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Abstract

During the freezing of sorbets, the concentration of sucrose and stabilizing macromolecules increases in the unfrozen phase. Rheological properties of this unfrozen phase were studied, depending on nature and concentration of hydrocolloids in sucrose solutions at temperatures below zero. Three stabilizers were tested individually in sucrose-rich solutions: locust bean gum (LBG), hydroxypropylmethylcellulose (HPMC) and carboxymethylcellulose (CMC). The parameters of the Ostwald-de Waele model were determined and apparent viscosities of solutions were calculated at shear rates encountered during the process. Intrinsic viscosities and critical concentrations of entanglement were determined to evaluate the expansion of polymers in solutions and the transition of concentration regimes according to process conditions. Viscoelastic properties were also tested to study the possible cryogelation. For HPMC and LBG, the shear thinning behavior increased quite linearly with the concentration in stabilizer whereas CMC was highly shear thinning. Increasing sugar did not reveal large effect on these properties. The increase in apparent viscosity of the unfrozen matrix in process conditions was dependent on stabilizers; solutions containing LBG were less viscous than the others. Intrinsic viscosities revealed that HPMC and LBG became progressively less expanded as the concentration of sucrose increased whereas CMC tended to aggregate. Measurements of viscoelastic properties evidenced a dominant viscous behavior for HPMC and LBG systems whereas CMC systems showed dominant elastic behavior at frequencies higher than 0.1 Hz. The next challenge will be to better understand the potential link between the particular rheological behavior of hydrocolloids in process conditions and their possible influence on crystallization

mechanisms.

Keywords

Stabilizers; locust bean gum; hydroxypropylmethylcellulose; carboxymethylcellulose; rheology; sorbet.

1. Introduction

Sorbet is a frozen fruit juice with high sugar content stabilized by gum stabilizers (Marshall, Goff, & Hartel, 2003); this consists of air bubbles and ice crystals dispersed in an unfrozen matrix containing high concentrations of sugars and stabilizers. Before freezing, the mixture of ingredients or "mix" contains an average of 70%wt of water, almost 25%wt of sugar (sugars contained in fruit juices and added sugars) and up to 0.5%wt of stabilizers (Arbuckle, 1986; Clarke, 2004; Marshall, & Arbuckle, 1996; Stogo, 1998). The freezing step is the core of the manufacturing process of sorbets; it takes place in a scraped surface heat exchanger (SSHE) or freezer. The mix enters the freezer at approximately 4 °C and is converted into sorbet by simultaneous aerating, freezing and mixing to generate ice crystals and air bubbles. As the freezing proceeds, the unfrozen matrix becomes more and more concentrated in sugars and stabilizers and then increasingly viscous (Clarke, 2004). At the outlet of the exchanger, the sorbet contains an average of 40%wt of ice while the concentration of sugars and stabilizers in the unfrozen matrix is almost double that in the original mix. Its final temperature is between -5 °C and -6 °C (Marshall et al., 2003).

Stabilizers commonly used in the sorbet industry are natural polysaccharides, such as seed gums: guar gum (GG) and locust bean gum (LBG); cellulose derivatives: carboxymethylcellulose (CMC) and hydroxypropylmethylcellulose (HPMC); and microbial gum: xanthan gum (XG) (Thombare, Jha, Mishra, & Siddiqui, 2016). The presence of stabilizers facilitates the incorporation of air, the pumping and the filling of the molds after the freezing step. They would also slow down the migration of water and stabilize the formed foam (Arbuckle, 1986; Clarke, 2004; Marshall et al., 2003). Their influence on crystallization during the freezing step, i.e. initial size of the ice crystals and amount of frozen water, is still a subject of debate in the literature and results depends on the type of polymer, on the heat exchanger used and on the technique of analysis applied (Budiaman, & Fennema, 1987; Fernandez, Martino, Zaritzky, Guignon, & Sanz, 2007; Flores, & Goff, 1999; Goff, Caldwell, Stanley, & Maurice, 1993). The initial size of ice crystals would partly depend on the ability of the polymers to

bind water and increase the viscosity of the mix, or even gel on the vicinity of the crystal; but the physicochemical parameters involved are not formally identified. Effects of stabilizers during conservation and storage, especially on recrystallization process have also been studied by several authors; as with the initial formation of ice crystals, the results are controversial (Buyong, & Fennema, 1988; Flores, & Goff, 1999; Gaukel, Leiter, & Spieß, 2014; Kamińska-Dwórznicka et al., 2015; Regand, & Goff, 2003).

Only a few studies focus on the flow properties of solutions of stabilizers in a cold and sugar-rich environment and most of the shear rates ranges studied is far from the ones encountered during the freezing process in a SSHE where the shear can exceed 1000 s^{-1}. According to Flores, & Goff (1999), solutions containing sugars and stabilizers (0.26%wt of CMC, guar gum or xanthan gum) showed non-Newtonian behavior compared with the Newtonian behavior of unstabilized samples. Apparent viscosities recorded at 4 °C and 50 s^{-1} were 2 to 30 times higher for stabilized solutions than for non-stabilized solutions. Goff et al. (1993) performed thermomechanical analysis (TMA) with parallel plate rheometer attachments and reported that the viscosity of a 20% sucrose solution increased in the presence of 0.6% guar gum as the temperature decreased from 0 °C to -30 °C; from a certain temperature, samples were partially frozen. Bolliger, Wildmoser, Goff, & Tharp (2000) reported that apparent viscosities of an ice cream mix at 4 °C increased by a factor of 7 with addition of 0.2% guar gum. Similar results were obtained by Park, Hong, Kim, Choi, & Min (2006) with LBG added to an ice cream mix; apparent viscosities were recorded at 4 °C and 24 s^{-1}. In these studies, the concentrations of sugar and stabilizers did not represent what could be obtained during sorbet manufacturing when concentration and temperature evolve during the process. In order to understand the evolution of solution properties, it would be interesting to focus also on the intrinsic properties of stabilizing molecules, such as their intrinsic viscosity or critical concentrations of entanglement. Although many studies have been conducted, analyses have rarely been done in sugar solutions and never at temperatures below zero (Elfak, Pass, Phillips, & Morley, 1977; Richardson, Willmer, & Foster, 1998).

Some authors showed that cryogelation of stabilizers may affect the ice crystal growth rate, the morphology of growing ice crystals or inhibit the ice recrystallization (Blond, 1988; Goff, Ferdinando, & Schorsch, 1999; Muhr, & Blanshard, 1986). Patmore, Goff, & Fernandes (2003) analyzed viscoelastic properties of galactomannans in sugar solutions and at temperatures in some cases close to those encountered during the freezing process. They evidenced that, after one or more temperature cycles

from -1 °C to -15 °C, LBG formed weak gel structures when added at 0.3% to an ice cream mix containing sugars (24%) and non-fat milk solids. On the contrary, guar gum did not gel under the same conditions. In another study, strong gels were obtained with freeze-thaw gelation of 1% of LBG in sucrose solutions. Measurements, conducted at 5 °C after 24 hours of storage at -20 °C, showed that the strongest gels were obtained in the presence of 50% sucrose; this would be due to the reduction in water content with increasing concentration of sugar which would favor intramolecular interactions between LBG macromolecules (Doyle, Giannouli, Martin, Brooks, & Morris, 2006).

These studies show interesting rheological behavior of stabilizers in particular conditions but do not provide any information on changes in the rheological properties, either flow behavior or gelation, when the concentrations of sugars and stabilizers increase concurrently with a decrease in temperature i.e. during freezing. As a result, the literature does not make it possible to understand the effect of the polymers at the beginning of crystallization or during the freezing process.

In the present study, solutions containing different amount of sucrose and of stabilizers commonly used in sorbet recipes (HPMC or LBG or CMC) were formulated to mimic the unfrozen residual solution that increasingly concentrates in a freezer. Rheological analyses were carried out at temperature below zero to reproduce the conditions during the freezing process; these temperatures were always maintained slightly above the freezing point to avoid ice crystallization. The flow behavior of stabilizer solutions and their viscoelastic properties were analyzed; their intrinsic viscosity and their critical overlap concentration were determined to better understand their behavior and their evolution in concentrated sugar solutions at negative temperatures. These results were then analyzed considering the process conditions (temperature and shear rates) encountered in the SSHE.

2. Material and methods

2.1. Polymers and preparation of the mixes

HPMC was purchased from Dow® (Methocel™ K4M). Its viscosity in water was evaluated by Dow® at about 4000 mPa.s (2% at 20 °C). It contains 19 - 24% of methoxy groups and 7 – 12% of hydroxypropoxy groups. Sodium CMC was also obtained from Dow® (Walocel™ CRT 20000 PA). Its viscosity was evaluated by Dow® at 1900 – 2600 mPa.s (1% in water at 25 °C). Its degree of substitution was about 0.70 – 0.95. LBG was obtained from Cargill® (Viscogum™ FA 150). Its

viscosity in water was evaluated at 1% between 2500 and 3000 mPa.s. Sucrose was purchased from Béghin Say™. Solutions were prepared with deionized water (conductivity 17 $\mu S.m^{-1}$).

In order to simplify the composition of the mixes and to study specifically the effect of each stabilizer, only sucrose was used as sugar and stabilizers were studied individually. Two different mix compositions were analyzed. The first one mimicked the formulation of a mix at the beginning of the freezing step and the second one reproduced the unfrozen residual solution at the end of the freezing process. Before its freezing in a SSHE, a sorbet mix contains generally around 25%wt of sugars, so in this study the first type of mix was formulated with 25%wt of sucrose. The final temperature at the exit of the SSHE is around -6 °C (Marshall et al., 2003). At this temperature, the corresponding mass fraction of the sucrose in the unfrozen solution given by the liquidus curve of sucrose (phase diagram) is about 45% (Cerecero Enriquez, 2003). Therefore, in this study the second formulation of mix contained 45%wt of sucrose. Control mixes containing no sucrose were also prepared.

For each formulation, a range of stabilizer concentrations from 0,001%wt to 0.6%wt was studied. The mixes were prepared by dispersing sucrose and polymers in water under strong stirring at ambient temperature. The different solutions were obtained by successive dilutions from the higher to the lower concentration of stabilizer. The mixes were then cooled at 4 °C for at least 24 hours before rheological analysis. This ageing step is necessary to ensure the complete hydration and expansion of stabilizers in the solvent and thus their total dissolution (Clarke, 2004).

2.2. Rheological analysis at low temperature

2.2.1. Choice of temperatures for the analyses

The aim of this study was to analyze the rheological properties of the unfrozen part of a sorbet. As a consequence, it was necessary to avoid the freezing of the samples during the experiments while maintaining a temperature close to the freezing point. The two formulations differed from one another in their sucrose concentrations and consequently in their respective freezing temperatures. The temperature selected for analysis was around 0.4 °C above the freezing points of the different mixes. These freezing points were calculated by using the sucrose liquidus curve (Arellano salazar, 2012; Cerecero Enriquez, 2003). Table 1 shows the analytical conditions of the different mixes. A test was also performed at -1.5 °C for solutions containing 45% sucrose to separate the effect of the

147 concentration of sugar from the effect of temperature. Sucrose solutions without stabilizers were also
148 tested for viscosity measurement.

Table 1.
Temperatures used for the analysis of the different solutions.

Mix	Temperature of analysis (°C)
0% sucrose + stabilizer	0.4
25% sucrose + stabilizer	-1.5
45% sucrose + stabilizer	-1.5
	-5.6

149 ### 2.2.2. Flow behavior

150 All rheological characterizations were carried out with Physica MCR 301 rheometer (Anton
151 Paar®, Graz, Austria); coaxial cylinders (CC27, 1 mm gap) were used and a Peltier element enabled
152 the control of the temperature of samples. For the flow behavior study, a logarithmic shear rate ramp
153 down from 1000 s^{-1} to 0.1 s^{-1} and then up from 0.1 s^{-1} to 1000 s^{-1} was applied and the apparent
154 viscosity of the mixes was recorded; flow curves were then plotted. These curves allowed to visualize
155 the particular behavior of solutions containing hydrocolloids described by Graessley (1974): at a low
156 shear rate, viscosity did not change as a function of shear rate (Newtonian plateau), whereas at a
157 certain shear rate, a shear thinning behavior appeared. This is due to a progressive mechanical
158 disentangling of polymer chains as the shear rate increases.

159 For the shear thinning part of the curve, the evolution of the apparent viscosity η_{app} was
160 described by the Ostwald-de Waele model (equation 1) and the consistency index *K* and the flow
161 index *n* were calculated.

162 $$\eta_{app} = K\,\dot{\gamma}^{n-1} \qquad (1)$$

163 where $\dot{\gamma}$ is the shear rate.

164 Shear rates encountered in a scraped surface heat exchanger were calculated in the case of a
165 continuous ice cream freezer described by Hernández-Parra et al. (2018). The analogy with a power-
166 law fluid in a concentric cylinder viscometer was used (Steffe, 1996) and the shear rate was calculated
167 at two radial positions in the exchanger (at the central rotor and at 1mm of the wall, close to the
168 blades) with equation 2. The scraper rotational speed was considered to be 300 rpm.

169 $$\dot{\gamma} = \frac{2\Omega}{n}\,\frac{R^{2/n}}{R^{2/n} - r^{2/n}} \qquad (2)$$

where Ω is the rotor angular velocity (rad.s^{-1}), R is the tank radius (m) and r is the central rotor radius or the radius at 1mm of the wall (m), n the flow index determined for each condition. Apparent viscosities of solutions for these particular shear rates were then calculated thanks to power law equation (equation 1).

2.2.3. Intrinsic properties of the macromolecules

The viscosity at the Newtonian plateau observed at low shear rates enabled to access to certain properties of stabilizers such as their intrinsic viscosity and their critical overlap concentration. The concentration regimes were determined by plotting the specific viscosity η_{sp0} as a function of the concentration c of stabilizer. For LBG and HPMC, which are neutral polymers, their intrinsic viscosity $[\eta]$ was obtained by plotting η_{sp0}/c versus concentration according to the classical empirical equation proposed by Huggins (1942) (equation 3). The Huggins parameter λ depends on the solvent and represents a measure for the quality of the solvent and for the degree of solvation of molecules.

$$\frac{\eta_{sp0}}{c} = [\eta] + \lambda\,[\eta]^2 c \qquad (3)$$

As CMC is an anionic polymer, its intrinsic viscosity was determined with the equation established by Fedors (1979) (equation 4) which is more appropriate in this case, by plotting $\left[2(\eta_{rel}^{1/2} - 1)\right]^{-1}$ against $1/c$.

$$\left[2(\eta_{rel}^{1/2} - 1)\right]^{-1} = ([\eta]c)^{-1} - ([\eta]c_m)^{-1} \qquad (4)$$

where η_{rel} is the relative viscosity and c_m is a polymer concentration parameter. Arinaitwe, & Pawlik (2014) showed that this equation described well the behavior of anionic polyacrylamide and fitted well to experimental data from CMC samples. This equation was also applied to HPMC and LBG to compare the results with those obtained with the Huggins model.

2.2.4. Viscoelastic properties

The viscoelastic properties of the unfrozen solution at the exit of a freezer (0.6% of stabilizer in 45% sucrose solution) have been studied using oscillatory mode. Frequency sweeps from 100 to 0.1 Hz and 0.1% strain corresponding to the linear viscoelastic range (LVE) were performed at -5.6 °C. Storage modulus G' and loss modulus G'' were measured.

2.3. Statistics

Two samples of each mix were collected and the viscosity of each sample was analyzed in triplicate so each mix provided a set of six datasets. For every parameter, analysis of variance was used to determine significant differences ($p < 0.05$).

3. Results and discussion

3.1. Flow behavior at low temperature as a function of sucrose concentration

3.1.1. Flow index and consistency index

Figure 1 shows the influence of the concentration of the stabilizer, of the sucrose and of the temperature on the flow index *n* for each solution. First of all, it appears that, whatever the stabilizer and for all the conditions, *n* decreased with an increase in the stabilizer concentration. This result, in agreement with other studies (Rao, & Kenny, 1975; Speers, & Tung, 1986), was expected; the polymers used are shear thinning molecules so this effect is more pronounced when they are present in larger quantities. CMC evidenced a high exponential decrease of *n* while increasing the concentration of stabilizer compared to HPMC and LBG. This could be explained by the high stiffness of the CMC due to its charges.

The flow index of the studied polymers was not influenced by temperature in 45% sucrose solutions. A few studies in literature focused on effects of temperature on hydrocolloids flow properties but all of them were reported at positive temperatures and without sugar. The authors observed either a slight decrease or no change in the values of *n* when temperature decreased (Gómez-Díaz, & Navaza, 2003; Haddarah et al., 2014; Rao, & Kenny, 1975; Speers, & Tung, 1986).

Sucrose concentration had a noticeable effect on shear thinning behavior in the case of HPMC solutions: higher was the sucrose concentration and lower was the flow index. A possible hypothesis is that, because of its hygroscopicity, sucrose mobilized water; then sucrose would promote hydrophobic interactions between HPMC chains due to their substitutions. These interactions would be disrupted during shearing. In the case of LBG as for CMC, the effect of sucrose on their shear thinning properties seemed to be less important; interactions between macromolecules would be prevented by steric hindrance or electrostatic repulsion respectively for LBG and CMC. As far as we know, no

224 literature focused on changes in the flow properties of stabilized solutions related to the presence of
225 sugar and at temperature below zero.
226 According to these results and considering the freezing process, a sorbet mix, which generally
227 contains a minimum of 0.3%wt of stabilizers when entering the SSHE, already has shear thinning
228 properties at the beginning of the process. Moreover, the unfrozen residual solution becomes
229 increasingly shear thinning during the freezing step with the increase in the concentration of stabilizer
230 and sugar.

231 Figure 2 show changes in the consistency index *K* in systems containing HPMC, LBG or CMC.
232 First, regardless of the stabilizer and sugar concentration, *K* increased with an increase in the
233 concentration of the polymer. As the polymers analyzed were thickening molecules, this character was
234 expected to increase with an increase in their concentration; similar results have been obtained in
235 other studies (Rao, & Kenny, 1975; Speers, & Tung, 1986).

236 In the case of HPMC and LBG solutions, the evolution of the consistency index with the
237 concentration of the stabilizer showed similar trends: whatever the solution studied, *K* increased
238 exponentially with an increase in the concentration of the stabilizer (*K* is plotted on a logarithmic axis
239 on Figure 2). In the case of HPMC, the slope of the curves was nearly the same whatever the
240 concentration of sugar or the temperature. In this case, for a given polymer concentration, higher was
241 the concentration of sugar and higher was the value of *K*. This result is not surprising, the viscosity of
242 a sugar solution increases with an increase in sugar concentration. Concerning LBG, the slope of the
243 curves was not the same: the variation of *K* according to the concentration of LBG was greater in
244 25%wt sucrose solutions than in 45%wt or in 0% sucrose solutions. At 0.6%wt of LBG, similar values
245 of *K* were obtained in all systems containing sucrose, regardless of the concentration of sucrose or the
246 temperature. It revealed a specific behavior of LBG; this effect could be related to specific
247 conformational properties of this polymer at high concentration in sucrose solutions. In the case of
248 CMC solutions, unlike with HPMC and LBG, *K* changed linearly according to the polymer
249 concentration (*K* is plotted on a logarithmic axis on Figure 2), with a change of the linear slope
250 between 0.1%wt and 0.3% wt of stabilizer. This difference may be due to negative charges carried by
251 CMC molecules which could induce particularities in the conformational properties of CMC; this will be
252 discussed in section 3.2.

In order to consider only the effect of the stabilizer on the consistency of the solution regardless of the effect of the solvent, the relative consistency index K_{rel} was calculated; it is defined as the ratio of the consistency to the viscosity of the solvent i.e. water or sucrose solutions analyzed at the corresponding temperature (data not shown). For all stabilizers, K_{rel} increased with an increase in the concentration in polymer and decreased when the concentration in sucrose increased. This suggests that the presence of sucrose had an influence on the thickening properties of stabilizers; polymers were allowed to develop better thickening properties with a lower concentration of sugar. With 45% of sucrose water would not be available enough to hydrate high concentrations of stabilizers.

Regarding the effect of temperature, the consistency index of solutions containing 45%wt of sucrose appeared to be close at -1.5 °C and -5.6 °C whatever the polymer. Some authors reported a significant increase (by a factor of 1.5 to 2) in the consistency index of solutions of stabilizers with a decrease in temperature (Gómez-Díaz, & Navaza, 2003; Haddarah et al., 2014; Marcotte, Taherian, & Ramaswamy, 2001; Rao, & Kenny, 1975; Speers, & Tung, 1986). These studies were performed at positive temperature between 5 °C and 80 °C and the results may be explained by the greater range of temperatures studied than that experienced in the present study. As for K, a change in temperature from -1.5 °C to -5.6 °C in 45% sucrose solutions did not significantly affect K_{rel}.

The general trends in K show that the unfrozen residual solution of a sorbet becomes increasingly viscous during the freezing step mostly due to the increase in the concentration of stabilizers and sugar.

3.1.2. *Apparent viscosity as a function of the process conditions*

The shear rates to which the mixes are subjected during the freezing process were calculated according to equation 3 and using the flow properties defined for each stabilizer in the section 3.1.1. The smallest shear rate of about 100 s^{-1} was encountered on the central axis of the rotor of the exchanger at the beginning of the process when the mix contains 25% of sugar and 0.3%wt of stabilizer at -1.5 °C. Conversely, the highest shear rate about 1000 s^{-1} was calculated at 1 mm of the inner wall close to the blades, with the mix characteristics encountered at the end of the process i.e. 45% of sucrose and 0.6%wt of stabilizer at -5.6 °C. The apparent viscosities of mixes were then calculated using the Ostwald-de Waele equation (equation 1) at the corresponding shear rates at the beginning or at the end of the process, in the center or at the wall of the exchanger and for the corresponding concentrations of stabilizers. Results are listed in Table 2.

The apparent viscosity systematically increased between the beginning and the end of the freezing process. These results, in agreement with another study (Arellano, Flick, Benkhelifa, & Alvarez, 2013) were expected as the concentration in sugars and polymers increases during freezing (freeze-concentration of the liquid phase). Then, η_{app} was always lower at the wall of the exchanger than at the center due to the higher shear rate and the shear thinning behavior of the mixes. At the beginning of the freezing process, the apparent viscosity of CMC solution was higher than the one of HPMC and LBG; indeed, the consistency index *K* was higher for this gum despites the higher sensitivity to shearing (lower flow index *n*). At the end of the process, when sucrose concentration was high, the apparent viscosity of LBG solutions was twice lower than the one of HPMC and CMC; it was found previously for this gum that the consistency index *K* increased less with sugar concentration. At high concentration, LBG gum seemed to exhibit specific conformational properties in sugar solutions.

Table 2.
Apparent viscosities of solutions as a function of freezing process conditions.

Process step	Conditions	Stabilizer	n	K (Pa.s^n)	η_{app} (Pa.s)	
					Radial position in the exchanger	
					Center	Wall
Beginning	25% sucrose -1.5°C 0.3% stab	HPMC	0.80	0.15	0.06	0.04
		LBG	0.75	0.15	0.05	0.03
		CMC	0.56	1.13	0.14	0.06
End	45% sucrose -5.6°C 0.6% stab	HPMC	0.52	7.50	0.76	0.30
		LBG	0.56	2.89	0.36	0.15
		CMC	0.42	13.3	0.72	0.27

These results show that, during the freezing process, the nature of the gum in the mix will have an influence on its apparent viscosity: this could affect the diffusive and thermal properties of the mix and finally, have an impact on the size of ice crystals at the output of a SSHE.

3.2. Intrinsic properties of stabilizers related to process conditions

Critical overlap concentrations and intrinsic viscosities were obtained by analyzing the viscosities in the Newtonian part of the flow curves of solution. A common method to identify concentration regimes is to plot the specific viscosity as a function of the polymer concentration (Fig. 3.).

For HPMC and LBG (Fig. 3 (A) and (B)) the curve presented a discontinuity in the concentration dependence of specific viscosities that defined the initial onset of the overlap of the polymer. The

303 critical overlap concentrations C* of HPMC and LBG was estimated to be about 0.22%wt and 0.18%wt
304 respectively. For these two stabilizers, C* did not vary with the process conditions (concentration of
305 sugar or temperature). In addition, there was no difference in the specific viscosity between the
306 different systems studied even when the HPMC or LBG concentration exceeded C*; this indicates that
307 the viscosity due to the presence of HPMC or LBG would not be influenced by sugar or temperature
308 and that a cold sucrose solution would be a good solvent for these two polymers. These results are
309 consistent with Richardson et al. (1998) who measured a critical concentration C* of LBG equal to
310 0.1%wt in solutions with sucrose concentrations ranging from 1% to 40% at 25 °C. Concerning CMC
311 (Fig. 3 (C)), C* was estimated at about 0.005%wt of stabilizer in 25% sucrose solutions. This value,
312 about forty times lower than those obtained for HPMC and LBG, would be due to the chain stretching
313 induced by charges carried by CMC macromolecules (Colby, 2010). In pure water or with 45% of
314 sucrose, C* could not have been obtained by plotting the specific viscosity against the concentration;
315 no change of slope was obtained in the range of studied concentrations. This could be due to specific
316 behavior of macromolecules in such condition as discussed later in this section.
317 Scaling laws have been defined for polymer solutions and each concentration regime is
318 characterized by a power law $\eta_{spO} \sim [polymer]^a$. For uncharged polymers such as LBG and HPMC
319 solvated in a good solvent, the values of the parameter *a* should be respectively 1.3, 3.9 and 3.75 for
320 the semi-dilute non-entangled, the semi-dilute entangled and the concentrated regimes (Colby, 2010).
321 Regarding the obtained values of the power law exponents for LBG and HPMC, they were in the same
322 order of magnitude despite the particular conditions of this study in terms of sugar concentration and
323 temperature. In the range of concentrations studied, solutions went from non-entangled semi diluted
324 regime to entangled macromolecular regime.
325 For polyelectrolyte solutions without salt, such as CMC in the conditions of this study, the power
326 law exponents are predicted to be respectively 0.5, 1.5 and 3.75 for the semi-dilute non-entangled, the
327 semi-dilute entangled and the concentrated regimes (Lopez, Colby, Graham, & Cabral, 2017). Values
328 of the same order of magnitude were obtained in 25% sucrose solutions. The exponent 1.3 of the
329 equation in other conditions would define that the entangled regime is already reached at a
330 concentration in CMC as low as 0.001% in water or in 45% sucrose solutions.
331 In the case of sorbets, since the concentration of stabilizer is twice as high in the unfrozen residual
332 solution at the end of the freezing step as in the original sorbet mix, if the initial concentration of

stabilizer is higher than $C^*/2$ then the solution will change from non-entangled to entangled polymer solution during the process. The viscosity of the unfrozen solution will increase linearly since the stabilizer concentration reached C^*, then it will increase exponentially above C^* (Lapasin, & Pricl, 1999). Since the concentration C^* of CMC seems significantly smaller, the change of behavior will take place earlier in the process in the case of a mix stabilized with this polymer.

The intrinsic viscosities [η] for HPMC, LBG and CMC are given in Table 3. As it was obtained thanks to the Huggins equation for HPMC and LBG, values of Huggins parameters λ are also recorded for these two polymers. The intrinsic viscosities of CMC were obtained using the equation of Fedors. Fedors model was also applied to HPMC and LBG (data not shown), the intrinsic viscosities were consistent when using both model.

Table 3
Intrinsic viscosities of HPMC, LBG and CMC and Huggins parameters of HPMC and LBG.

Solvent & temperature	[η] (cl/g)			λ	
	HPMC*	LBG*	CMC**	HPMC	LBG
45% sucrose -5.6 °C	69.9 ± 3.8a	50.6 ± 3.1c	801 ± 27e	1.1	1.4
45% sucrose -1.5 °C	67.7 ± 4.5a	48.3 ± 2.9c	623 ± 13f	1.1	1.6
25% sucrose -1.5 °C	84.1 ± 2.1b	78.3 ± 4.6b,d	497 ± 32g	0.7	0.7
0% sucrose 0.4 °C	71.5 ± 4.4a,d	76.3 ± 6.7b,d	684 ± 31f	1.4	0.9

*Values for HPMC and LBG were obtained with the Huggins equation **Values for CMC were obtained thanks to the Fedors equation. (Different lower case letters indicate significant differences between values, $p < 0.05$)

For HPMC as for LBG, intrinsic viscosity decreased as the concentration in sucrose increased from 25% to 45%, whereas the temperature had no effect. Intrinsic viscosity [η] of HPMC was estimated at about 70 cl/g in 45%wt sucrose systems whereas in 25% sucrose solution at -1.5 °C, it was found to be equal to 84 cl/g. Bustamante, Navarro-Lupión, & Escalera (2005) found a value of the intrinsic viscosity of HPMC close of those obtained is this study (80.9 cl/g in water at ambient temperature). Concerning LBG, [η] was about 78 cl/g with 25%wt of sucrose and 50 cl/g with 45%wt of sucrose whatever the temperature. The presence of sugar decreases the amount of water available for solvation of polymer; this could cause a fold of macromolecules as long as the freezing takes place. Elfak et al. (1977) also observed a decrease in the intrinsic viscosity of LBG with an increase in the sucrose concentration: [η] was 68 and 53 cl/g with respectively 20% or 40% of sucrose. Richardson et al. (1998) also obtained a decrease of [η] from 153 cl/g in a 20% sucrose solution to

354 114.7 cl/g in a 40% sucrose solution. The difference in the absolute values of intrinsic viscosity
355 between these studies should be due to a difference in molecular weight; furthermore they were both
356 conducted at ambient temperature.

357 The Huggins coefficient increased when the sugar concentration increased; λ exceeded 1 in
358 solutions containing 45%wt of sucrose whatever the temperature of analysis. This confirms that
359 solvation of LBG and HPMC is progressively less satisfactory as the residual solution concentrates
360 during the freezing process.

361 Concerning CMC, the intrinsic viscosities were always much higher than those observed for
362 HPMC and LBG. The pH of solutions was measured and it was found to be close to neutrality. At this
363 pH, 99% of the carboxylic groups would be dissociated and it is likely that electrostatic repulsions
364 occurred. Either the molecular weight of CMC was much larger or the chain of CMC was particularly
365 expanded. On the other hand, the intrinsic viscosity of CMC increased when the sugar concentration
366 increased and the temperature decreased. It is also possible that the presence of sucrose and the
367 decrease in temperature encouraged interactions between unsubstituted regions of the polymer
368 chains by decreasing solvation and increasing stiffness of the molecule. Therefore the intrinsic
369 viscosity obtained would be that of aggregates of extended molecules; the aggregation would be due
370 to the interactions between unsubstituted zones while the expansion would be due to the electrostatic
371 repulsions between dissociated carboxylic groups. The higher intrinsic viscosity of CMC at 0% sucrose
372 than at 25% of sucrose tends to evidence that polymer association would persist even in more diluted
373 solution due to unsubstituted part in the chain. These results are consistent with the analysis of the
374 critical concentration of entanglement. Values of the same order of magnitude were obtained in
375 another study (Arinaitwe, & Pawlik, 2014) ; the authors evidenced a low effect of substitution but a
376 high effect of molecular weight. However, the authors did not observe any effect of temperature on the
377 intrinsic viscosity of CMC.

378 Another method to evaluate the critical overlap concentration is to consider the inverse of the
379 intrinsic viscosity (Weissberg, Simha, & Rothman, 1951). Since this study allowed to obtain an intrinsic
380 viscosity per studied system, an interval of C* was calculated for each stabilizer. For LBG and HPMC
381 the determined C* were slightly lower than the ones obtained through the specific viscosity versus
382 concentration curve (between 0.12% and 0.15% for HPMC, between 0.13% and 0.21% for LBG). It
383 could highlight that the polymer may tend to compress before entanglement (Richardson et al., 1998).

For CMC there was a more important discrepancy between the two methods (2 to 4 fold higher when considering the inverse of the intrinsic viscosity which evaluated C* between 0.01% and 0.02%). This could result from the difficulty to assess C* through the change in slope of viscosity versus concentration.

3.3. Viscoelastic properties of the final unfrozen phase

The viscoelastic properties of solutions were also analyzed since they could have some strong effects on the freezing mechanisms of a sorbet mix (Marshall et al., 2003). Results obtained with 45% sucrose solutions and 0.6% stabilizer at -5.6 °C are shown in figure 4.

HPMC and LBG showed typical macromolecular solution behavior (Fig.4 (A) and (B)): G" was larger than G' over the entire frequency range but they approached each other at higher frequencies. Concerning CMC (Fig.4 (C)), the mechanical spectra was representative of a concentrated solution with G'' close to G' at low frequency, a cross-over and then G' predominating at higher frequencies, showing for these frequencies a clear tendency for more solid-like behavior; interactions between polymer were dominant. These results are consistent with the observed increased in intrinsic viscosity mentioned above. Doyle, Giannouli, Martin, Brooks, & Morris (2006) systematically obtained gels by freezing and thawing solutions containing LBG, at higher concentration than in the present study (1%) and for several concentrations of sucrose. In that study, the strength of the gel seemed to depend on the sucrose concentration (with a maximum strength obtained for 50% sucrose) and on the galactose content of LBG molecules which prevent the intermolecular associations through mannan sequences by steric hindrance. As a result, it is not surprising that two different LBG samples with probably different mannose/galactose ratios have different viscoelastic properties; different LBG concentrations and different methods of sample preparation can also explain these differences.

Although the ice crystallization phenomena in such polymers solutions has not been clearly related to the viscoelastic properties of polymer solutions, he bonds between the CMC molecules at the origin of the solid properties of the system may have a different effect on crystallization than the predominantly liquid systems obtained with HPMC or LBG. This could influence the diffusion properties of water or sucrose molecules or promote mechanical resistance to crystal growth (Blond, 1988; Goff et al., 1999; Muhr, & Blanshard, 1986).

4. Conclusions

As shown by flow behavior data, the unfrozen phase of a sorbet containing sugars and stabilizers becomes increasingly shear thinning and viscous as the freezing step proceeds. Apparent viscosities of solutions calculated at shear rates encountered in a scraped surface heat exchanger indicate that the unfrozen phase is more viscous in the center of the exchanger than that near the walls and not in the same proportion according to the stabilizer. Compared to HPMC and CMC, LBG provides less increase in viscosity as the sugar and stabilizer concentration increase. This could be explained by a less solvation of hydrocolloids in sucrose solutions. The intrinsic viscosity of LBG decreases twice more than that of HPMC. CMC reveals a high shear thinning behavior and it seems more expanded as concentrations in polymer and sucrose increase. Moreover CMC solution shows dominant elastic behavior while HPMC and LBG give dominant viscous behavior.

These results will be confronted with analyzes of the size of the ice crystals during the process and at the end of freezing step. It aimed to link the action of hydrocolloids on rheological properties of the mixes and their possible influence on crystallization processes and finally on the size of ice crystals. As polymers do not exhibit the same flow behaviors or tendencies to create a gel, blends of hydrocolloids could also be analyzed as they are mainly used in the industry. They may exert possible synergistic effects at temperature below zero and with addition of sucrose.

Funding

This work was supported by the French Ministry of Higher Education, Research and Innovation.

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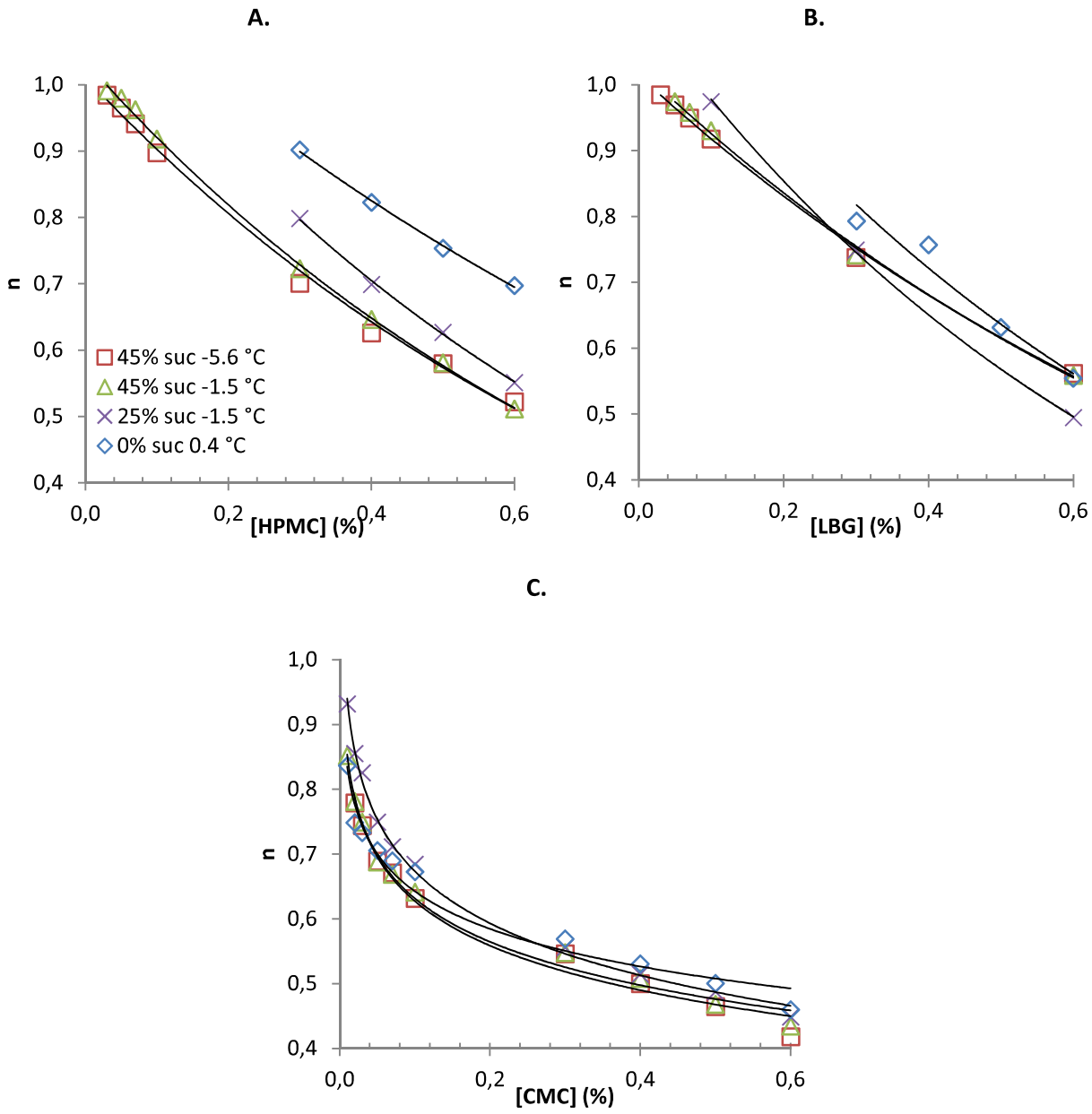

542 **Fig. 1.** Evolution of the flow index versus concentration of HPMC (A), LBG (B) and CMC (C) solutions
543 at several concentrations of sucrose (suc: sucrose) and temperatures.

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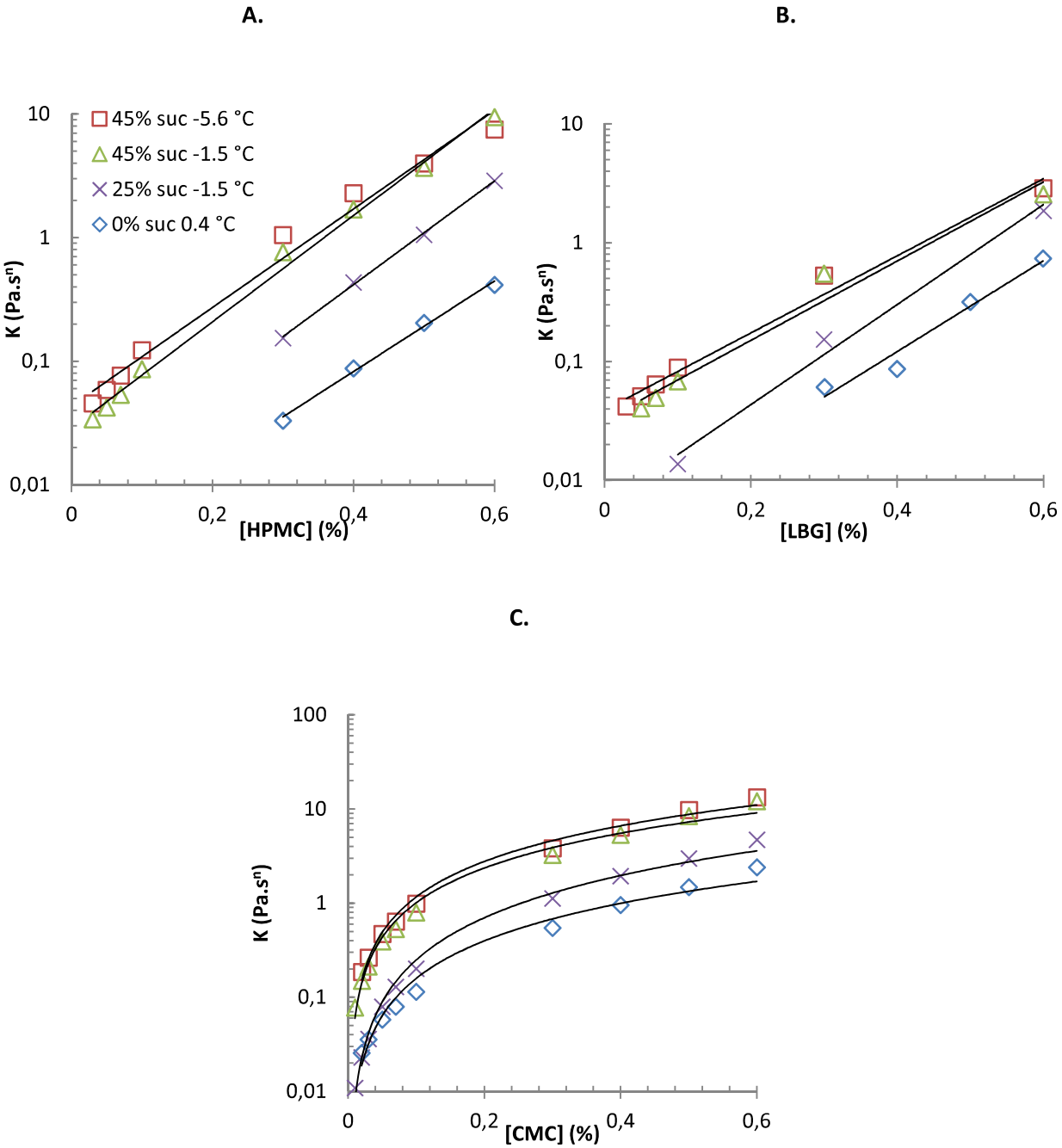

Fig. 2. Evolution of the consistency index versus concentration of HPMC (A), LBG (B) and CMC (C) solutions at several sucrose concentrations (suc: sucrose) and temperatures. The ordinate is shown in logarithmic scale.

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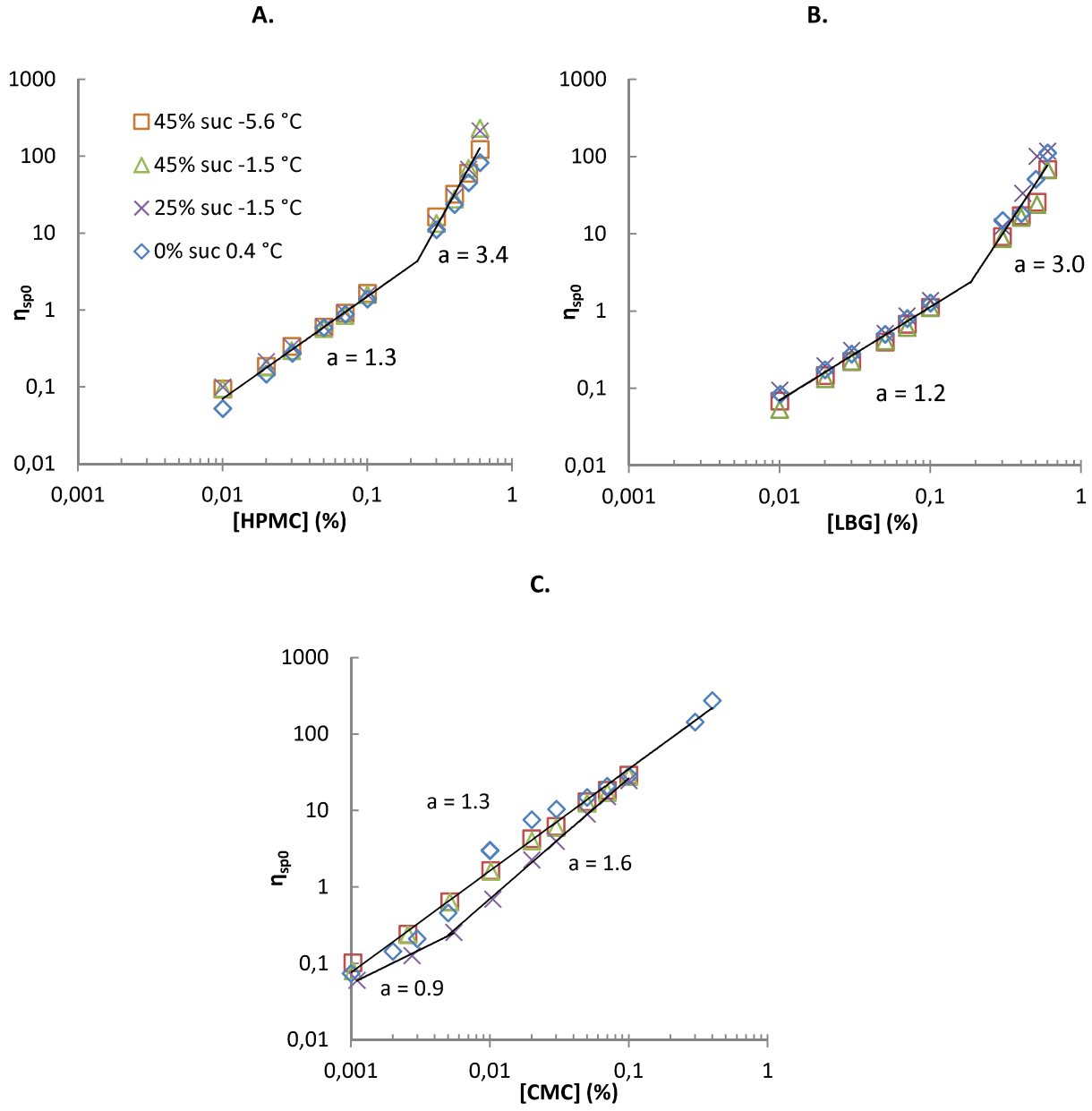

549 **Fig. 3.** Specific viscosity versus concentration of stabilizers at several sugar concentrations and
550 temperatures for HPMC (A), LBG (B) and CMC (C). The axes are shown in logarithmic scale. Lines
551 represent the best power law fits, the power law exponents *a* are provided below the corresponding
552 curve.

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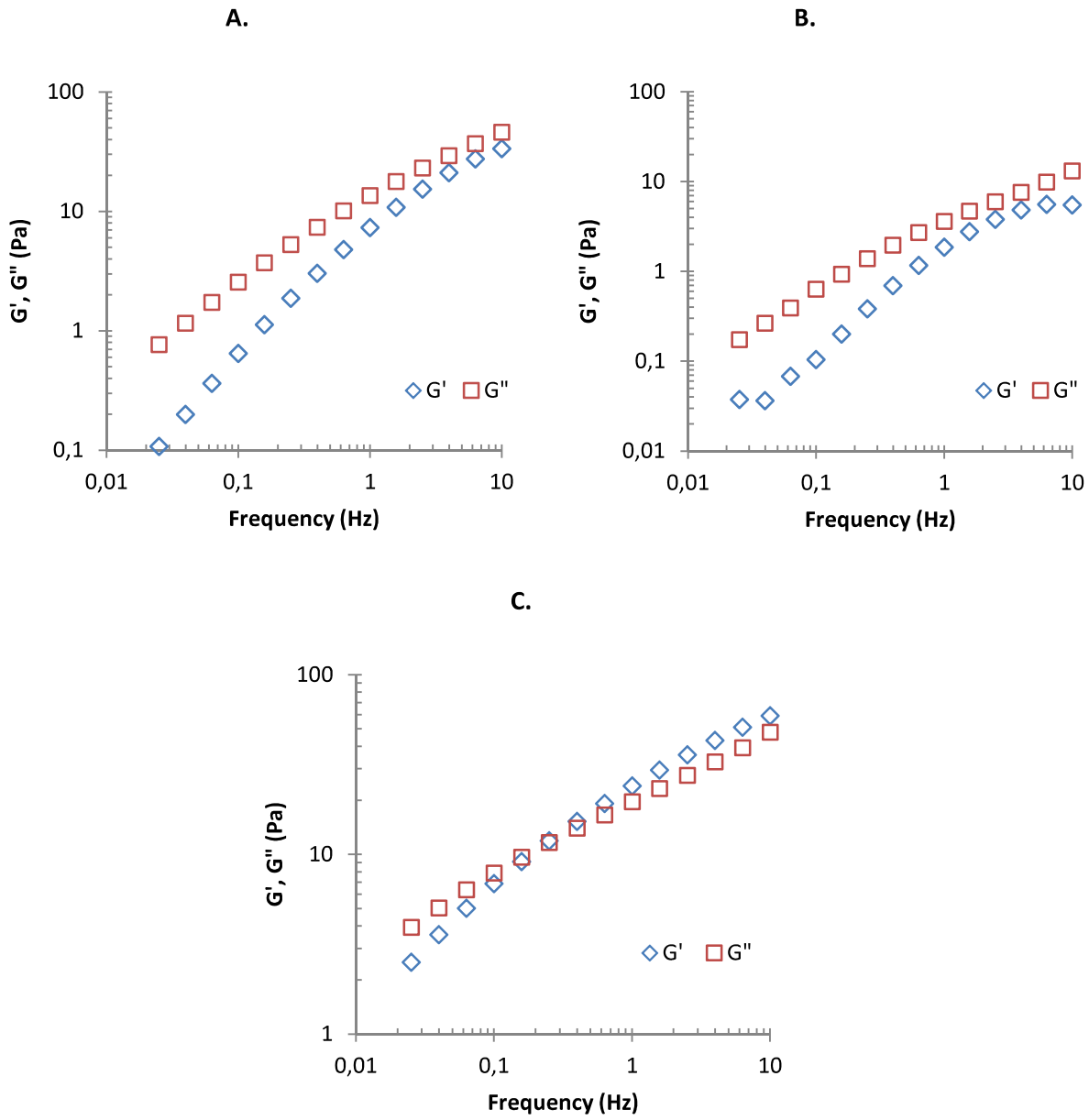

Fig. 4. Storage (G') and loss (G") moduli as a function of frequency (0.03 – 10 Hz) at -5.6 °C for 0.6%wt stabilizer in 45%wt sucrose solution (A), HPMC (B) LBG (C) CMC.

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555