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1 **Gellan gum fluid gels. Influence of the nature and concentration of gel-promoting**
2 **ions on rheological properties.**

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30 **Abstract**

31 Low-acyl gellan gum fluid gels were obtained using two different gel-promoting cations
32 under the same processing conditions and their rheological properties were investigated.
33 For that reason, stress and frequency sweeps measurements and flow curves tests were
34 carried out. Small amplitude oscillatory shear assays demonstrated that these materials
35 exhibit weak gel behaviour despite the shape of their mechanical spectra being similar to
36 those obtained from strong gels. However, the existence of a weak gel structure was
37 confirmed by the fact that the difference between the elastic and viscous components was
38 of only one order of magnitude. In addition, a reduction in the storage and lost modules
39 and the viscosity as a function of the applied shear was observed with increasing cation
40 concentration. Finally, in order to produce fluid gels, a higher concentration of the
41 monovalent cation was required than when divalent cations were employed in the low-
42 acyl gellan gum fluid gels formulation.

43

44 **Keywords**

45 Low-acyl gellan gum, fluid gel, Rheology, Viscoelasticity, Very shear thinning, Gel-
46 promoting cation.

47

48 **Introduction**

49 It is well known that fluid gels can be produced by polysaccharides capable of forming
50 strong gels. This is possible when a strong gel manufactured under quiescent conditions
51 is disturbed by submitting the sample to mechanical energy [1]. Consequently, the
52 resulting sample shows a heterogeneous microstructure consisting of an irregularly-
53 shaped cluster with gel-like behaviour suspended in an aqueous phase whose
54 polysaccharide concentration is smaller than that present in the microgels formed. Among
55 the biopolymers which can produce fluid gels are gellan gum [2, 3], agar, K-carrageenan,
56 whey protein [4] or alginate [5]. Norton et al. [6] proposed a model to explain the form
57 and stability of fluid gels. The latter model establishes a as a consequence of a gelation

58 stage takes place the particles or clusters form when the biopolymers aqueous solution is
59 cooled under mechanical treatment. The cluster sizes are dependent of the shear
60 conditions. Following, the molecular ordering is attained. The particle size and volume
61 fraction achieved are as a function of the applied shear during process and the polymer
62 concentration in the fluid gel formulation. In addition, the fluid gels stability is maintained
63 while it is not submitted at the melting temperature.

64 Although the sample presents rheological behaviour somewhere between that of a strong
65 gel and weak gel, it is closer to the latter. These rheological properties make possible the
66 current and future applications of fluid gels as suspension [3] and satiety [7] agents,
67 emulsion stabilizers [8]. Additionally, other applications can be mentioned in
68 pharmaceutical and biomedical fields such topical administration of diclofenac [9] or in
69 the paint formulation [10]. In the food industry, low-acyl gellan gum, as a fluid gel, is
70 widely used, since this biopolymer has been utilized as a food additive in the USA from
71 1992 and, in addition, its use is currently authorized in other countries. The code
72 established by The International Numbering System for food additives for gellan gum is
73 INS 418 [11].

74 Gellan gum is a biopolysaccharide obtained by microbial fermentation from
75 *Sphingomonas elodea* (ATCC 31461) [3] which can produce strong gels when gel-
76 promoting ions are added to the gellan gum solution under cooling conditions. The
77 disturbance of the formation of this strong gel gives rise to the development of a fluid gel,
78 as mentioned above. The nature and ionic strength of gel-promoting ions chosen to
79 prepare the fluid gels determine their final rheological properties. The main applications
80 of gellan gum as a fluid gel are as a suspending agent in some drinks, such as citrus drinks
81 or chocolate milk. On another hand, it is also utilized to suspend coloured particles in
82 translucent drinks [12].

83 The main objectives of this work are the study of the effect of the nature of the salt
84 employed to provide gel-promoting ions and the influence of the cation concentration on
85 the rheological properties of fluid gels containing 0.2 wt% gellan gum. For these
86 purposes, small amplitude oscillatory shear and steady-state measurements were carried
87 out.

88

89 **Materials and methods**

90

91 **Materials**

92 Low-acyl gellan gum (Kelcogel® FTM) cordially provided by CP-Kelco (San Diego,
93 USA) was employed as obtained and it has molecular weight of $2\text{-}3\cdot 10^5$ Da. This
94 substance will be designated as LA-gellan in the rest of this paper. Its concentration in
95 the fluid gels formulation was 0.2 wt %. To acquire Na⁺ or Ca²⁺ gel-promoting ions,
96 99.5% purity NaCl [3] supplied from Panreac (Barcelona, Spain) and 98% purity CaCl₂
97 provided by Merck were used. CaCl₂ concentrations assessed were $9.0\cdot 10^{-3}$ M, $1.1\cdot 10^{-2}$
98 M, $1.3\cdot 10^{-2}$ M, $1.6\cdot 10^{-2}$ M and $1.8\cdot 10^{-2}$ M, and NaCl concentrations studied were 0.22 M,
99 0.24 M and 0.27M. Deionised water was always utilized and 0.1 wt % sodium azide was
100 used to preserve the fluid gels.

101

102 **Fluid gel preparation**

103 LA-gellan fluid gels were prepared in batches of 600 g following the steps suggested by
104 Sworn (2009), as was done in a previous work [13]. In order to disperse the LA-gellan
105 gum powder, it was added slowly to a vessel placed within a water-bath at 80° C. The
106 hydration step was carried out at 80° C while stirring at 700rpm for 25 min was maintained
107 using an Ika-Visc MR-D1 homogenizer (Ika, Germany) equipped with a sawtooth-type
108 impeller. The impeller diameter/container diameter ratio was 0.85. Once the 25 minutes
109 had elapsed, the required amount of CaCl₂ or NaCl was added and the solution was
110 maintained under mechanical treatment at 80° C for 5min. Water loss by evaporation was
111 corrected by adding the appropriate quantity of deionised water. Afterwards, the sample
112 vessel was placed in a thermostatic bath at 20°C and the gelation step was carried out by
113 submitting the solution to mechanical treatment under 700 rpm with the aforementioned

114 Ika-Visc homogenizer for 1500s [13, 14, 15]. The cooling rate was 2.4°C/min. Finally,
 115 the fluid gels were stored at 4.5 °C for at least 48 h before performing the rheological
 116 study.

117

118 **Rheological Characterization**

119 In order to perform stress sweep and frequency sweep measurements, a controlled-stress
 120 rheometer AR2000 (TA Instruments, Crawley, United Kingdom) was employed. These
 121 tests were carried out at 20 °C. A parallel plate with serrated surfaces, 40mm diameter
 122 and a measuring gap of 1mm was used as a sensor system. It should be noted that in order
 123 to avoid wall depletion phenomena, sensor systems with rough surfaces were required,
 124 since in previous works it was demonstrated that the gellan gum fluid gel structure
 125 consists of microgels in aqueous phase, this being a heterogeneous microstructure [1]. To
 126 prevent losses as a consequence of evaporation during measurements, a thin film of Dow-
 127 Corning 200® (Dow Chemical Co.) silicon oil fluid (kinematic viscosity, 20 cSt) was
 128 applied to enclose the plate rim. The estimation of the dynamic linear viscoelastic range
 129 (DLVR) was performed by stress sweeps under oscillatory shear measurements at three
 130 different frequencies (0.1, 1, 3 Hz), from 0.008 to 3 Pa. The frequency sweep tests were
 131 conducted in the 3-0.01 Hz frequency range as this is within the linear range of response.
 132 Flow behaviour was studied using a Haake RS100 controlled stress rheometer (Thermo
 133 Scientific, Karlsruhe, Germany), with a parallel plate sensor system with serrated surfaces
 134 (60mm diameter and a measuring gap of 1mm). The shear rate variation with the plate
 135 radius in the flow curves data was corrected by using the following equations [16]:

136

$$137 \quad \eta_{corr}(\dot{\gamma}_R) = \eta_N [1 + (m/4)]$$

138 (1)

$$139 \quad \tau_{corr}(\dot{\gamma}_R) = \eta_N [1 + (m/4)] \cdot \dot{\gamma}_R$$

140 (2)

141 where, $\eta_{newt} = (2 \cdot H / (\pi \cdot R^4)) \cdot (M / \Omega)$; $m = d(\log \eta_{newt}) / d(\log \dot{\gamma}_R) = n_{PL} - 1$; $\dot{\gamma}_R$ is the rim
 142 shear rate; τ_{corr} is the corrected shear stress; H is the gap between plates; Ω is the angular
 143 velocity; R is the plate radius, M is the torque applied, η_{newt} is the viscosity calculated at
 144 the rim of the parallel plate geometry and n_{PL} is the power law flow index.

145 The measurements were carried out in the 0.5-33Pa shear stress range by a step-wise
146 procedure.

147 The samples were maintained in a rest state in the measuring gap for 600 s of equilibration
148 time, before conducting the rheological test, in order to avoid any effects of recent
149 mechanical history after the loading procedure.

150 Each type of measurement was carried out at least 4 times and in all of them, fresh sample
151 was used.

152 In order to determine the existence of the significant differences between the results in
153 this work, the standard deviations of all assessed parameters are shown in each table. For
154 this purpose, the ANOVA ONE WAY method using Statgraphic Plus software was used.

155

156 **Results and discussion**

157

158 *Dynamic linear viscoelastic range (DLVR)*

159 Fig. 1 shows the influence of the Ca^{2+} concentration on the stress sweep results obtained
160 to determine the DLVR at the three studied frequencies chosen in order to avoid
161 destruction of the sample structure [12]. This Figure exhibits constant values of G' and
162 G'' up to a certain shear stress, the critical stress, which is related to the inception of the
163 non-linear zone characterized by the dependence of the shear stress applied on the
164 viscoelastic moduli. The microstructural reorganization before breakdown entails energy
165 dissipation which brings about an increase in G'' values up to a peak value at the
166 beginning of the non-linear response [16, 17]. It is interesting to mention that, from that
167 moment, the G' value began to decrease. As can be observed in Fig.1, the Ca^{2+}
168 concentration had no influence on the extension of the linear viscoelastic range. The
169 critical stress values shown in Table 1 demonstrate that there is a slight decrease in their
170 values as the frequency increases. However, this tendency is not clear in the critical strain
171 values. Additionally, data show a decrease in the viscoelastic modules with an increase
172 in the Ca^{2+} concentration.

173

Figure 1

174

Table 1

175 Similar behaviour is observed when the stress sweep measurements were carried out over
176 the gellan gum fluid gels containing Na^+ as a gel-promoting cation (Fig.2), that is, there
177 was a decrease in the G' and G'' values with an increase in the cation concentration.

178 However, there was a slight reduction in the DLVR with increasing- Na^+ concentration.
179 This is also supported by Table 2.

180 Figure 2

181 Table 2

182

183 *Mechanical spectra*

184 The frequency sweep results are displayed in Fig.3. The data show the storage module
185 (G') is larger than the loss module (G'') over the whole frequency range studied. In
186 addition, the mechanical spectra of gellan gum fluid gels containing both gel-promoting
187 cations exhibited the typical behaviour shown by strong gels which present a) a slow
188 frequency dependence on G' characteristic slopes and b) a minimum of G'' in the mid-
189 section of the frequency range. However, they cannot be considered strong gels since
190 there is only a difference of one order of magnitude between the storage module values
191 and the loss module values. Additionally, as can be observed, both an increase in Ca^{2+}
192 concentration (Fig.3a) and Na^+ concentration (Fig.3b) provoked a fall in the viscoelastic
193 moduli. However, this trend started to be significant when the value of Ca^{2+} reached
194 $1.8 \cdot 10^{-2}$ M, while significant differences in the case of Na^+ were found for the sample
195 containing 0.27 M NaCl.

196 Figure 3a

197 Figure 3b

198 This effect of the concentration of the gel-promoting ions on the mechanical spectra is
199 due to the fact that the gellan gum is an anionic biopolymer and an increase in the cation
200 concentration causes a rise in the charge screen effect resulting in a decrease in the
201 repulsive interactions between the gellan gum macromolecules. Previous works have
202 reported that the existence of cations in solutions of polyelectrolyte provokes the
203 screening of the charge along the chains of polysaccharide involving a little and closely
204 packed structure resulting in a decrease in their rheological parameters [18, 19]. In
205 addition, the presence of inorganic salts with a degree of hydration causes the thickness
206 formation around the polysaccharide molecules provoking a reduction in these parameters
207 [20].

208 Fig.3a shows the occurrence of a minimum peak in the G'' curves of the order of
209 magnitude of 0.6 rad/s which makes it possible to estimate the plateau module value, G_N^0 ,
210 [21, 22]. The plateau module gives an idea of the level of the interactions among the
211 gelled particles forming the fluid gel. Fig.3c illustrates the plateau module, G_N^0 , as a

212 function of the CaCl_2 concentration. The decrease in the G_N^0 in $1.8 \cdot 10^{-2}$ M CaCl_2 indicates
213 that the concentration needed to form the gels is exceeded. This fact can be associated
214 with the charge screen effect between the gellan macromolecules since it is an anionic
215 polyelectrolyte.

216 Figure 3c

217 Additionally, it can be observed that the mechanical spectra shape did not change in the
218 CaCl_2 concentration range studied, indicating the existence of the same microstructure.
219 This fact is supported by the representation of exponent (n') of the power equation which
220 relates G' to the angular frequency ($G' \sim \omega^{n'}$) (Fig.3d). The value of n' was practically
221 constant at about 0.02 which is very close to zero. This result is typical of strong gels.
222 However, according to the criteria proposed by Ross-Murphy [23], the gellan gum fluid
223 gels cannot be classified as strong gels since the strong gels undergo shear-induced
224 fracture under flow, their linear viscoelastic region is broad and the differences between
225 G' and G'' are great enough to support the occurrence of a self-supporting gel. Here, the
226 difference between G' and G'' was of only one order of magnitude, which is more
227 characteristic of weak gels and justifies the fluid gel consistency.

228

229 Figure 3d

230 Moreover, it must be noted that smaller Ca^{2+} concentrations lead to similar, or even
231 higher, G' and G'' values in the mechanical spectra than those shown by the samples
232 involving higher Na^+ concentrations in their formulation (Fig.3). This fact has been
233 attributed to the ionic strength and the nature of the salt employed [24]. The single
234 divalent ion is capable of substituting each monovalent ion-water-monovalent ion
235 interaction between two carboxylates [25].

236

237 *Steady state test*

238 The influence of the concentration of gel-promoting ions can be observed in Fig.4 (Ca^{2+}
239 cations in Fig.4a and Na^+ cations in Fig.4b) where the viscosity is plotted against the shear
240 stress.

241 It must be mentioned that the most noticeable aspect of the flow curves, for both Ca^{2+} and
242 Na^+ , is their “very shear thinning” [26] behaviour for all concentrations studied. This
243 behaviour is characterized by showing high plateau viscosity values at low shear stresses
244 and zero shear viscosity. However, as reported in several works [14,15] the high time
245 necessary to achieve the real steady state at low shear stresses or rates makes it necessary

246 to appeal to creep compliance measurements. Therefore, in most cases, the apparent
 247 Newtonian viscosity observed in the flow curves, which must be obtained by means of
 248 creep compliance tests [27]. The viscosities shown at the smallest shear stresses represent
 249 the tendency to reach an apparent Newtonian viscosity as a result of the experimental
 250 design, which was flow curve with a protocol with 5 minutes per point. Nevertheless, this
 251 apparent Newtonian viscosity obtained from flow curves do not correspond with the
 252 steady state response at low shear stresses since at least 60 minutes per shear stress test
 253 are required to reach it [28]. In addition, it is possible to observe in Fig.4 the existence of
 254 a critical shear stress or “yield stress” from which a little increase in the shear stress value
 255 provokes a decrease in viscosity of 5 orders of magnitude for Ca^{2+} , and 6 orders of
 256 magnitude in the case of Na^+ .

257 Figure 4

258 Table 3a

259 Table 3a exhibits the practical yield stress as a function of the concentration of gel-
 260 promoting ions. These results indicate a general tendency of decreasing practical yield
 261 stress as cation concentrations increase.

262 In Fig.5 the influence of the corrected shear stress was plotted as a function of shear rate.
 263 In addition, the fit of the results to a Herschel-Bulkley equation (3) has been included:

$$264 \tau - \tau_0 = k \cdot \dot{\gamma}^n \quad (3)$$

265 Moreover, this equation becomes the following (4) when $\dot{\gamma} = 1 \text{ s}^{-1}$ and $K = \tau_1 - \tau_0$:

$$266 \tau = \tau_0 + (\tau_1 - \tau_0) \cdot \dot{\gamma}^n \quad (4)$$

267 Where K is the consistency index ($\text{Pa} \cdot \text{s}^{-n}$) and its units are dependent of the flow index,
 268 n , τ is the shear stress and τ_0 is the yield stress predicted by the Herschel-Bulkley equation
 269 (Pa). The parameters obtained from this equation are shown in Table 3.

270 Figure 5

271 Table 3

272 Both Fig.5 and Table 3 support the fact that the data were fairly well fitted to the Herschel-
 273 Bulkley equation. The yield stresses obtained from Herschel-Bulkley were smaller than
 274 those estimated from the graph. The yield stress values of the Herschel-Bulkley equation

278 exhibited a slight tendency to decrease as the concentration of gel-promoting ions
279 increased for both cations studied. This result is coherent with those observed in
280 frequency sweep measurements due to the increase in the charge screen effect when the
281 cation concentration increases, as mentioned above [18,19]. Additionally, the index flow
282 values shown in Table 3b were typical of materials presenting shear thinning behaviour.
283 Moreover, a slight tendency to increase with Ca^{2+} concentration was observed. However,
284 this effect was not so evident in the case of Na^+ .

285

286 **Conclusions**

287 In this work, the influence of the nature of the gel-promoting cations and their
288 concentration on the gellan gum fluid gel rheological behaviour was assessed. The extent
289 of the dynamic linear viscoelastic range was not affected by the Ca^{2+} concentration.
290 However, increasing Na^+ concentration provoked a slight fall in the DLVR extension. On
291 the other hand, critical shear stresses were smaller as the frequency increased. Mechanical
292 spectra of fluid gels containing both cations, Ca^{2+} or Na^+ , exhibited a typical strong gel
293 shape. Nevertheless, the difference between the storage module and the loss module was
294 more characteristic of weak gels. The data correspond to a rubber-like region of
295 relaxation. In the case of Ca^{2+} , the plateau modulus showed a slight decrease with
296 increasing concentration, but the decrease was significant at 0.2 wt % Ca^{2+} .

297 Steady state tests made it possible to determine that gellan gum fluid gel showed a “very
298 shear thinning” behaviour for all formulations studied. This fact made it possible to
299 estimate the practical stress values. In addition, the flow curves were well fitted to the
300 Herschel-Bulkley equation. However, the yield stress values obtained from the latter
301 equation were higher than those estimated from the graph.

302 This study confirms that the rheological properties of gellan gum fluid gels, such as the
303 predominance of the storage module over the loss module, extremely great apparent
304 viscosity at low shear and the existence of a yield stress, make it an excellent stabilizer of
305 dispersions.

306

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311

312 **Conflict of interest**

313 There no was conflicts of interest to declare

314

315 **References**

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395

396 **Table captions**

397 **Table 1.** Determination of dynamic linear viscoelastic region at studied frequencies (0.1,
398 1 and 3 Hz) for fluid gels containing 0.2 wt% LA-gellan gum and CaCl₂ as gel-promoting
399 ions. Temperature: 20°C

400 **Table 2.** Determination of dynamic linear viscoelastic region at studied frequencies (0.1,
401 1 and 3 Hz) for fluid gels containing 0.2 wt% LA-gellan gum and NaCl as gel-promoting
402 ions. Temperature: 20°C

403 **Table 3a.** Determination of practical yield stress for fluid gels containing 0.2wt % and
404 NaCl or CaCl₂ as gel-promoting ions. T=20°C

405 **Table 3b.** Fitting parameters of the Herschel-Bulkley equation for fluid gels containing
406 0.2 wt% LA-gellan gum and CaCl₂ or NaCl as gel-promoting ions, prepared by different
407 mechanical protocols. Temperature: 20°C. E stands for standard error of fitting
408 parameters

409

410 **Tables**

411

412 Table 1. Determination of dynamic linear viscoelastic region at studied frequencies (0.1,
413 1 and 3 Hz) for fluid gels containing 0.2 wt% LA-gellan gum and CaCl₂ as gel-promoting
414 ions. Temperature: 20°C

415

| [CaCl ₂] M | τ_c (Pa) | | | | | | γ_c | | | | | |
|----------------------------|---------------|---------------|------|-------------|------|-------------|------------|---------------|-------|-------------|-------|-------------|
| | 0.1Hz | SD (0.1Hz) | 1Hz | SD (1Hz) | 3Hz | SD (3Hz) | 0.1Hz | SD (0.1Hz) | 1Hz | SD (1Hz) | 3Hz | SD (3Hz) |
| 9.0·10⁻³ | 0.30 | 0.04 | 0.10 | 0.06 | 0.10 | 0.13 | 0.006 | 0.002 | 0.001 | 0.000 | 0.004 | 0.002 |
| 1.1·10⁻² | 0.30 | 0.11 | 0.10 | 0.10 | 0.04 | 0.04 | 0.005 | 0.003 | 0.002 | 0.001 | 0.002 | 0.001 |
| 1.3·10⁻² | 0.20 | 0.05 | 0.20 | 0.00 | 0.06 | 0.03 | 0.004 | 0.001 | 0.005 | 0.001 | 0.003 | 0.001 |
| 1.6·10⁻² | 0.30 | 0.12 | 0.10 | 0.03 | 0.06 | 0.02 | 0.006 | 0.003 | 0.004 | 0.001 | 0.004 | 0.000 |
| 1.8·10⁻² | 0.20 | 0.02 | 0.10 | 0.00 | 0.05 | 0.02 | 0.004 | 0.000 | 0.003 | 0.001 | 0.009 | 0.001 |

416

417 Table 2. Determination of dynamic linear viscoelastic region at studied frequencies (0.1,
418 1 and 3 Hz) for fluid gels containing 0.2 wt% LA-gellan gum and NaCl as gel-promoting
419 ions. Temperature: 20°C.

420

| [NaCl] M | τ_c (Pa) | | | | | | γ | | | | | |
|-------------|---------------|---------------|---------|-------------|---------|-------------|-----------|---------------|-------|-------------|-------|-------------|
| | 0.1 Hz | SD (0.1Hz) | 1 Hz | SD (1Hz) | 3 Hz | SD (3Hz) | 0,1 Hz | SD (0.1Hz) | 1 Hz | SD (1Hz) | 3 Hz | SD (3Hz) |
| 0.22 | 1.60 | 0.50 | 0.80 | 0.34 | 0.80 | 0.37 | 0.061 | 0.001 | 0.039 | 0.002 | 0.035 | 0.000 |
| 0.24 | 1.60 | 0.45 | 0.64 | 0.12 | 0.20 | 0.01 | 0.075 | 0.003 | 0.022 | 0.001 | 0.038 | 0.001 |
| 0.27 | 0.64 | 0.03 | 0.40 | 0.09 | 0.16 | 0.03 | 0.029 | 0.001 | 0.021 | 0.000 | 0.017 | 0.002 |

421

422 Table 3a. Determination of practical yield stress for fluid gels containing 0.2wt % and NaCl or
423 CaCl₂ as gel-promoting ions. T=20°C.

424

| CaCl ₂ (M) | Practical yield stress (Pa) | NaCl (M) | Practical yield stress (Pa) |
|----------------------------|--------------------------------|-------------|--------------------------------|
| 9.0·10⁻³ | 7.3 | 0.22 | 6.4 |
| 1.1·10⁻² | 4.3 | 0.24 | 6.4 |
| 1.3·10⁻² | 4.5 | 0.27 | 4.8 |

| | |
|---------------------|-----|
| $1.6 \cdot 10^{-2}$ | 2.7 |
| $1.8 \cdot 10^{-2}$ | 4.1 |

425

426 Table 3b. Fitting parameters of the Herschel-Bulkley equation for fluid gels containing
 427 0.2 wt% LA-gellan gum and CaCl₂ or NaCl as gel-promoting ions, prepared by different
 428 mechanical protocols. Temperature: 20°C. E stands for standard error of fitting
 429 parameters

430

| CaCl ₂ | τ_0 (Pa) | E_{τ_0} | $\tau_1 - \tau_0$ | $E_{\tau_1 - \tau_0}$ | n | En | R ² |
|---------------------|---------------|--------------|-------------------|-----------------------|------|-------|----------------|
| M | | | (Pa) | | | | |
| $9.0 \cdot 10^{-3}$ | 3.5 | 0.7 | 0.83 | 0.34 | 0.45 | 0.06 | 0,978 |
| $1.1 \cdot 10^{-2}$ | 2.5 | 0.6 | 0.20 | 0.08 | 0.63 | 0.05 | 0,986 |
| $1.3 \cdot 10^{-2}$ | 2.6 | 0.5 | 0.11 | 0.05 | 0.69 | 0.06 | 0,983 |
| $1.6 \cdot 10^{-2}$ | 2.1 | 0.4 | 0.05 | - | 0.81 | 0.06 | 0,988 |
| $1.8 \cdot 10^{-2}$ | 2.4 | 0.6 | 0.12 | 0.07 | 0.71 | 0.08 | 0,983 |
| NaCl | τ_0 (Pa) | E_{τ_0} | $\tau_1 - \tau_0$ | $E_{\tau_1 - \tau_0}$ | n | En | R ² |
| M | | | (Pa) | | | | |
| 0.22 | 2.36 | 0.51 | 0.06 | - | 0.75 | 0.010 | 0.979 |
| 0.24 | 3.68 | 0.08 | 0.04 | - | 0.82 | 0.001 | 0.999 |
| 0.27 | 1.90 | 0.31 | 0.10 | - | 0.71 | 0.004 | 0.990 |

431

432

433

Figure captions

434

435 **Fig.1a.** Stress sweep tests performed at 0.1Hz for fluid gels containing 0.2 wt% LA-gellan
 436 gum and CaCl₂ as gel-promoting ions. Temperature: 20°C

437

438 **Fig.1b.** Stress sweep tests performed at 1Hz for fluid gels containing 0.2 wt% LA-gellan
 439 gum and CaCl₂ as gel-promoting ions. Temperature: 20°C

440

441 **Fig.1c.** Stress sweep tests performed at 3 Hz for fluid gels containing 0.2 wt% LA-gellan
 442 gum and CaCl₂ as gel-promoting ions. Temperature: 20°C

443

444 **Fig.2a.** Stress sweep tests performed at 0.1Hz for fluid gels containing 0.2 wt% LA-gellan
445 gum and NaCl as gel-promoting ions. Temperature: 20°C

446

447 **Fig.2b.** Stress sweep tests performed at 1Hz for fluid gels containing 0.2 wt% LA-gellan
448 gum and NaCl as gel-promoting ions. Temperature: 20°C

449

450 **Fig.2c.** Stress sweep tests performed at 3Hz for fluid gels containing 0.2 wt% LA-gellan
451 gum and NaCl as gel-promoting ions. Temperature: 20°C

452

453 **Fig.3a.** Mechanical spectra obtained at fixed shear stress of 0.02 Pa for fluid gels
454 containing 0.2 wt% LA-gellan gum and CaCl₂ as gel-promoting ions. The error bars at
455 different frequencies have been included to indicate the reproducibility of the test.
456 Temperature: 20°C

457

458 **Fig.3b.** Mechanical spectra obtained at fixed shear stress of 0.1Pa for fluid gels containing
459 0.2 wt% LA-gellan gum and NaCl as gel-promoting ions. The error bars at different
460 frequencies have been included to indicate the reproducibility of the test. Temperature:
461 20°C

462

463 **Fig.3c.** CaCl₂ concentration dependence on the plateau module (G_N^0) for fluid gels
464 containing 0.2 wt% LA-gellan gum and CaCl₂ as gel-promoting ions. Temperature: 20°C

465

466 **Fig.3d.** CaCl₂ concentration dependence on exponent (n') of the power equation which
467 relates G' to the angular frequency ($G' \sim \omega^{n'}$) for fluid gels containing 0.2 wt% LA-gellan
468 gum and CaCl₂ as gel-promoting ions. Temperature: 20°C

469

470 **Fig.4a.** Corrected shear stress dependence of viscosity for fluid gels containing 0.2 wt%
471 LA-gellan gum and CaCl₂ as gel-promoting ions. Temperature: 20°C

472

473 **Fig.4b.** Corrected shear stress dependence of viscosity for fluid gels containing 0.2 wt%
474 LA-gellan gum and NaCl as gel-promoting ions. Temperature: 20°C

475

476 **Fig.5a.** Shear rate dependence of corrected shear stress for fluid gels containing 0.2 wt%
477 LA-gellan gum and CaCl_2 as gel-promoting ions and fitting curve of the Herschel-
478 Buckley model. Temperature: 20°C

479

480 **Fig.5b.** Shear rate dependence of corrected shear stress for fluid gels containing 0.2 wt%
481 LA-gellan gum and NaCl as gel-promoting ions and fitting curve of the Herschel-Buckley
482 model. Temperature: 20°C

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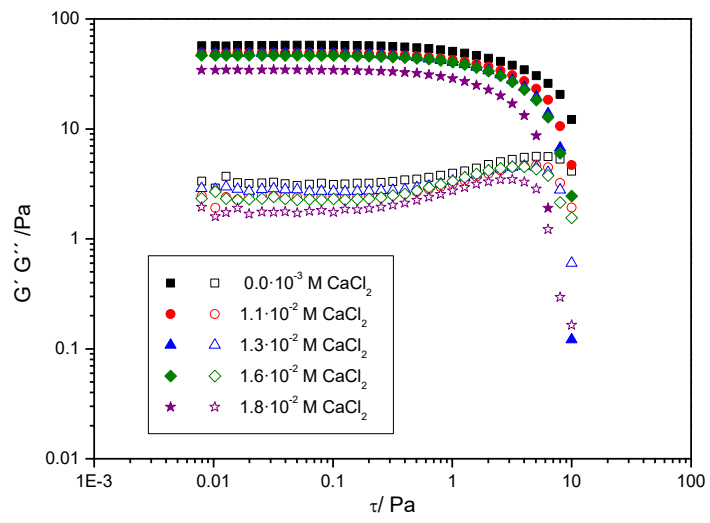


Figure 1a

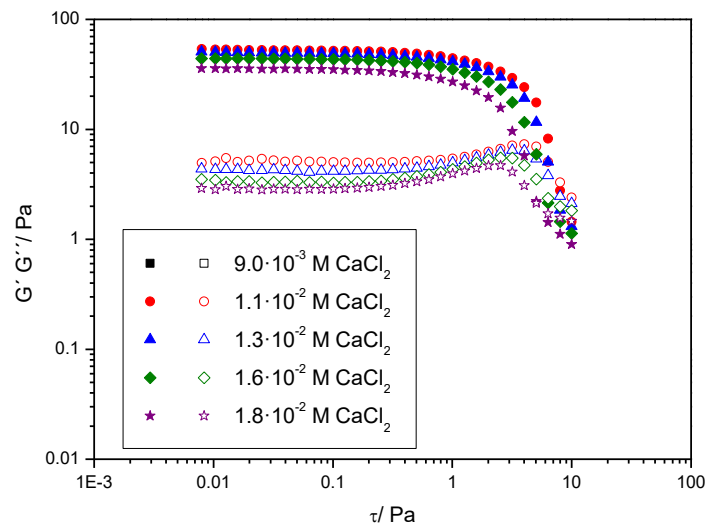


Figure 1b

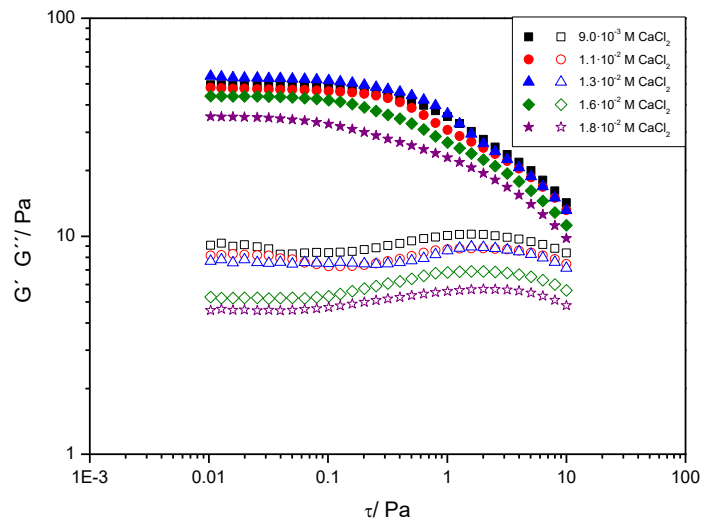


Figure 1c

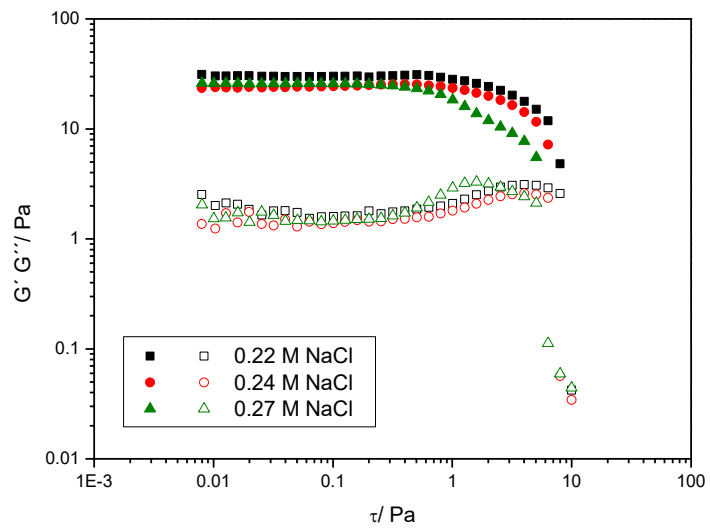


Figure 2a

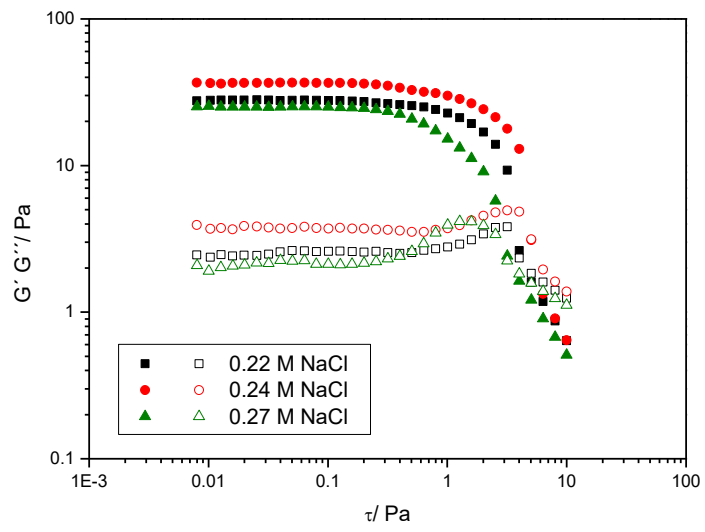


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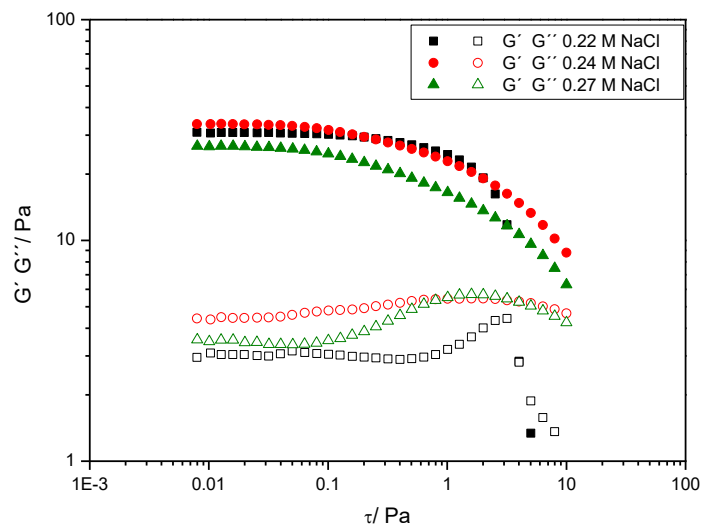


Figure 2c

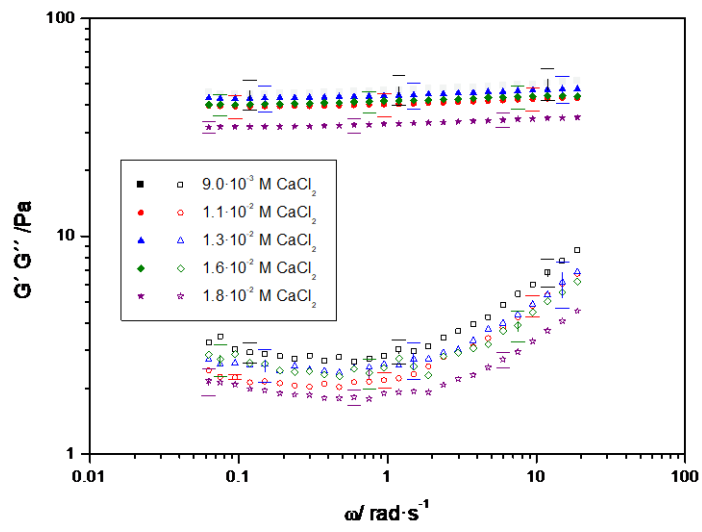


Figure 3a

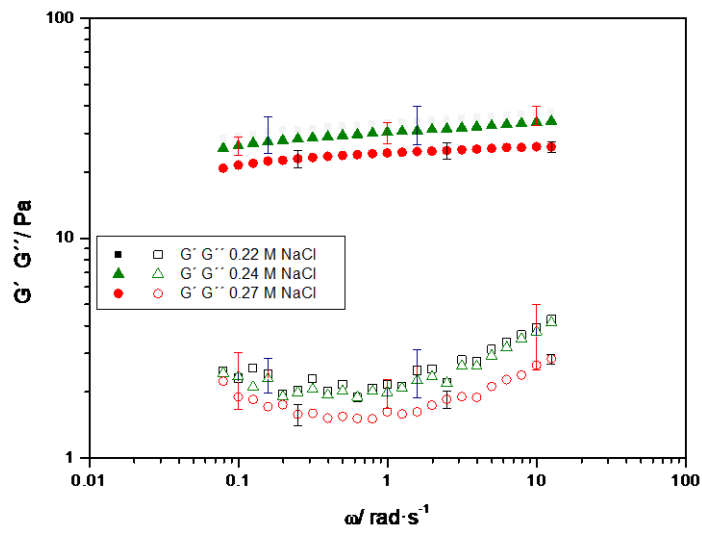


Figure 3b

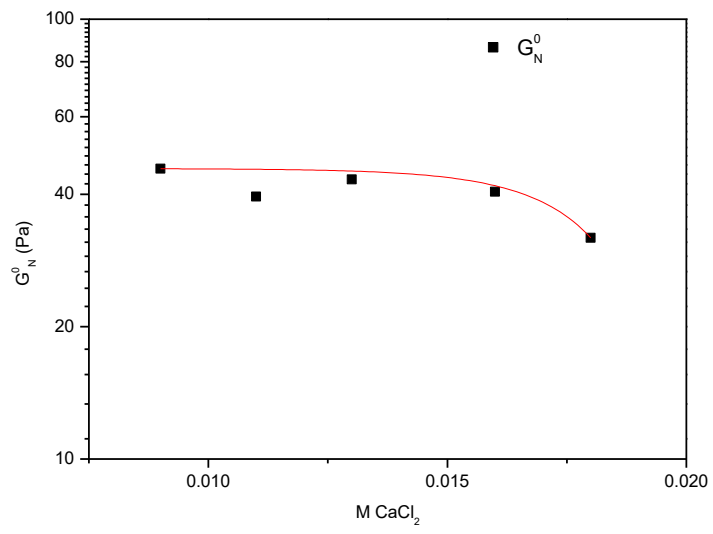


Figure 3c

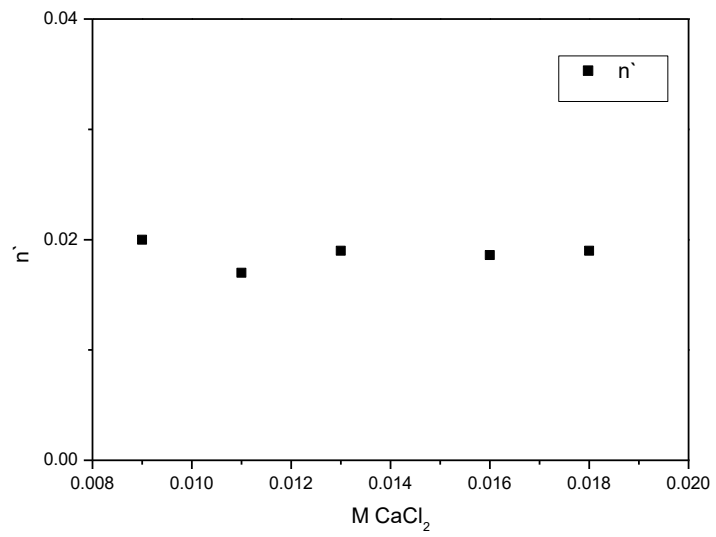


Figure 3d

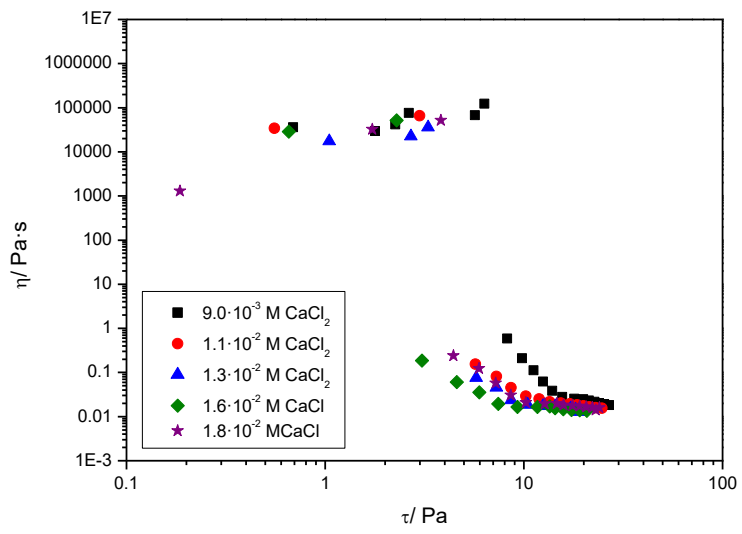


Figure 4a

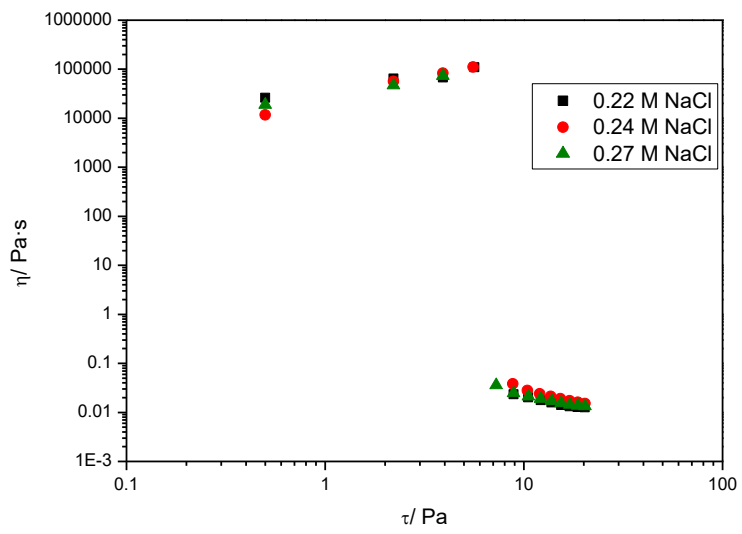


Figure 4b

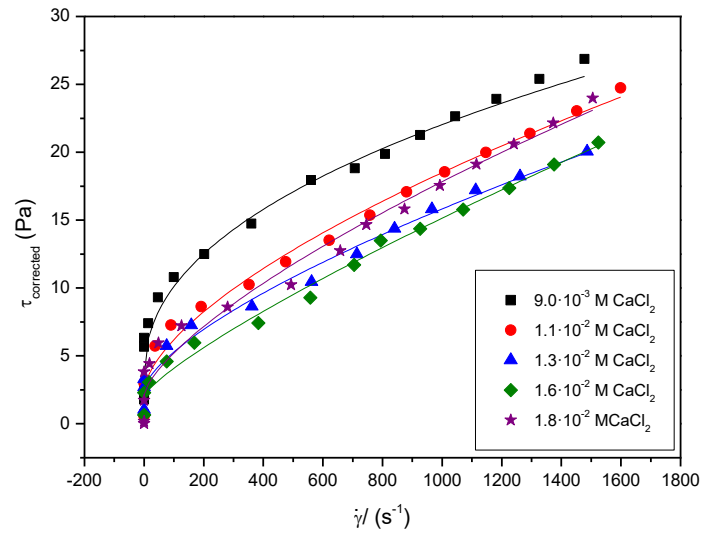


Figure 5a

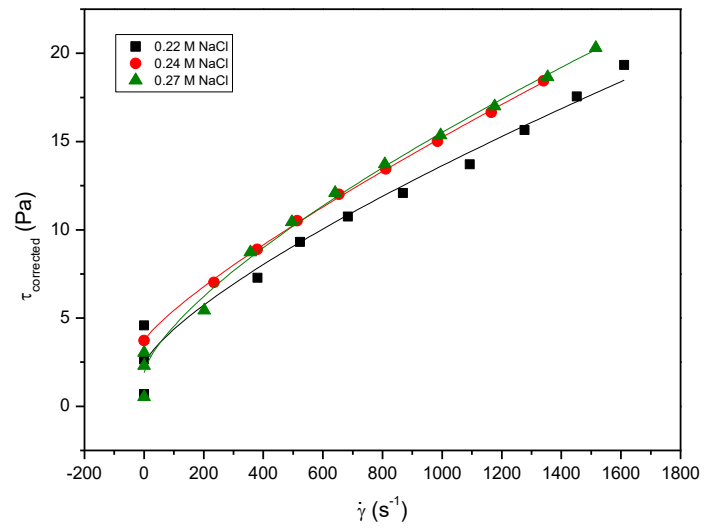


Figure 5b