− 2.84*	*+ 2.63*
	Standard deviation	*± 0.33*	*± 0.84*	*± 0.34*			

Table 4
Surface tension monitoring at 25 °C, for vanillin/ι-carrageenan system by varying its ratio (mass concentration of vanillin was fixed at 0.02% whereas that of the ι-carrageenan was modulated from 0.002 to 0.2%). Differences of surface tension between complex and either guest or host were obtained by calculation and are printed in italics.

	Ratio (V/ιC)	1	2	3	*4*	*5*	*6*
		$\gamma_{Vanillin}$ (mN/m)	$\gamma_{i\text{-}carrageenan}$ (mN/m)	$\gamma_{Inclusion\ complex}$ (mN/m)	$\Delta_{complex\text{-}Vanillin}$ *(mN/m)*	$\Delta_{Complex\text{-}\iota\text{-}carrageenan}$ *(mN/m)*	$Average_{Host\&Guest}$ *(5 + 6)/2 (mN/m)*
a	10/1	64.90	55.80	36.83	*− 28.07*	*− 18.97*	*− 23.52*
	Standard deviation	*± 0.12*	*± 0.27*	*± 0.16*			
b	5/1	64.90	55.70	40.90	*− 24.00*	*− 14.80*	*− 19.40*
	Standard deviation	*± 0.12*	*± 0.11*	*± 0.23*			
c	1/1	64.90	51.00	45.63	*− 19.27*	*− 5.37*	*− 12.32*
	Standard deviation	*± 0.12*	*± 0.15*	*± 0.27*			
d	1/5	64.90	49.40	47.67	*− 17.23*	*− 1.73*	*− 9.48*
	Standard deviation	*± 0.12*	*± 0.12*	*± 0.19*			
e	1/10	64.90	48.27	46.10	*− 18.80*	*− 2.17*	*− 10.49*
	Standard deviation	*± 0.12*	*± 0.84*	*± 0.29*			

lowering of wavenumber suggests that vanillin remains in the water media during complexation. In that case, the most likely explanation would be a possible complexation in the interstitial spaces of the helix.

It should also be noted that, in the case of inclusion complex (1/10: V/ιC w/w), no band shifting was observed. Consequently, the lowering of surface tension seems mainly due to the presence of inclusion complexes in solution.

For the previous system made with vanillin and Hylon VII (1/10 w/w), infra-red spectroscopy highlighted a hydrogen bond between aldehyde (vanillin) and hydroxyl groups from amylose. An NMR analysis was also carried out with the same system but, with H_2O/D_2O (90/10 v/v) as a solvent, signals of amylose were not correctly resolved,

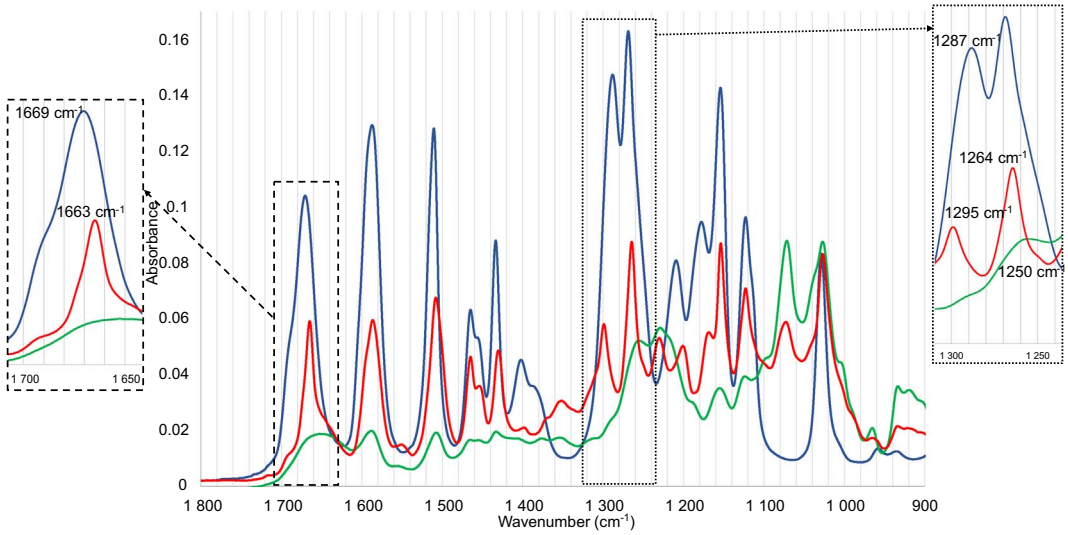

Fig. 5. Infra-red spectra of vanillin (blue solid line), ι-carrageenan (green solid line) and vanillin/ι-carrageenan inclusion complex (R = 10/1; red solid line, multiplied by 3). Insert left: Focus on the aldehyde C═O stretching band. Insert right: Focus on the vanillin OH phenolic group, free and H-bonded (in the case of complex), followed by the ι-carrageenan O═S═O stretching band. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

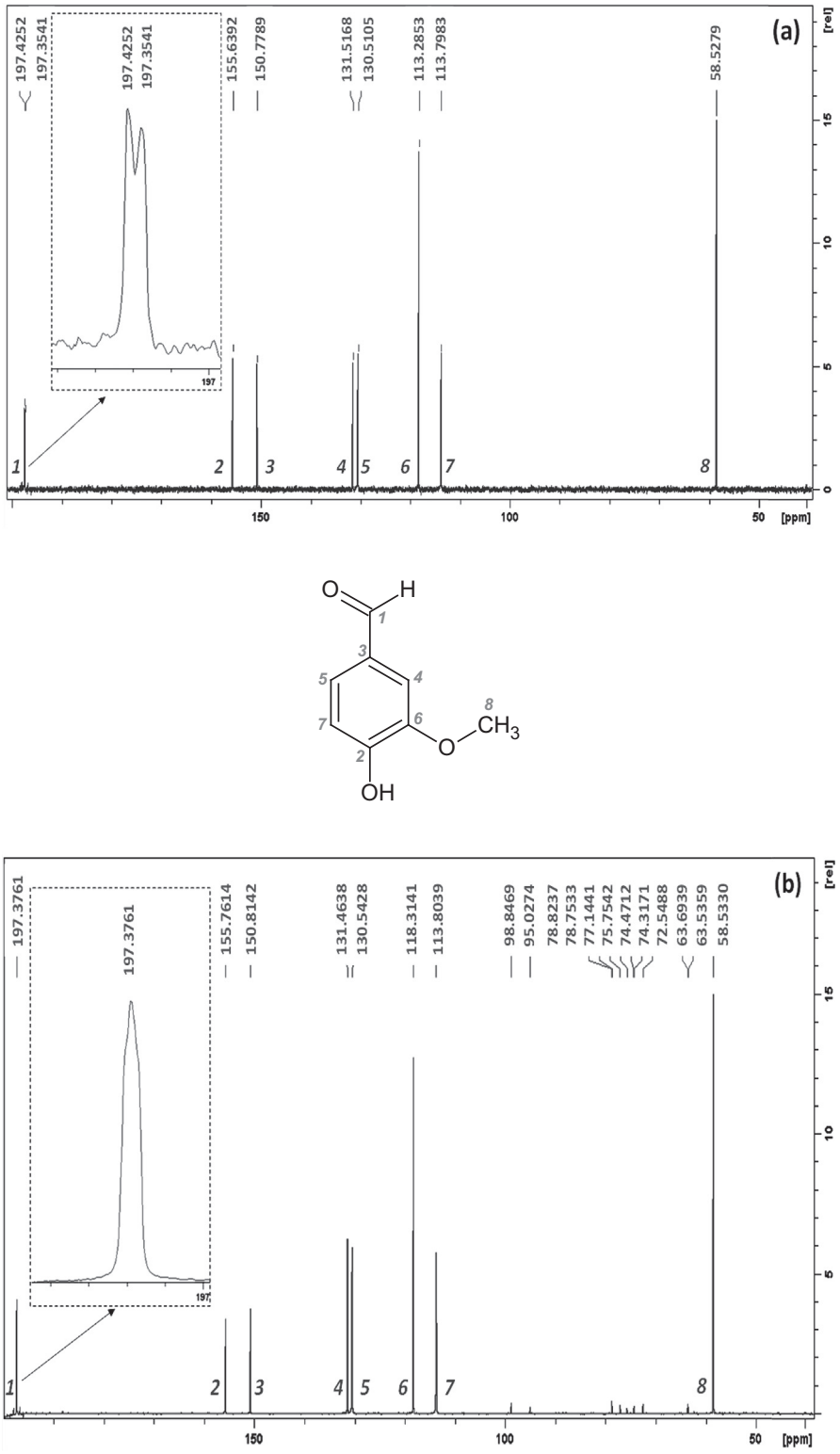

Fig. 6. ^{13}C NMR spectra (800 MHz; TSP as reference); (a): vanillin and (b): vanillin/ι-carrageenan inclusion complex (V/ιC: 1/10 w/w). Insert in both figures: Focus on the aldehyde peak ((a): duplication and (b): average singlet). Numbers indicated correspond to their respective position within the molecular skeleton of vanillin (central).

preventing a possible structure determination or an observation of interactions between substrates. It is known that linear homoglycans (i.e. cellulose and amylose) dissolve either poorly or not at all in water, which explains this observation (Cheng & Neiss, 2012). A dissolution of amylose or vanillin/amylose complex in organic solvents is not recommended in that case due to a possible break of intermolecular hydrogen bonds and thus to a dissociation of the assembly in solution.

By using ι-carrageenan as the host, this problem did not appear and NMR experiments were carried out in correct conditions (Van de Velde, Pereira, & Rollema, 2004). In order to show a possible complexation between vanillin and ι-carrageenan and confirm previous observations in ATR-FTIR, three concentrated samples were monitored: inclusion complex in a ratio 10/1 (V/ιC w/w) and both substrates at the same mass concentration as the complex (i.e. V: 1% and ιC: 0.1%). In comparison with raw substrates, a ^{1}H NMR spectrum of the inclusion complex was not significant. Nevertheless, complexation effects were

brought out by ^{13}C NMR analysis and some changes could be underlined, especially between pure vanillin and complex (shown in Fig. 6 a and b respectively; ι-carrageenan peaks are located with small intensities between 63 and 99 ppm). First, the signal of carbonyl changed in shape due to the complexation (carbon number 1): two peaks were present in raw vanillin (located at 197.35 and 197.42 ppm) whereas, in the case of inclusion complex, a broad signal was observed (197.38 ppm). The first two peaks may first correspond to a coexistence of free vanillin and dimers or trimers of vanillin in aqueous solution. Such specific assemblies, stabilized by hydrogen bonds, have been well described in the case of solid vanillin (Akinchan, 2002). It is thus possible that these interactions remain stable in solution. According to this hypothesis, the observed peak for the inclusion complex could be due to a global complexation of structures of vanillin with ι-carrageenan in solution and intermolecular hydrogen bonds. The second probable explanation for the observation of two peaks is a π-π stacking of vanillin molecules in solution. This effect has already been observed by ^{1}H NMR when the concentration of vanillin was up to 50 mM (Bogdan, Floare, & Pirnau, 2009). Typically in these experimental conditions, vanillin molar concentration was 65 mM. Additionally, a temperature dependence study of vanillin at two levels (25 °C and 65 °C; not shown) evidenced a slight shielding of few vanillin's aromatic protons, which corroborated the presence of these weak interactions (Sun et al., 2006). Then, a meaningful peak shifting was also detected for the phenolic function of vanillin (carbon number 2; 155.64 and 155.76 ppm for inclusion complex). The deshielding effect (+ 24 Hz), especially localized on the quaternary carbon, was suggestive of an electronic impoverishment (low electronic density) of the O—H bond. This implies a weak interaction, such as a hydrogen bond, between vanillin and ι-carrageenan. This agrees with the ATR-FTIR interpretations and confirms a good match between these analytical methods. A similar phenomenon has already been reported in the literature for interactions between vanillin and gallic acid (Jung, De Ropp, & Ebeler, 2000). All the other peaks were little affected by the complexation, whether against vanillin or ι-carrageenan.

3.2.4. Behaviour in water

For this set of experiments, the upper solubility of vanillin was pushed forward from the theoretical value (10 g/L). In the case of cyclodextrins it is known that complexation enhances the guest solubility (Atipairin & Sawatdee, 2015). In the system investigated here, the same effect was obtained. As shown in Fig. 7a, when vanillin was added above its solubility limit (> 1%) in water, crystals remained in solution. When ι-carrageenan was used as a medium in an amount that was one tenth that used for, vanillin, isotropic solutions were obtained (Fig. 7b). This effect was still observed up to 4% of vanillin in solution. It is important to note that the inclusion complexes obtained in these conditions were stable for at least 7 days. Beyond this time, some crystals of vanillin started to appear at the bottom, indicating a possible evolution leading to destabilization of the complex.

The surface tension curve of vanillin/ι-carrageenan inclusion complex (RV/iC = 10/1) presented in Fig. 8 exhibits two main parts. The left one (for lower concentrations) shows a rapid decrease of surface tension until 0.5%. Beyond this point, γ values decrease slowly and are stable at around 1%. This kind of behaviour could correspond to a progressive saturation of the interface or to a possible self-assembly of the inclusion complex in solution. The break occurs at a mass concentration of the complex of 0.69%. Raw substrates were also analysed but did not present this particular type of shape and, compared to the first system with vanillin and Hylon VII, only one break was observed. All of these observations lead to the conclusion that (i) many possibilities exist for inclusion complexes to be made starting from non-emulsifier substrates and (ii) each association has a specific behaviour in solution.

3.2.5. Foam stability

In order to validate the emulsifying properties of both inclusion complexes V/H: 1/10 and V/ιC: 10/1, the foaming abilities of solutions were investigated. For this purpose, gas dispersions were produced using two syringes connected together by a rubber hose. The same general procedure was repeated whatever the solution and has been described in the Materials and methods section. Before proceeding, all raw substrates in solution were investigated separately (vanillin 1% and 10%, Hylon VII 10% and ι-carrageenan 1% wt.). None of the raw substrates generated foams in those conditions. Thus, they could not be considered as emulsifiers. Indeed, especially for both polysaccharides and despite their low surface tension measured (65.8 mN/m for Hylon VII and 46.2 mN/m for ι-carrageenan) this result indicates that interfacial stabilization is a multifactorial approach and only γ values are not sufficient to explain why a dispersion remains stable over time.

As far as inclusion complexes are concerned, reliable foams were produced in both cases as shown in Fig. 9 (9a: V/H and 9b: V/ιC). In the case of vanillin/Hylon VII complex, the foam remained stable for just a few minutes (estimated at 3 min) but, with vanillin/ι-carrageenan complex, the resulting foam persisted for at least 60 min before complete destabilization. These results are in accordance with observation

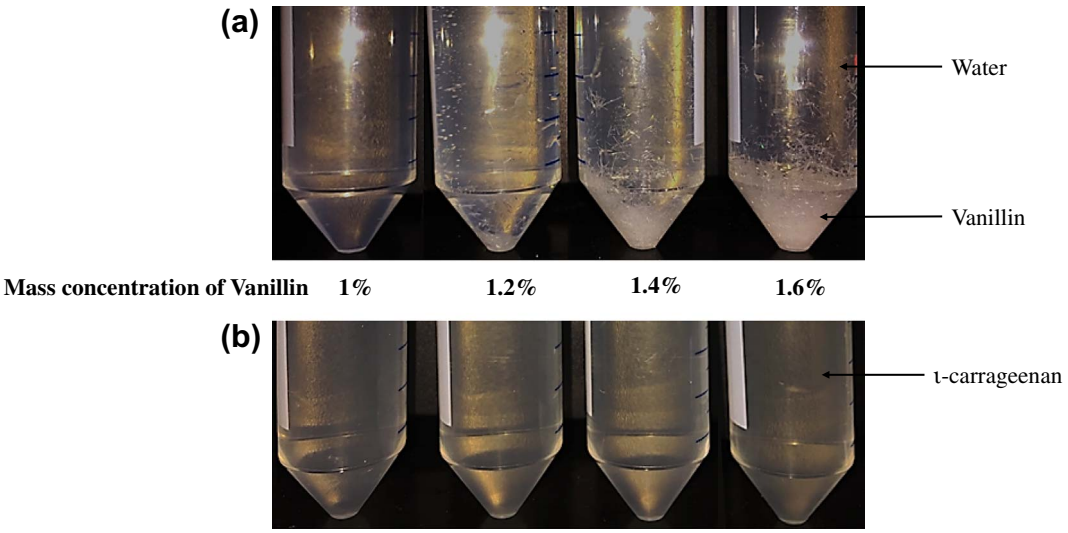

Fig. 7. Solubility of vanillin at ambient temperature above the theoretical solubility (10 g/L); (a): Dispersant: Water – Starting from 1.2%, crystalline vanillin is observed and (b): Dispersant: ι-carrageenan (V/ιC: 10/1 w/w) – Isotropic solutions are obtained beyond 1%.

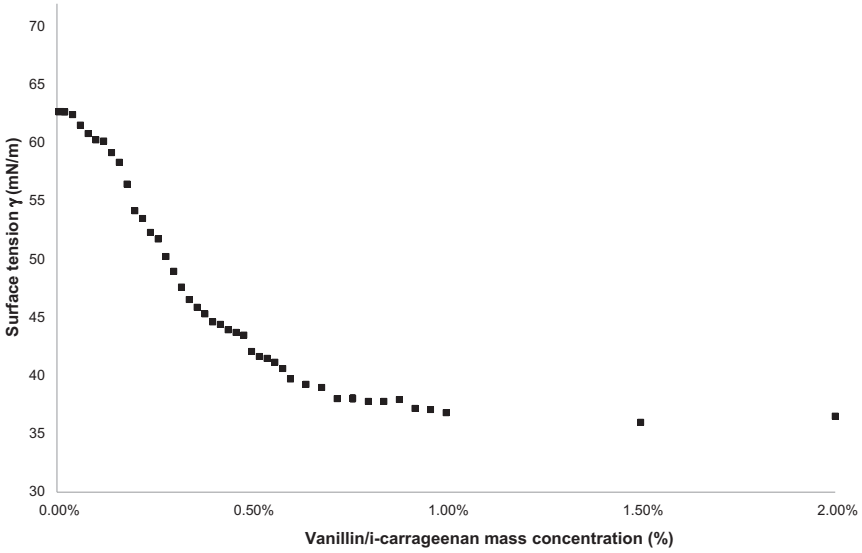

Fig. 8. Surface tension curve of vanillin/ι-carrageenan inclusion complex ($R_{V/iC}$ = 10/1) in water at 25 °C.

made by Patel et al. (2013). Indeed, methylcellulose is not a surface active agent and has only a gelling behaviour when used alone. In that case, the coarsening time (τ) of the foam has been calculated at 27.8 min. By associating tannic acid, the τ value has increased up to 83.3 min that suggest a surface active stabilization thanks to the inclusion complex. By comparison, these results indicate that emulsifying properties can be considered for both systems and that the inclusion complex structure is responsible of the interfacial stabilization. Nevertheless, the moderate stabilization of the foam with the Hylon VII system indicated that the corresponding breaks observed in Fig. 4 were mainly due to progressive interface saturation. If we consider the vanillin/ι-carrageenan system, the observed break is more indicative of a CAC and a complex closer to a regular emulsifier.

4. Conclusion

The main goal of these experiments was the synthesis of supramolecular assemblies between helical polysaccharides and flavouring molecules, which can interact with each other according to several mechanisms. Based on literature results as well as a "host-guest" screening, two systems made from vanillin/Hylon VII (amylose) and vanillin/ι-carrageenan exhibited a surface-active property due to an inclusion complexation. For both systems, intermolecular hydrogen bonds were highlighted by infrared spectroscopy and by ^{13}C NMR. These analyses revealed that complexation mechanisms were different for the two systems. Vanillin was preferentially located inside the amylose helix whereas it was preferentially located in the interstitial spaces of ι-carrageenan. In addition, for each system, complexation occurred for different mass ratios: ten times as much amylose as vanillin was needed but, with ι-carrageenan, the mass required was one tenth that of vanillin. Then, when their respective concentrations in water were varied, both complexes exhibited an emulsifying behaviour in solution by the presence of one or two breaks in the graph of surface tension vs mass concentration. In the last step of this study, foams were generated with both systems. In the case of vanillin/Hylon VII, stability was quite limited whereas, in the case of vanillin/ι-carrageenan, shelf life could reach 60 min before complete destabilization. Thus, it is reasonable to assume that the break corresponded to a CAC whereas, in the other system made with Hylon VII, two breaks were more indicative of a progressive saturation of the interface. All these results on structure

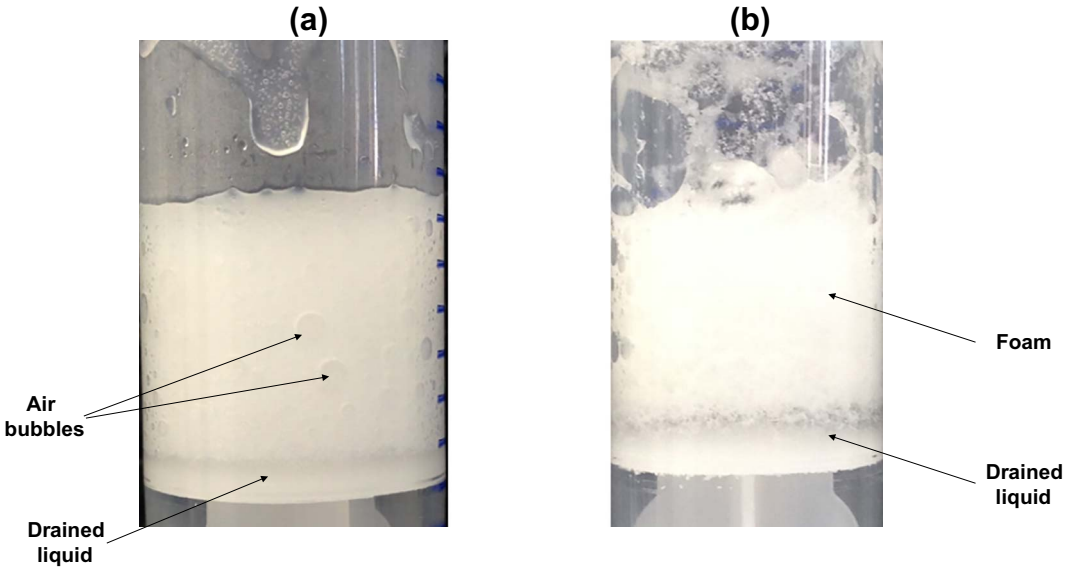

Fig. 9. Foams obtained with solutions of inclusion complexes and produced through two syringes connected together by a rubber hose; (a): vanillin/Hylon VII (1/10 w/w) and (b): vanillin/ι-carrageenan (10/1 w/w).

determination as well as the physicochemical approach are promising, that should be developed and open up new interesting perspectives on this research area.

As a continuation of the work presented here, it will be interesting to investigate other guest molecules and to correlate their structure with the formation of, or failure to form, inclusion complexes in solution and also their respective emulsifying abilities in other dispersion like emulsions. From a food chemistry point of view, this work opens up interesting opportunities, either to replace emulsifiers commonly used as additives (especially with amylose) or even to limit their use by adding an emulsifying activity to a regular thickening agent.

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