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# 1 Rheological properties of stabilizers at low temperatures in concentrated sucrose 2 solutions

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## 12 **Abstract**

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

32 mechanisms.

## 33 **Keywords**

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

## 36 **1. Introduction**

37 Sorbet is a frozen fruit juice with high sugar content stabilized by gum stabilizers (Marshall, Goff,  
38 & Hartel, 2003); this consists of air bubbles and ice crystals dispersed in an unfrozen matrix containing  
39 high concentrations of sugars and stabilizers. Before freezing, the mixture of ingredients or “mix”  
40 contains an average of 70%wt of water, almost 25%wt of sugar (sugars contained in fruit juices and  
41 added sugars) and up to 0.5%wt of stabilizers (Arbuckle, 1986; Clarke, 2004; Marshall, & Arbuckle,  
42 1996; Stogo, 1998). The freezing step is the core of the manufacturing process of sorbets; it takes  
43 place in a scraped surface heat exchanger (SSHE) or freezer. The mix enters the freezer at  
44 approximately 4 °C and is converted into sorbet by simultaneous aerating, freezing and mixing to  
45 generate ice crystals and air bubbles. As the freezing proceeds, the unfrozen matrix becomes more  
46 and more concentrated in sugars and stabilizers and then increasingly viscous (Clarke, 2004). At the  
47 outlet of the exchanger, the sorbet contains an average of 40%wt of ice while the concentration of  
48 sugars and stabilizers in the unfrozen matrix is almost double that in the original mix. Its final  
49 temperature is between -5 °C and -6 °C (Marshall et al., 2003).

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

61 bind water and increase the viscosity of the mix, or even gel on the vicinity of the crystal; but the  
62 physicochemical parameters involved are not formally identified. Effects of stabilizers during  
63 conservation and storage, especially on recrystallization process have also been studied by several  
64 authors; as with the initial formation of ice crystals, the results are controversial (Buyong, & Fennema,  
65 1988; Flores, & Goff, 1999; Gaukel, Leiter, & Spieß, 2014; Kamińska-Dwórznička et al., 2015;  
66 Regand, & Goff, 2003).

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

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



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

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

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

## 112 **2. Material and methods**

### 113 **2.1. Polymers and preparation of the mixes**

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

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

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

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

## 137 **2.2. Rheological analysis at low temperature**

### 138 *2.2.1. Choice of temperatures for the analyses*

139 The aim of this study was to analyze the rheological properties of the unfrozen part of a sorbet. As  
140 a consequence, it was necessary to avoid the freezing of the samples during the experiments while  
141 maintaining a temperature close to the freezing point. The two formulations differed from one another  
142 in their sucrose concentrations and consequently in their respective freezing temperatures. The  
143 temperature selected for analysis was around 0.4 °C above the freezing points of the different mixes.  
144 These freezing points were calculated by using the sucrose liquidus curve (Arellano salazar, 2012;  
145 Cerecero Enriquez, 2003). Table 1 shows the analytical conditions of the different mixes. A test was  
146 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<sup>-1</sup> to 0.1 s<sup>-1</sup> and then up from 0.1 s<sup>-1</sup> to 1000 s<sup>-1</sup> 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  $\eta_{app}$  was  
160 described by the Ostwald-de Waele model (equation 1) and the consistency index  $K$  and the flow  
161 index  $n$  were calculated.

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

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.

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

170 where  $\Omega$  is the rotor angular velocity (rad.s<sup>-1</sup>),  $R$  is the tank radius (m) and  $r$  is the central rotor radius  
171 or the radius at 1mm of the wall (m),  $n$  the flow index determined for each condition. Apparent  
172 viscosities of solutions for these particular shear rates were then calculated thanks to power law  
173 equation (equation 1).

### 174 **2.2.3. Intrinsic properties of the macromolecules**

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

$$182 \quad \frac{\eta_{sp0}}{c} = [\eta] + \lambda [\eta]^2 c \quad (3)$$

183 As CMC is an anionic polymer, its intrinsic viscosity was determined with the equation established  
184 by Fedors (1979) (equation 4) which is more appropriate in this case, by plotting  $[2(\eta_{rel}^{1/2} -$   
185  $1)]^{-1}$  against  $1/c$ .

$$186 \quad [2(\eta_{rel}^{1/2} - 1)]^{-1} = ([\eta]c)^{-1} - ([\eta]c_m)^{-1} \quad (4)$$

187 where  $\eta_{rel}$  is the relative viscosity and  $c_m$  is a polymer concentration parameter. Arinaitwe, & Pawlik  
188 (2014) showed that this equation described well the behavior of anionic polyacrylamide and fitted well  
189 to experimental data from CMC samples. This equation was also applied to HPMC and LBG to  
190 compare the results with those obtained with the Huggins model.

### 191 **2.2.4. Viscoelastic properties**

192 The viscoelastic properties of the unfrozen solution at the exit of a freezer (0.6% of stabilizer in  
193 45% sucrose solution) have been studied using oscillatory mode. Frequency sweeps from 100 to 0.1  
194 Hz and 0.1% strain corresponding to the linear viscoelastic range (LVE) were performed at -5.6 °C.  
195 Storage modulus  $G'$  and loss modulus  $G''$  were measured.

## 196        **2.3.        Statistics**

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

## 200        **3. Results and discussion**

### 201        **3.1.        Flow behavior at low temperature as a function of sucrose** 202        **concentration**

#### 203        *3.1.1. Flow index and consistency index*

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

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

217        Sucrose concentration had a noticeable effect on shear thinning behavior in the case of HPMC  
218        solutions: higher was the sucrose concentration and lower was the flow index. A possible hypothesis is  
219        that, because of its hygroscopicity, sucrose mobilized water; then sucrose would promote hydrophobic  
220        interactions between HPMC chains due to their substitutions. These interactions would be disrupted  
221        during shearing. In the case of LBG as for CMC, the effect of sucrose on their shear thinning  
222        properties seemed to be less important; interactions between macromolecules would be prevented by  
223        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.

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

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

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

### 272 ***3.1.2. Apparent viscosity as a function of the process conditions***

273 The shear rates to which the mixes are subjected during the freezing process were calculated  
274 according to equation 3 and using the flow properties defined for each stabilizer in the section 3.1.1.  
275 The smallest shear rate of about 100 s<sup>-1</sup> was encountered on the central axis of the rotor of the  
276 exchanger at the beginning of the process when the mix contains 25% of sugar and 0.3%wt of  
277 stabilizer at -1.5 °C. Conversely, the highest shear rate about 1000 s<sup>-1</sup> was calculated at 1 mm of the  
278 inner wall close to the blades, with the mix characteristics encountered at the end of the process i.e.  
279 45% of sucrose and 0.6%wt of stabilizer at -5.6 °C. The apparent viscosities of mixes were then  
280 calculated using the Ostwald-de Waele equation (equation 1) at the corresponding shear rates at the  
281 beginning or at the end of the process, in the center or at the wall of the exchanger and for the  
282 corresponding concentrations of stabilizers. Results are listed in Table 2.

283 The apparent viscosity systematically increased between the beginning and the end of the  
 284 freezing process. These results, in agreement with another study (Arellano, Flick, Benkhelifa, &  
 285 Alvarez, 2013) were expected as the concentration in sugars and polymers increases during freezing  
 286 (freeze-concentration of the liquid phase). Then,  $\eta_{app}$  was always lower at the wall of the exchanger  
 287 than at the center due to the higher shear rate and the shear thinning behavior of the mixes. At the  
 288 beginning of the freezing process, the apparent viscosity of CMC solution was higher than the one of  
 289 HPMC and LBG; indeed, the consistency index  $K$  was higher for this gum despite the higher  
 290 sensitivity to shearing (lower flow index  $n$ ). At the end of the process, when sucrose concentration was  
 291 high, the apparent viscosity of LBG solutions was twice lower than the one of HPMC and CMC; it was  
 292 found previously for this gum that the consistency index  $K$  increased less with sugar concentration. At  
 293 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 <sup>n</sup> )	$\eta_{app}$ (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

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

### 297 3.2. Intrinsic properties of stabilizers related to process conditions

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

301 For HPMC and LBG (Fig. 3 (A) and (B)) the curve presented a discontinuity in the concentration  
 302 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  $\eta_{sp0} \sim [polymer]^a$ . 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

333 stabilizer is higher than  $C^*/2$  then the solution will change from non-entangled to entangled polymer  
 334 solution during the process. The viscosity of the unfrozen solution will increase linearly since the  
 335 stabilizer concentration reached  $C^*$ , then it will increase exponentially above  $C^*$  (Lapasin, & Prici,  
 336 1999). Since the concentration  $C^*$  of CMC seems significantly smaller, the change of behavior will take  
 337 place earlier in the process in the case of a mix stabilized with this polymer.

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

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

Solvent & temperature	$[\eta]$ (cl/g)			$\lambda$	
	HPMC*	LBG*	CMC**	HPMC	LBG
45% sucrose -5.6 °C	69.9 ± 3.8a	50.6 ± 3.1c	801 ± 27e	<u>1.1</u>	<u>1.4</u>
45% sucrose -1.5 °C	67.7 ± 4.5a	48.3 ± 2.9c	623 ± 13f	<u>1.1</u>	<u>1.6</u>
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	<u>1.4</u>	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,  $p < 0.05$ )

343 For HPMC as for LBG, intrinsic viscosity decreased as the concentration in sucrose increased  
 344 from 25% to 45%, whereas the temperature had no effect. Intrinsic viscosity  $[\eta]$  of HPMC was  
 345 estimated at about 70 cl/g in 45%wt sucrose systems whereas in 25% sucrose solution at -1.5 °C, it  
 346 was found to be equal to 84 cl/g. Bustamante, Navarro-Lupi3n, & Escalera (2005) found a value of the  
 347 intrinsic viscosity of HPMC close of those obtained in this study (80.9 cl/g in water at ambient  
 348 temperature). Concerning LBG,  $[\eta]$  was about 78 cl/g with 25%wt of sucrose and 50 cl/g with 45%wt of  
 349 sucrose whatever the temperature. The presence of sugar decreases the amount of water available  
 350 for solvation of polymer; this could cause a fold of macromolecules as long as the freezing takes  
 351 place. Elfak et al. (1977) also observed a decrease in the intrinsic viscosity of LBG with an increase in  
 352 the sucrose concentration:  $[\eta]$  was 68 and 53 cl/g with respectively 20% or 40% of sucrose.  
 353 Richardson et al. (1998) also obtained a decrease of  $[\eta]$  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;  $\lambda$  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).

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

### 388 **3.3. Viscoelastic properties of the final unfrozen phase**

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

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

406 Although the ice crystallization phenomena in such polymers solutions has not been clearly  
407 related to the viscoelastic properties of polymer solutions, the bonds between the CMC molecules at  
408 the origin of the solid properties of the system may have a different effect on crystallization than the  
409 predominantly liquid systems obtained with HPMC or LBG. This could influence the diffusion  
410 properties of water or sucrose molecules or promote mechanical resistance to crystal growth (Blond,  
411 1988; Goff et al., 1999; Muhr, & Blanshard, 1986).

## 412 **4. Conclusions**

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

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

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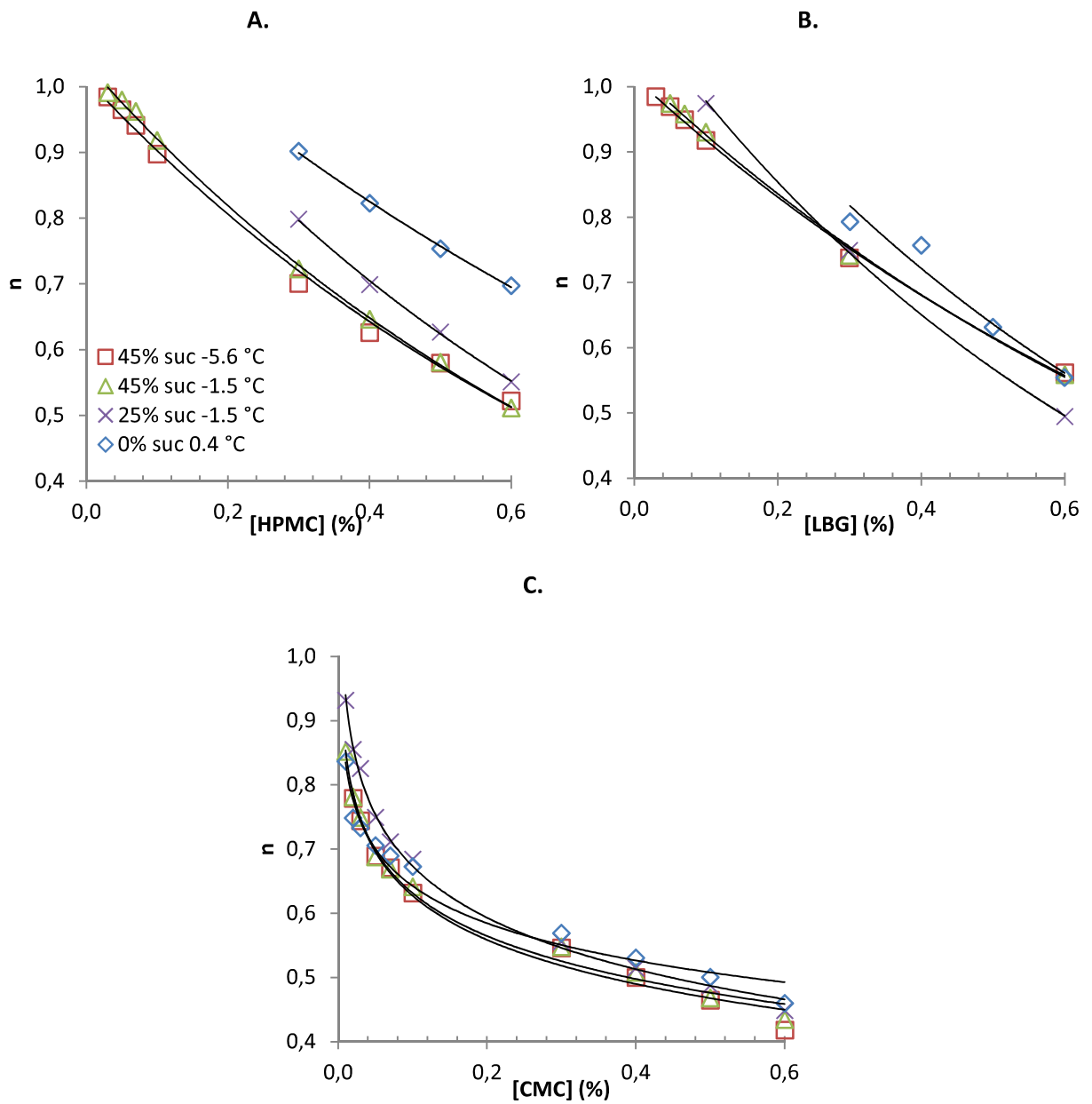
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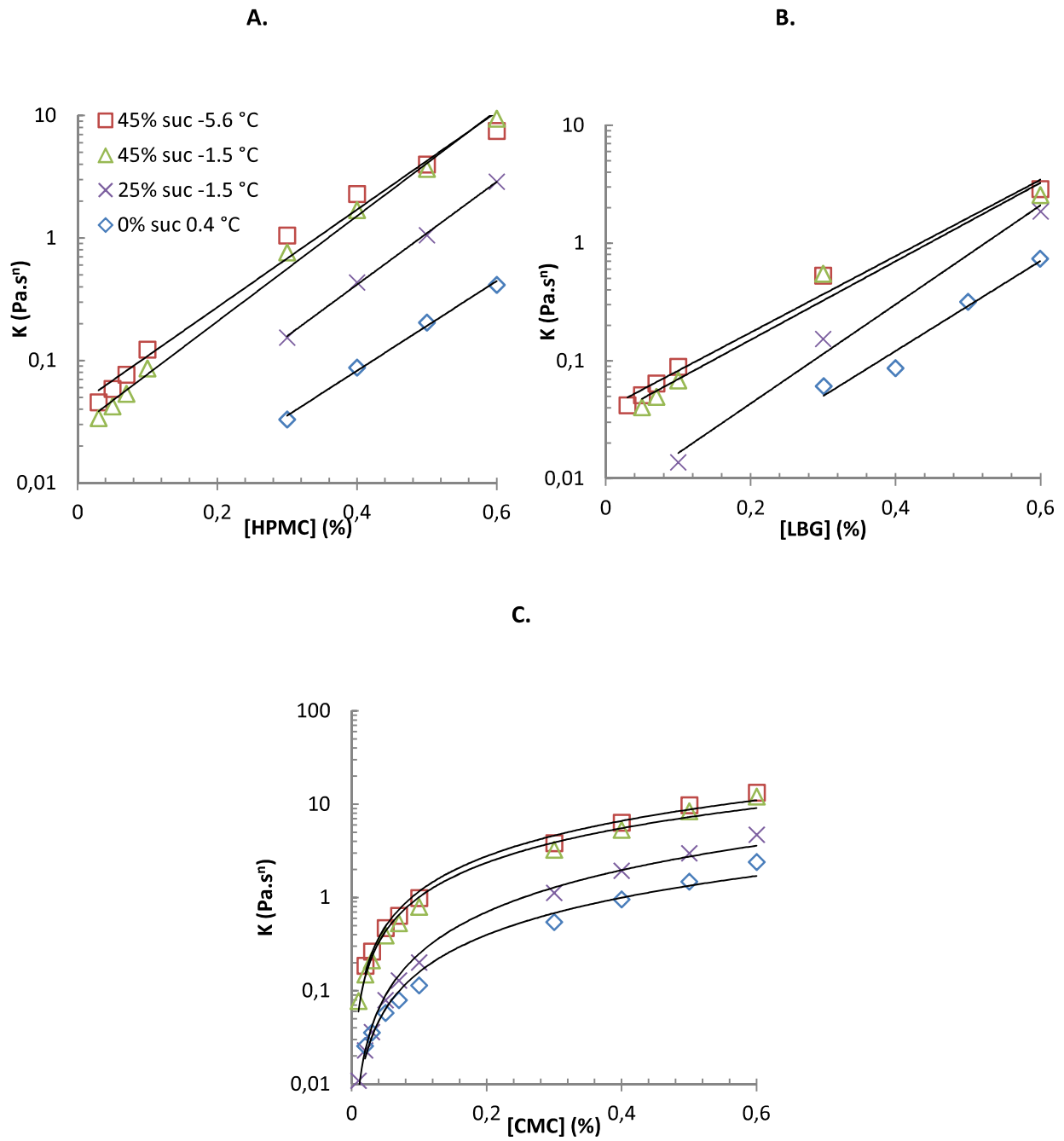


542 **Fig. 1.** Evolution of the flow index versus concentration of HPMC (A), LBG (B) and CMC (C) solutions  
 543 at several concentrations of sucrose (suc: sucrose) and temperatures.

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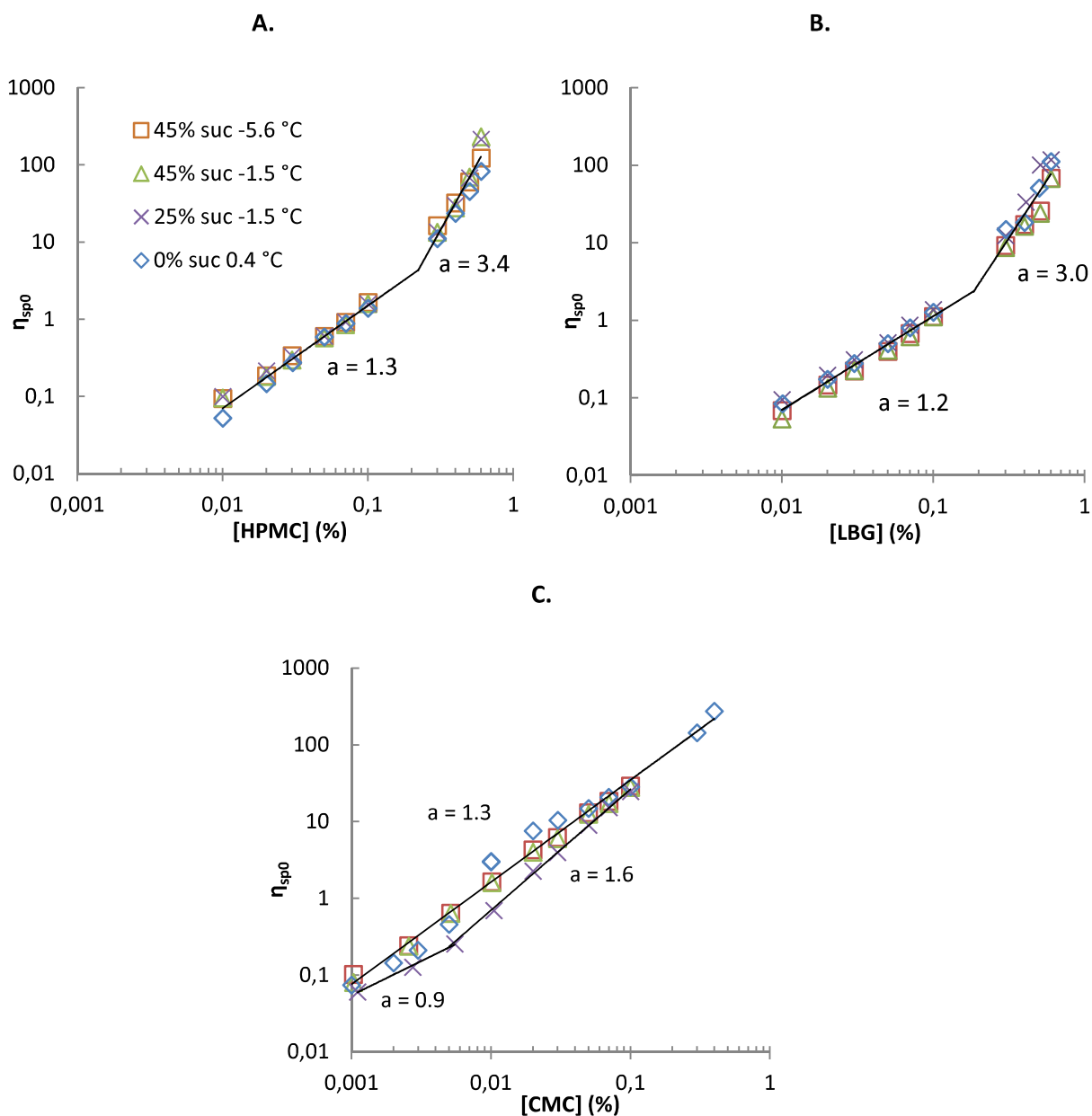




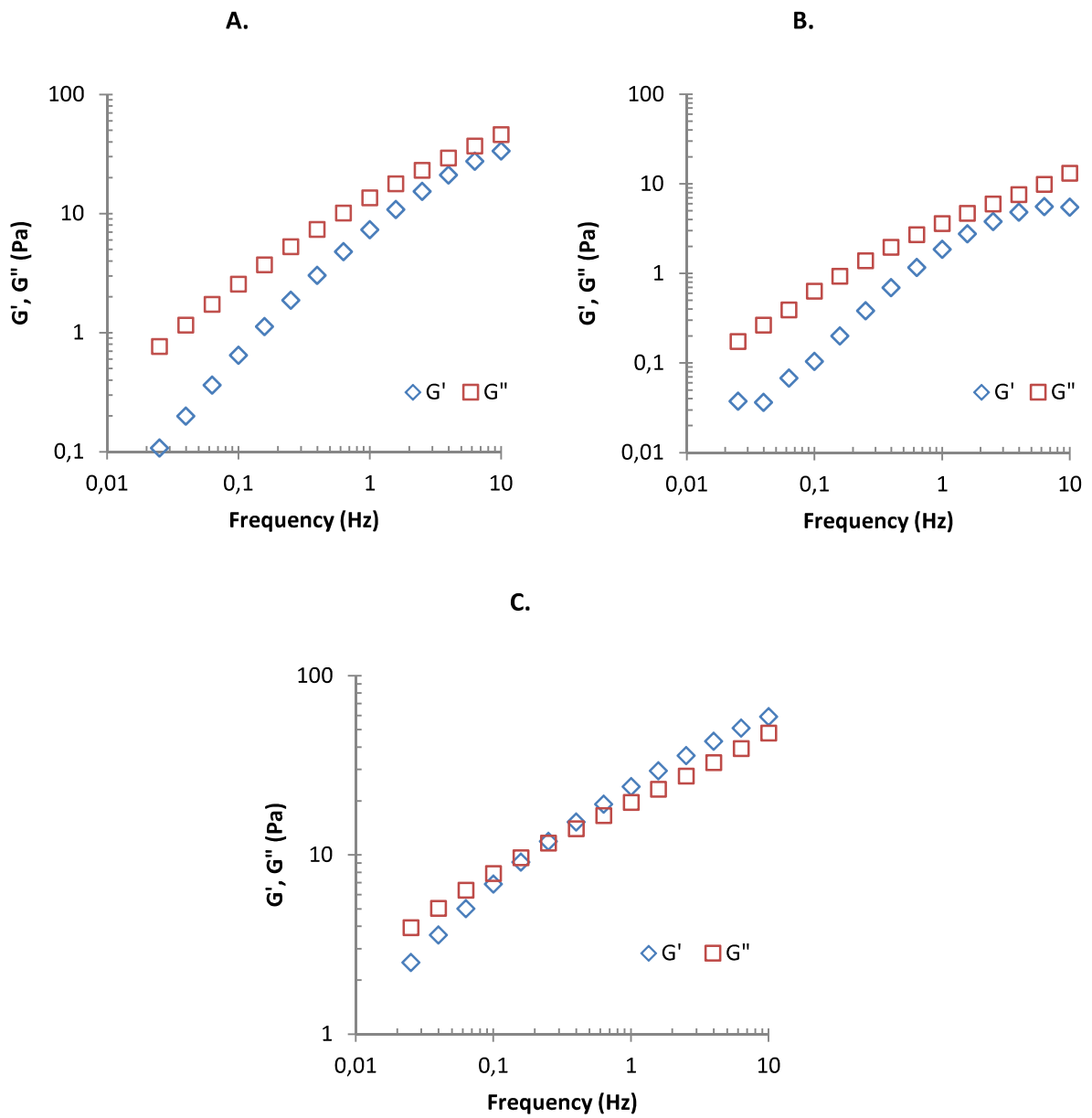
**Fig. 2.** Evolution of the consistency index versus concentration of HPMC (A), LBG (B) and CMC (C) solutions at several sucrose concentrations (suc: sucrose) and temperatures. The ordinate is shown in logarithmic scale.

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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.



**Fig. 4.** Storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of frequency (0.03 – 10 Hz) at  $-5.6\text{ }^{\circ}\text{C}$  for 0.6%wt stabilizer in 45%wt sucrose solution (A), HPMC (B) LBG (C) CMC.

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