

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Flow Properties of Lambda Carrageenan in Aqueous Systems

Andrea Rivera del Rio, Mariana Ramírez-Gilly and Alberto Tecante

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/65785>

Abstract

Small amplitude oscillatory and steady shear measurements at 25°C were used to investigate the rheological behavior of λ -carrageenan solutions at pH 7.0 ± 1.0 without and with added sodium counterion. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, show the typical behavior of macromolecular solutions in which the viscous character predominates. The steady shear flow exhibits a Newtonian zero-shear viscosity (η_0) region followed by a shear-thinning zone. Viscosity data can be well described by the Carreau-Yasuda model. Without added Na^+ , the intrinsic viscosity, $[\eta]$, and the critical overlap concentration, C^* , are 204 dL/g and 0.21%, respectively. With 20 mmol/dm³ Na^+ , $[\eta] = 14.7$ dL/g and $C^* = 0.38\%$. For concentrations below C^* , the viscous character is more sensitive to the presence of added Na^+ , and the opposite occurs when the concentration exceeds C^* . The dynamic moduli and viscosity increase with the increase of polysaccharide concentration, but they decrease with added Na^+ , confirming the polyelectrolyte nature of λ -carrageenan. Empirical shift factors were used to obtain master curves for the dynamic moduli and apparent viscosity for different polysaccharide and added Na^+ concentrations.

Keywords: carrageenan, polysaccharides, rheology, viscoelasticity, viscosity

1. Introduction

Recently, the nondigestible polysaccharides of natural origin have received great interest from the perspective of human health although they have been widely used for a long time [1, 2]. Carrageenans are among these polysaccharides. They are nondigestible linear sulfated polysaccharides extracted from red algae (*Rhodophyta*) of the genera *Chondrus*, *Gigartina*, *Iridaea*, *Eucheuma*, and *Hypnea* [3]. They are useful in the food industry as glazing, gelling, emulsifying, thickening, stabilizing, wetting, and bulking agents in a wide range of processed

foods such as dairy products, meat, drinks, condiments, infant formula, and animal feed [3, 4]. Carrageenans are in the list of authorized additives at the level of Good Manufacturing Practices [4] and should be used in sufficient quantity to act as emulsifiers, stabilizers, or thickeners in food [5]. The kappa and iota types of carrageenans form gels under particular conditions, while lambda carrageenan will not form a gel but can only be used as a thickener and stabilizer. λ -Carrageenan is used to clarify beverages and improve the texture of cosmetic products as creams. It is used as a thickener in dairy products and as a stabilizer in water-based systems. Also, it can act as an asymmetric selector in the separation by capillary electrophoresis of the enantiomers of tryptophan derivatives and racemic mixtures of beta blockers, used as medications for heart disease [6]. In particular, λ -carrageenan oligosaccharides with a low degree of polymerization, e.g., λ -carrageptose, have shown high activity against blood vessel growth, i.e., angiogenesis, tumor proliferation, and endothelial cell invasion [1]. However, there is a fierce controversy because oligosaccharides with molecular weights in the range of 10–40 kDa obtained from hydrolysis of λ -carrageenan have been reported to be potentially carcinogenic [2].

The functionality of carrageenans resides mainly in their structure and polyelectrolyte properties that allow them to interact with other components; they are anionic polysaccharides highly unstable in their free acid form and are commonly commercialized as a mixture of sodium, potassium, and calcium salts. Carrageenans are composed of alternating units of β -D-galactopyranoside linked to position 3 (G units) and α -D-galactopyranoside attached to position 4 (D units) or 3,6-anhydrogalactose attached to position 4 (DA units). They form repetitive disaccharide “ideal” units, commonly called carrabioses, giving rise to each type of carrageenan. According to IUPAC rules, the name of λ -carrageenan is carrageenane 2,6,2'-trisulfate (G2S-D2S, 6S) (**Figure 1**). The λ -carrageenan lacks DA units and has a 4C_1 conformation that causes the creation of twisted zones or segments in the polysaccharide chain. As a consequence, the formation of helices is not possible and gels are not formed but only viscous solutions. As it occurs with the other types, the solubility of λ -carrageenan depends on temperature, pH of the solvent, type, and concentration of counterions, and other solutes. λ -Carrageenan is soluble in water at room temperature because

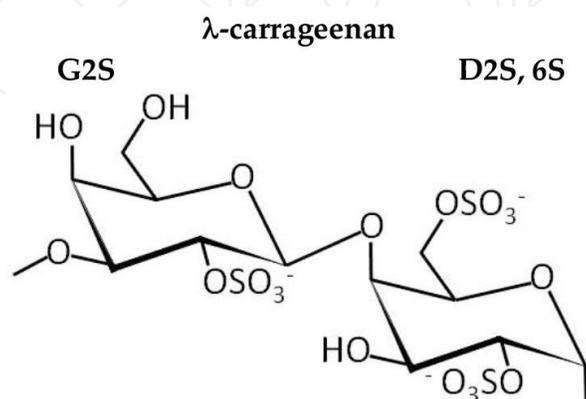


Figure 1. Ideal structure of the repeating unit of λ -carrageenans in its anionic form. G2S = 3-linked β -D-galactopyranose 2-sulfate; D2S, 6S = 4-linked α -D-galactopyranose 2,6 disulfate.

the polysaccharide-polysaccharide interactions are weak [7]. Most of the early investigations were focused on the characterization of the structure and size of λ -carrageenan by infrared spectrometry, nuclear magnetic resonance, and light scattering [8–10]. The synergistic effects on the rheological properties of λ -carrageenan combined with other polysaccharides, such as locust bean gum [11], whey protein concentrate [12], and inulin [13], have been studied in complex food systems. However, to the best of our knowledge, the different aspects investigated in this work for λ -carrageenan have not been previously reported.

Rheological techniques are widely used for the characterization of products and food additives. The variation of shear stress with shear rate or apparent viscosity with shear rate indicates if the flow behavior is Newtonian, shear-thinning, or both. Small-amplitude oscillatory tests within the zone of linear viscoelasticity (ZLV) are used to determine the variation of the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, with angular frequency and allow the viscoelasticity of the material to be characterized.

The objective of this work is to discuss the flow behavior and viscoelastic properties of λ -carrageenan in aqueous solution, without or with the addition of sodium to characterize the polyelectrolyte behavior of the polysaccharide, and evaluate the effect of its concentration and that of the counterion on these behaviors. The overlap concentrations separating the dilute from the semidilute regimes were also determined. The flow behavior was described with empirical models. Shift factors for generating master curves of the mechanical spectra and flow curves are proposed for different λ -carrageenan and added Na^+ concentrations. These results are useful to understand better the thickening properties of this important polysaccharide.

2. Experimental

A food-grade commercial preparation of λ -carrageenan as provided by a local supplier (FMC Biopolymer, Mexico) was used without further treatment. Other materials included sodium chloride ACS reagent grade (Mallinckrodt Baker, Mexico) and deionized water. The content (ppm) of sodium, potassium, calcium, and magnesium ions in the commercial preparation of the polysaccharide, determined by atomic absorption, was $\text{Na}^+ = 30,863$; $\text{K}^+ = 15,595$; $\text{Ca}^{2+} = 972$, and $\text{Mg}^{2+} = 1882$.

2.1. Preparation of λ -carrageenan solutions

λ -Carrageenan solutions with concentrations of 0.002, 0.006, 0.01, 0.08, 0.5, 0.8, 1.0, 1.5, and 2.0% by weight were prepared without and with added Na^+ considering the moisture content of the polysaccharide. The necessary amount of λ -carrageenan to make 50 g of a solution was dispersed as fine rain with a vibrating spatula in the appropriate solvent at 70°C under magnetic stirring at 1000 rpm (Barnstead International, model Super-Nuova SP131825, USA) until complete dissolution. The water that evaporated was compensated with the corresponding solvent. The solutions were stored in refrigeration at 3°C until analysis. Solutions with 0.002–2.0% λ -carrageenan were prepared in 0, 20, 30, 50, 70, 80, 100, 120, and 140 mmol/dm³ NaCl. Besides, 1.5 and 2.0% λ -carrageenan solutions were prepared in 160, 180, 200, 220, 240,

and 260 mmol/dm³ Na⁺. Only for 2.0% λ -carrageenan, solutions with 300, 350, and 400 mmol/dm³ Na⁺ were prepared too. The pH was 7.0 \pm 1.0.

2.2. Ionic strength of λ -carrageenan solutions without and with added sodium counterion

Given the anionic nature of λ -carrageenan, the ionic strength of the aqueous environment is crucial. **Table 1** shows the range of total ionic strength of all solutions without and with added Na⁺, the range of contribution of added Na⁺ to the total ion strength, the amount of sodium ion required to neutralize the charges in the different polysaccharide solutions, and the concentration of Na⁺ present in the commercial preparation.

The contribution of the internal counterions to the total ionic strength becomes significant only for high levels of the polysaccharide. Below 0.5% λ -carrageenan, the total ionic strength is practically given by the added Na⁺, regardless of the concentration of added Na⁺. Above 0.5% λ -carrageenan, the contribution of added Na⁺ depended on the concentrations of the polysaccharide and added Na⁺. The contribution of the internal counterions is always greater than that of added Na⁺ for concentrations of added Na⁺ \leq 30 mmol/dm³. On the other hand, the Na⁺/ λ -carrageenan stoichiometric ratio is 4.76 meq/g. This value can be obtained considering a molecular weight of 630.41 for the sodium salt of the repeating unit of λ -carrageenan and indicates the amount of sodium ion needed to neutralize the charges in 1 g of polysaccharide.

2.3. Rheometry

The rheological behavior of λ -carrageenan solutions without and with added Na⁺ was determined in a rheometer (ARES-RFS III, TA Instruments, Delaware, USA) using the Couette double-wall concentric cylinders fixture with a diameter ratio of 0.95, and 1.0 mm gap between

C _{λC} (%)	I _{min} –I _{max} ^a	Contribution (%) ^b	Na ⁺ _{nc} (meq)	Na ⁺ _{cp} (meq/mL)
0.002	0.024–70.0	99.8–99.9	0.00952	2.98 × 10 ⁻⁵
0.006	0.072–70.1	99.3–99.9	0.0286	8.95 × 10 ⁻⁵
0.01	0.119–70.1	98.8–99.8	0.0476	1.49 × 10 ⁻⁴
0.08	0.95–71.0	91.3–98.7	0.381	1.19 × 10 ⁻³
0.50	5.97–76.0	62.6–92.1	2.38	7.46 × 10 ⁻³
0.80	9.50–79.5	51.3–88.1	3.81	1.19 × 10 ⁻²
1.0	11.9–81.9	45.7–85.5	4.76	1.49 × 10 ⁻²
1.5	17.9–87.9	35.8–79.6	7.14	2.24 × 10 ⁻²
2.0	23.9–93.9	29.5–74.5	9.52	2.98 × 10 ⁻²

^aFor 0–140 mmol/dm³ added Na⁺.

^bFor 20–140 mmol/dm³ added Na⁺.

Table 1. Range of total ionic strength (mmol/dm³) of λ -carrageenan solutions, range of contribution (%) of added Na⁺ to the total ionic strength, the amount (meq) of Na⁺ necessary to neutralize the charges in λ -carrageenan solutions (Na⁺_{nc}), and concentration (meq/mL) of Na⁺ present in the commercial preparation (Na⁺_{cp}).

cylinders. All determinations were performed in duplicate at $25 \pm 0.5^\circ\text{C}$. Rheological data are presented as means of at least two repetitions with a standard deviation not greater than 5.0%.

The viscoelastic properties were determined by small-amplitude oscillatory shear tests. Strain sweeps were run from 0.1 to 100% strain (γ) at a constant angular frequency (ω) of 6.28 rad/s to determine the zone of linear viscoelasticity. Frequency sweeps were done in the ZLV from 0.1 to 100 rad/s to determine the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$.

The flow properties were determined from steady angular shear tests in the range of 0.03–300 s^{-1} . Flow curves (η vs. $\dot{\gamma}$) for each concentration of λ -carrageenan and added Na^+ were obtained. Experimental data were fitted to the Cross model [14]

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^{1-n}} \quad (1)$$

and the Carreau-Yasuda equation [15]

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + (\lambda\dot{\gamma})^a\right)^{\frac{n-1}{a}} \quad (2)$$

using the nonlinear regressions routines of SigmaPlot© programming software. Only regressions with $r^2 > 0.9960$ were considered.

2.3.1. Intrinsic viscosity and critical concentration

The intrinsic viscosity was determined from the graphical representation of the Huggins and Kraemer equations, given by Eqs. (3) and (4), respectively,

$$\eta_{\text{red}} = [\eta] + k'[\eta]^2 C \quad (3)$$

$$\eta_{\text{inh}} = [\eta] + k''[\eta]^2 C \quad (4)$$

In these equations $\eta_{\text{red}} = \eta_{\text{sp}}/C$ is the reduced viscosity and $\eta_{\text{inh}} = (\ln \eta_{\text{rel}})/C$ is the inherent viscosity. The specific viscosity is defined as $\eta_{\text{sp}} = \eta_{\text{rel}} - 1$ and the relative viscosity as $\eta_{\text{rel}} = \eta/\eta_s$, i.e., the ratio of solution to solvent viscosities. The reduced and the inherent viscosities were calculated from the zero-shear viscosity, η_0 . The intrinsic viscosity is determined by extrapolation to zero concentration and the corresponding constants, k' and k'' , are determined from the respective slopes. The critical concentration, C^* , was determined from the graph η_{sp} vs. $C[\eta]_0$ as the point where there is a change in slope of the linear relationship between the plotted variables.

2.3.2. Master curves

Concentration-dependent shift factors on the ordinate and the abscissa of the flow curves (η vs. $\dot{\gamma}$) and frequency sweeps, $G'(\omega)$ and $G''(\omega)$ vs. ω , were determined empirically to obtain the corresponding master curve for each added Na^+ concentration and different λ -carrageenan concentrations. The 0.5% polysaccharide solution was used as a reference.

3. Results and discussion

3.1. Viscoelastic behavior of λ -carrageenan solutions without added sodium counterion

The variation with frequency of $G'(\omega)$ and $G''(\omega)$ for 0.006, 0.5, and 2.0% λ -carrageenan solutions is shown in **Figure 2**. The λ -carrageenan concentrations, 0.01, 0.08, 0.8, 1.0, and 1.5%, lie between 0.5 and 2.0%. The behavior displayed is characteristic of macromolecular solutions. The loss modulus is greater than the storage modulus, both depend on the angular frequency with a continuous rise, in the terminal zone $G'(\omega) \propto \omega^{1.6}$ and $G''(\omega) \propto \omega^{0.8}$, and the viscous character dominates. In solutions with 0.006, 0.01, and 0.08% λ -carrageenan moduli overcrossed, i.e., $G' = G''$, at frequencies of 10.0, 15.9, and 39.8 rad/s, respectively. These overcrossing points separate the behavior into a region predominantly viscous in which the loss modulus is superior, and an elastic domain in which the behavior is governed by the storage modulus. The reciprocal of the overcrossing frequency, ω_c , is related to the relaxation time of the macromolecular chains. This last time indicates the magnitude of the elastic character of the material. When ω_c becomes larger, the relaxation time becomes shorter, and the contribution of the elastic character diminishes.

For a given constant frequency both moduli increase with the increase of polysaccharide concentration, but this increase is not proportional. For example, at 10 rad/s $G'(\omega)$ increased 50 times when the polysaccharide concentration increased from 0.5 to 2.0%, while $G''(\omega)$ increased 20 times. The inverse occurs when λ -carrageenan concentration goes from 0.006 to 0.5%; $G'(\omega)$ increases about 5 times and $G''(\omega)$ does it 30 times. Therefore, at high polysaccharide concentrations, the contribution of the elastic character becomes more significant.

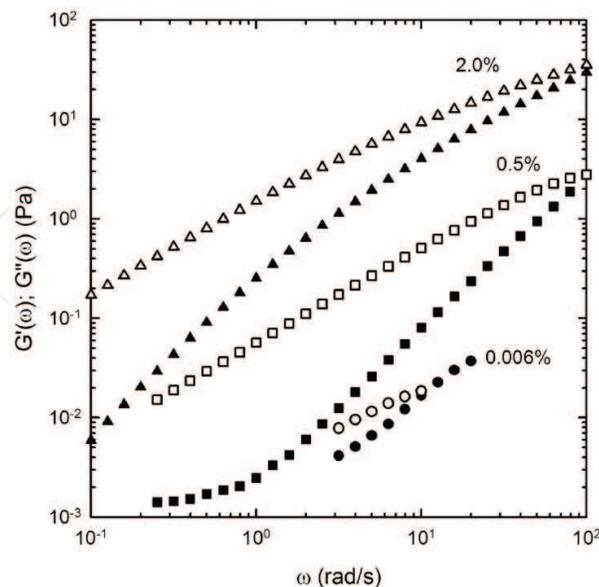


Figure 2. Variation of the storage modulus, $G'(\omega)$ (full symbols) and the loss modulus, $G''(\omega)$ (empty symbols) with angular frequency for solutions with 0.006, 0.5 and 2.0% λ -carrageenan without added Na^+ . Strains are 50, 40, and 20% for 0.006, 0.5, and 2.0%, respectively.

3.2. Steady flow behavior of λ -carrageenan solutions without added sodium counterion

The variation of apparent viscosity with a shear rate and λ -carrageenan concentration is shown in **Figure 3**. The dependence between these two quantities for a given shear rate is approximately $\eta \propto C^2$. The 0.002% λ -carrageenan solution exhibits Newtonian behavior. All other polysaccharide concentrations exhibit Newtonian behavior at low shear rates, a transition zone at intermediate shear rates and shear-thinning behavior at high shear rates. The end of the zero-shear Newtonian zone is displaced to lower shear rates when λ -carrageenan concentration increases. This behavior is typical of many polysaccharides used in the food industry and is closely related to the polymer-polymer and polymer-solvent interactions. The intrinsic viscosity and the overlap concentration are useful parameters to explain this behavior.

3.3. Intrinsic viscosity and critical concentration of λ -carrageenan solutions without added sodium counterion

The intrinsic viscosity, $[\eta]$, of a polymer is a measure of its contribution to the viscosity of a solution when the polymer concentration, C , tends to zero and depends on the conformation and molecular weight of the polymer in solution. The determination of this quantity from Huggins and Kraemer equations requires dilute solutions and a linear dependence of η_{sp}/C and $(\ln \eta_{rel})/C$ with concentration. The intrinsic viscosity for λ -carrageenan in aqueous solution without added Na^+ is around 204 dL/g. The repeating unit of λ -carrageenan has three sulfate groups. In the absence of external counterion, these groups repel each other and hence the polysaccharide chains are primarily unfolded. Therefore, this can explain the high intrinsic viscosity observed. The intrinsic viscosity is related to the hydrodynamic volume of a polymer in solution. A dimensionless quantity, called the coil-overlap parameter, is the product of intrinsic viscosity and polymer concentration ($C[\eta]_0$). This parameter is a measure of the total volume occupied by the polymer in solution [16].

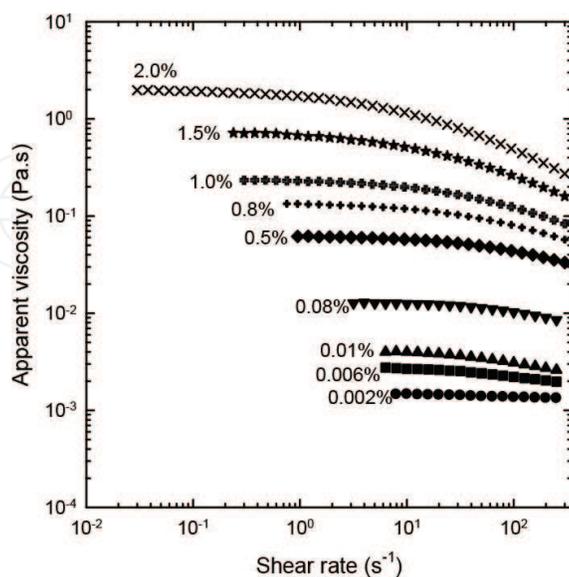


Figure 3. Variation of apparent viscosity with shear rate and λ -carrageenan concentration in the range of 0.002–2.0% without added Na^+ .

On the other hand, the critical concentration, C^* , indicates the transition from dilute to semi-dilute regimes and is closely related to the formation of entanglements between macromolecules. The critical concentration of λ -carrageenan in aqueous solution without added Na^+ is about 0.21%. Solutions with 0.002, 0.006, 0.01, and 0.08% λ -carrageenan can be considered dilute. These solutions exhibit a slight shear-thinning behavior (**Figure 3**); the zero-shear viscosity decreases about 30–35% along the range of shear rate. At low shear rate, polysaccharide strands are in a highly extended conformation due to electrostatic repulsion. When shear rate increases, the strands are aligned or oriented in the direction of flow and occupy a smaller volume, this explains the decrease in viscosity.

Solutions with 0.5, 0.8, 1.0, 1.5, and 2.0% λ -carrageenan are semidilute. The shear-thinning behavior becomes more evident than for dilute solutions (**Figure 3**). In these solutions, polysaccharide-polysaccharide interactions, in the form of overlaps and interlocks, become increasingly significant while polysaccharide-water interactions decrease. When the chains are deformed, the entanglements are disturbed. At low shear rate, there is enough time for new entanglements to be formed and their number to remain constant over time. Therefore, viscosity remains practically constant. This phenomenon gives rise to the zero-shear Newtonian region. The transition to the shear-thinning zone occurs when the shear rate is greater than the rate of formation of new entanglements [16]. As a consequence, there are fewer polymer-polymer interactions which facilitate the flow of the solution and cause the viscosity to decrease.

The rate of formation of new interactions is related to the concentration of polymer in solution. The space occupied by the polymer and particularly the available space are related to $C[\eta]_0$. The unoccupied space allows the chains to move freely, but when $C[\eta]_0$ increases motion becomes more restricted. That is the reason why upon increasing the concentration of polymer, the beginning of the transition to the shear-thinning region is displaced to lower shear rates [16].

3.4. Flow models of λ -carrageenan solutions without added sodium counterion

The Cross and the Carreau-Yasuda are two of the more traditional flow models. The regression parameters of the two models for each λ -carrageenan solution without added Na^+ are shown in **Table 2**. In both models, the increase in the zero-shear viscosity (η_0) is attributed to the increase in polysaccharide concentration. The parameters K and λ of the Cross and Carreau-Yasuda models, respectively, have the same meaning. They represent the time for which the shear-thinning region appears. They are different for each model but the Carreau-Yasuda model describes better the start of the shear-thinning region. The parameter n indicates the proximity to Newtonian behavior. The indirect relationship between polysaccharide concentration and n for the Carreau-Yasuda model means that for a higher polysaccharide concentration, the flow behavior deviates from Newtonian. This behavior is not observed with the Cross model, and the values of n do not explain the observed shear-thinning behavior.

The parameter a in the Carreau-Yasuda equation indicates how long and smooth the transition is from the Newtonian to the shear-thinning zone. This parameter takes bigger values for more dilute solutions, except for the 0.002% solution, in which the flow transition is not observed. In all cases, this change is long and smooth as observed experimentally. The

Cross					Carreau-Yasuda				
$C_{\lambda C}$ (%)	η_0 (Pa·s)	K (s)	n	r^2	η_0 (Pa·s)	λ (s)	a	n	r^2
0.002	0.0030	0.2789	0.944	0.9879	0.0017	0.0193	0.2047	0.939	0.9883
0.006	0.0030	0.0011	0.526	0.9967	0.0028	0.0466	1.3320	0.860	0.9984
0.01	0.0044	0.0022	0.396	0.9962	0.0041	0.0415	1.7380	0.813	0.9995
0.08	0.0131	0.0019	0.189	0.9976	0.0129	0.0160	1.2420	0.734	0.9990
0.5	0.0631	0.0029	0.343	0.9997	0.0627	0.0069	0.7295	0.531	0.9998
0.8	0.1392	0.0061	0.384	0.9997	0.1377	0.0107	0.6746	0.489	0.9999
1.0	0.2414	0.0095	0.363	0.9997	0.2387	0.0225	0.7329	0.525	0.9999
1.5	0.7602	0.0305	0.408	0.9997	0.7593	0.0323	0.6028	0.413	0.9998
2.0	2.0080	0.0633	0.377	0.9998	2.0110	0.0581	0.6147	0.361	0.9999

Table 2. Regression parameters of the Cross and Carreau-Yasuda models for different λ -carrageenan concentrations without added Na^+ .

Carreau-Yasuda model describes better the flow behavior of the λ -carrageenan solutions without added Na^+ . In addition, it provides more information because it contains the parameter a . However, both models have some limitations. If the experimental data do not allow the zero-shear and shear-thinning regions to be observed, the values of the parameters K , λ , and a will be somehow unrealistic because the models are unable to predict the beginning of the shear-thinning region and its shape. It is because of this the values of the parameters for the 0.002% λ -carrageenan solution are less in agreement, as shown by the corresponding regression coefficients, with experimental observations.

The power-law model is used to describe only the shear-thinning region. The description of the flow curves with this model requires the experimental data to be adjusted to Eq. [5].

$$\eta = k\dot{\gamma}^{n-1} \quad (5)$$

Table 3 shows the parameters obtained with such fitting and the good correlations obtained. This proficiency of the model is not surprising, but the limitations in comparison with the Cross

$C_{\lambda C}$ (%)	k (Pa·s ^{n})	n	r^2
0.5	0.1331	0.76	0.9971
0.8	0.2881	0.72	0.9955
1.0	0.5350	0.68	0.9960
1.5	1.708	0.59	0.9982
2.0	4.556	0.51	0.9987

Table 3. Regression parameters of the power-law model for different λ -carrageenan concentrations without added Na^+ .

and Carreau-Yasuda equations are evident. The consistency index, k , is directly related to viscosity. As the polysaccharide concentration is increased, the values of k increase, and if the behavior becomes Newtonian, the consistency index is the viscosity. The parameter n , called flow behavior index, has the same meaning that in the Cross and Carreau-Yasuda models. Values close to 1 indicate a close-to-Newtonian behavior. Lower polysaccharide concentrations result in a behavior closer to Newtonian, as expected and predicted by the Cross and Carreau-Yasuda models.

3.5. Viscoelastic behavior of λ -carrageenan solutions with added sodium counterion

Figure 4 shows the effect of added Na^+ on the dynamic moduli. The ratios $G'(\omega)/G'_0(\omega)$ and $G''(\omega)/G''_0(\omega)$ are plotted against the total ionic strength for different polysaccharide concentrations at a given angular frequency. In these ratios, $G'(\omega)$ and $G''(\omega)$ are the storage and loss modulus, respectively, of the solutions with added Na^+ , while $G'_0(\omega)$ and $G''_0(\omega)$ are the corresponding moduli without added Na^+ . Drastic reductions in the dynamic moduli occur when the total ionic strength increases. Reductions are so drastic for 20, 30, 50, 70, 80, 100, 120, and 140 mmol/dm^3 added Na^+ that the dynamic moduli for solutions with polysaccharide concentrations in the dilute regime, i.e., 0.002, 0.006, and 0.01%, cannot be detected by using the rheometer. Only for 0.08% λ -carrageenan dynamic moduli can be determined, and the characteristic behavior of macromolecular solutions in which the loss modulus is greater than the storage modulus is observed. The viscous character dominates and moduli depend on frequency. The increase in ionic strength by addition of Na^+ reduced $G'(\omega)$ 39% and $G''(\omega)$ 81%. The previous value represents an almost three-fold reduction in $G'(\omega)$ for the same polysaccharide concentration but without added Na^+ . This behavior illustrates the polyelectrolyte character of λ -carrageenan which is responsible for the sensitivity of viscoelasticity to the addition of the counterion. In addition, the viscous character is the most sensitive.

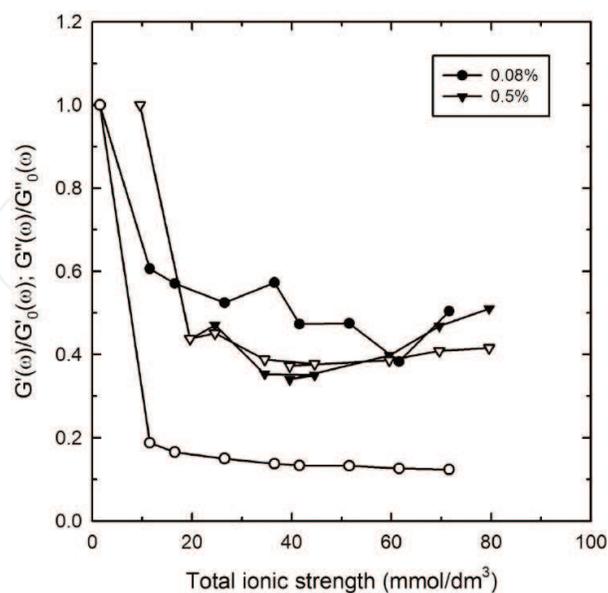


Figure 4. Variation of the ratio of storage moduli with added Na^+ to storage moduli without added Na^+ (full symbols), and the ratio of loss moduli with added Na^+ to loss moduli without added Na^+ (empty symbols) with the total ionic strength for 0.08 and 0.5% λ -carrageenan solutions ($\omega = 6.31$ rad/s). Lines are included as a visual guide.

After an initially noticeable decrease, the dynamic moduli remain practically constant with the increase in the total ionic strength, that is, for concentrations greater than 20 mmol/dm³ Na⁺. On the other hand, this concentration is superior to the stoichiometric counterion/poly-saccharide ratio and is sufficient to screen all the charges in the macromolecule.

The effect of the total ionic strength on 0.5% λ -carrageenan solutions can also be seen in **Figure 4**. In this case, the rate of diminution due to the increase in the total ionic strength is 60% for both moduli in comparison with a solution with the same polysaccharide concentration but without added Na⁺. Moduli decrease and then become practically independent of Na⁺ concentration. However, above 45 mmol/dm³ approximately, the moduli increase around 10%. At this point, it is possible that ions start to compete for water associated with the polysaccharide because ions are not hydrated enough as they are added to the solution which for 0.5% λ -carrageenan is in the semidilute regime. The addition of Na⁺ can lead to the formation of a new more elastic structure than the one observed when there is enough water to hydrate all molecules and ions in solution.

The effect of the increase in ionic strength on 0.8% λ -carrageenan solutions is observed in **Figure 5**. The dynamic moduli decrease about 25–30% for 20 mmol/dm³ Na⁺ ($I_{\text{total}} = 19.5$ mmol/dm³) as compared with systems without added Na⁺ ($I_{\text{total}} = 9.50$ mmol/dm³), and a minimum is observed when the ionic strength due to the counterions is 44.5 mmol/dm³. At this point $G'(\omega)$ decreases 35% and $G''(\omega)$ decreases 45%. From a total ionic strength of 44.5 mmol/dm³, the storage and loss moduli increased up to 86 and 65% of their values without added Na⁺, respectively. These changes mean that $G'(\omega)$ increases 21% from its low to its maximum value and $G''(\omega)$ increases 11%. Also, $G'(\omega)$ decreases less and recovers more than $G''(\omega)$.

For 1.0% λ -carrageenan solutions, the diminution in the presence of added Na⁺ is almost 30% as compared with solutions without added Na⁺. The minimum $G'(\omega)$ occurs for a total ionic

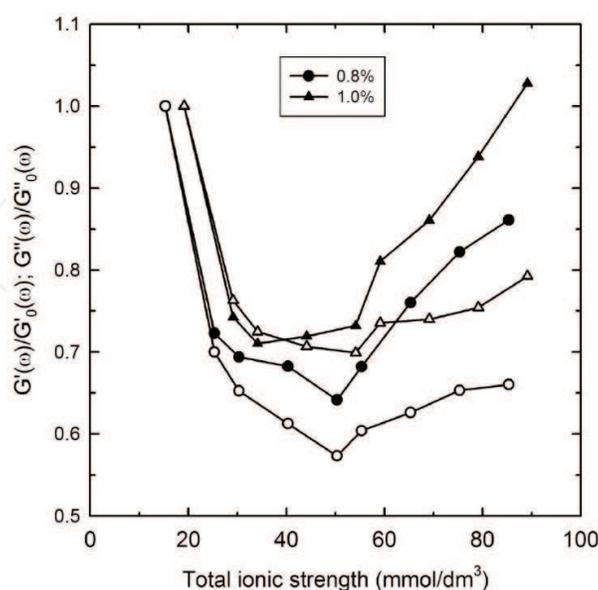


Figure 5. Variation of the ratio of storage moduli with added Na⁺ to storage moduli without added Na⁺ (full symbols), and the ratio of loss moduli with added Na⁺ to loss moduli without added Na⁺ (empty symbols) with the total ionic strength for 0.8 and 1.0% λ -carrageenan solutions ($\omega = 6.31$ rad/s). Lines are included as a visual guide.

strength of 26.9 mmol/dm^3 and decreases 27% as compared with 11.9 mmol/dm^3 . The minimum $G''(\omega)$ takes place for 46.9 mmol/dm^3 and decreases 30% compared with 11.9 mmol/dm^3 . $G'(\omega)$ and $G''(\omega)$ increase up to 103 and 79%, respectively, from these minimum values as compared with those without added Na^+ . This means that $G'(\omega)$ increases 30% and $G''(\omega)$ increases 7% from their corresponding minimum to maximum values. The increase in storage modulus is more significant than the loss modulus, so the presence of added Na^+ affects the elastic character more than the viscous one in the semidilute regime, unlike the dilute regime in which the viscous character is more sensitive than the elastic one. This behavior may be due to the above-stated reason, i.e., the competition between the counterions and the macromolecules for water to become hydrated that occurs when the solution begins to saturate. This competition increases the association of the polysaccharide chains that form structures with a certain degree of rigidity that favors the elastic nature of the behavior.

In the case of 1.5 and 2.0% λ -carrageenan solutions with added Na^+ , a respective decrease of 10% for $I_{\text{total}} = 32.9 \text{ mmol/dm}^3$ and 7% for $I_{\text{total}} = 38.9 \text{ mmol/dm}^3$ in the dynamic moduli is also observed in comparison with $0 \text{ mmol/dm}^3 \text{ Na}^+$ ($I_{\text{total}} = 17.9 \text{ mmol/dm}^3$ for 1.5% λ -carrageenan and $I_{\text{total}} = 23.9 \text{ mmol/dm}^3$ for 2.0% λ -carrageenan) (Figure 6). The λ -carrageenan is a highly flexible polyelectrolyte which means that by screening its charges, the hydrodynamic volume of the polymer is significantly reduced causing a corresponding decrease in its dynamic moduli. Although this occurs, the polysaccharide concentration is so high that the reduction of the moduli is smaller than the one observed for lower polysaccharide concentrations.

The decrease in dynamic moduli for 1.5% λ -carrageenan solutions continues until the total ionic strength is 32.9 mmol/dm^3 . From this point $G'(\omega)$ and $G''(\omega)$ increases up to 189 and 113%, respectively, regarding a solution with the same concentration of polysaccharide but without added Na^+ . Also, in the 2.0% λ -carrageenan solutions, the minimum dynamic moduli are achieved for a total ionic strength of 33.9 mmol/dm^3 , and $G'(\omega)$ and $G''(\omega)$

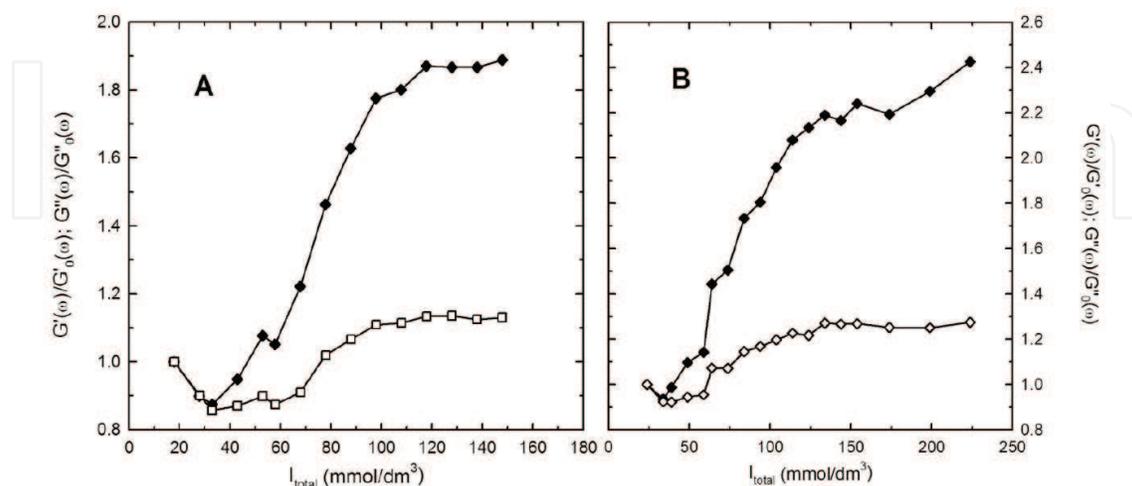


Figure 6. Variation of the ratio of storage moduli with added Na^+ to storage moduli without added Na^+ (full symbols), and the ratio of loss moduli with added Na^+ to loss moduli without added Na^+ (empty symbols) with the total ionic strength for 1.5% (A) and 2.0% (B) λ -carrageenan solutions ($\omega = 6.31 \text{ rad/s}$). Lines are included as a visual guide.

increase to 242 and 127%, respectively, regarding the corresponding solutions without added Na⁺.

3.6. Steady flow behavior of λ-carrageenan solutions with added sodium counterion

Solutions were also examined under steady angular shear to observe the effect of added Na⁺ on their thickening properties. Newtonian behavior with a viscosity close to 1 mPa s was found in the range of 6–300 s⁻¹ for 0.002, 0.006, and 0.01% λ-carrageenan solutions with 20 mmol/dm³ Na⁺ ($I_{\text{total}} \approx 10 \text{ mmol/dm}^3$). This behavior indicates that the ionic strength is sufficient for screening the charges of all chains and their hydrodynamic volume decreases in such a way that all the flow resistance of the pure solvent is not altered. The λ-carrageenan concentration is low enough for available water to interact with the polysaccharide and added Na⁺. The viscosity remains constant with the increase in ionic strength to a level close to 70 mmol/dm³.

In the case of the 0.08% λ-carrageenan solution with 20 mmol/dm³ Na⁺ ($I_{\text{total}} = 10.95 \text{ mmol/dm}^3$), the presence of the external counterion causes a decrease of 80% in the viscosity regarding the same polysaccharide concentration without added Na⁺ ($I_{\text{total}} = 0.95 \text{ mmol/dm}^3$). However, this polysaccharide concentration is sufficiently high for the viscosity not to drop close to that of the solvent. This decrease is maintained constant regardless of the amount of added Na⁺ as shown in **Figure 7**. In this figure, the viscosity ratio is plotted against the total ionic strength. This ratio is the quotient of the zero-shear viscosity of the solution with added Na⁺ and the zero-shear viscosity of the solution without added Na⁺ for the same polysaccharide concentration and a given shear rate.

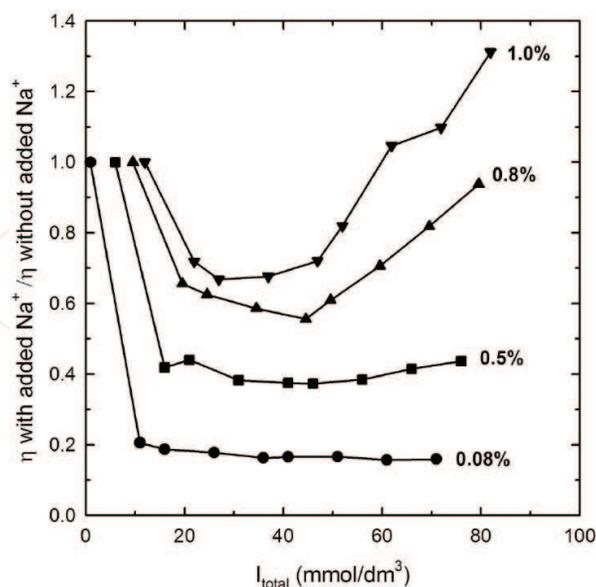


Figure 7. Variation of the ratio of apparent viscosities with added Na⁺ to apparent viscosities without added Na⁺ with the total ionic strength for 0.08 ($\dot{\gamma} = 10 \text{ s}^{-1}$), 0.5, 0.8, and 1.0% ($\dot{\gamma} = 3.8 \text{ s}^{-1}$) λ-carrageenan solutions. Lines are included as a visual guide.

In solutions with 0.5% λ -carrageenan, a similar behavior is observed. The viscosity decreases 60% when the concentration of added Na^+ is 20 mmol/dm³ ($I_{\text{total}} = 15.97$ mmol/dm³), compared with a solution of equal carrageenan concentration without added Na^+ ($I_{\text{total}} = 5.97$ mmol/dm³). This decrease remains constant until the ionic strength is 55.97 mmol/dm³. Beyond this value, a slight increase in viscosity of about 5% is observed.

For 0.8 and 1.0% λ -carrageenan solutions, viscosity decreases of 34 to 28%, respectively, are observed with the addition of 20 mmol/dm³ Na^+ ; $I_{\text{total}} = 19.5$ and 21.90 mmol/dm³, respectively. The viscosity reduction continues until a minimum is reached when the ionic strength is 44.5 and 26.9 mmol/dm³, for 0.8 and 1.0% λ -carrageenan, respectively. From these minimum viscosity ratios, the viscosity of the 0.8% λ -carrageenan solutions increases linearly ($r^2 = 0.9983$) with the increase in the concentration of added Na^+ , and recovers 96% of the viscosity without added Na^+ .

For 1.0% λ -carrageenan solutions, viscosity increases from the minimum ratio up to 132% of its value without added Na^+ . However, this increase in viscosity is not linear ($r^2 = 0.9697$). The decrease in viscosity with added Na^+ highlights the polyelectrolyte property of λ -carrageenan and is due to charge screening of the polysaccharide chains. In the absence of external Na^+ , the chains are highly unfolded due to electrostatic repulsion between the sulfate groups. In the presence of external Na^+ , the negative charges of the polysaccharide chain are screened, and a more compact conformation can be adopted. The hydrodynamic volume decreases, and so does the viscosity of the solution. The maximum increase in viscosity observed primarily for 0.8 and 1.0% λ -carrageenan solutions with the addition of more Na^+ , which in turn implies that an increase in viscosity in the shear-thinning region is due to the presence of excess external Na^+ , i.e., additional to that necessary to screen all the charges of the sulfate groups. The excess Na^+ is hydrated and competes with the polysaccharide for water molecules, which results in a decrease in polysaccharide-water interactions and increases the polysaccharide-polysaccharide interactions forming semiordered and more elastic structures that increased the viscosity. The amount of polysaccharide in 1.0% λ -carrageenan solutions becomes important. A minimum viscosity appears when the ionic strength is 26.9 mmol/dm³. Competition for the solvent begins probably at this point. Therefore, viscosity increases from this ionic strength to the extreme concentration of added Na^+ for the same reason explained previously.

For solutions with concentrations higher than 1.0% polysaccharide, a different behavior is observed (**Figure 8**). The viscosity of 1.5% λ -carrageenan solutions without added Na^+ decreases 12% when the ionic strength is 32.9 mmol/dm³ in comparison with $I_{\text{total}} = 17.9$ mmol/dm³ without external Na^+ . That is the minimum viscosity observed.

For the 2.0% λ -carrageenan solutions, a minimum is observed for an ionic strength of 33.9 mmol/dm³ which corresponds to a 12% decrease (**Figure 8B**) regarding 23.9 mmol/dm³ without added Na^+ . From these minimum values, viscosity suddenly increases with increasing the addition of Na^+ . Hydration of the Na^+ counterions and the formation of semiordered and more elastic structures might explain the growth in viscosity to 200 and 270% for 1.5 and 2.0% λ -carrageenan, respectively. It is possible that for higher external Na^+ concentrations ($I_{\text{total}} > 87\text{--}94$ mmol/dm³) more ordered structures are formed which have a greater resistance to flow and remain up to very high added Na^+ concentrations. It is presumed that if the addition of

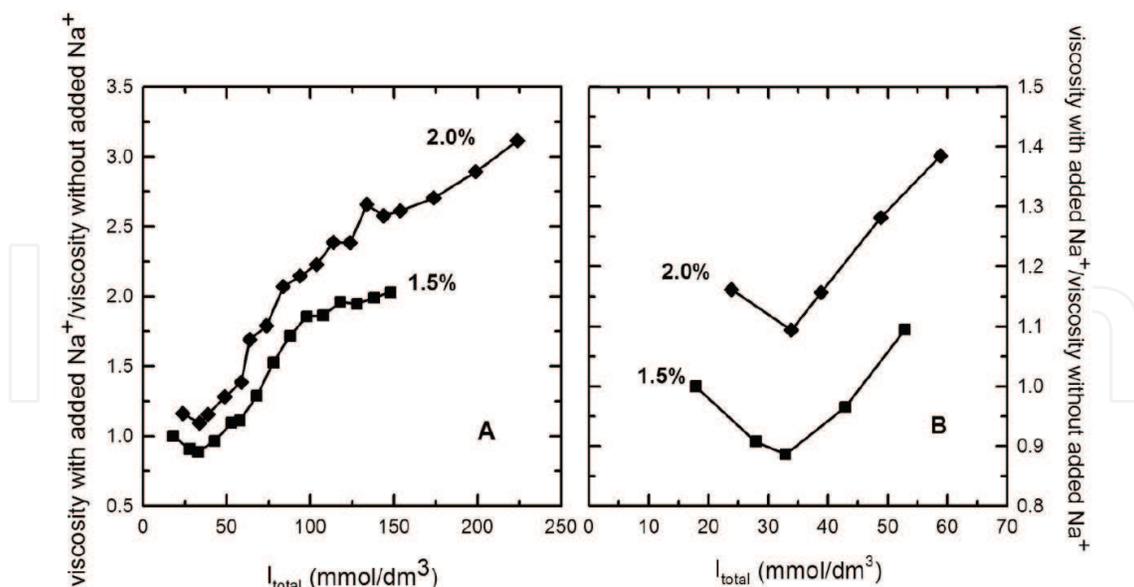


Figure 8. (A) Variation of the ratio of apparent viscosities with added Na^+ to apparent viscosities without added Na^+ with the total ionic strength for 1.5 and 2.0% λ -carrageenan solutions ($\dot{\gamma} = 9.5 \text{ s}^{-1}$). (B) Initial section of (A) corresponding to $I_{total} = 18\text{--}59 \text{ mmol/dm}^3$ ($0\text{--}70 \text{ mmol/dm}^3$ added Na^+). Lines are included as a visual guide.

Na^+ continued, a state would be reached in which precipitation of the polysaccharide chains would occur. It is worth noting that only the shear-thinning region was observed, and the infinite-shear Newtonian region was not observed. It is for this reason that the viscosities in **Figure 8** correspond to a shear rate in the former zone.

3.7. Intrinsic viscosity and critical concentration of λ -carrageenan solutions with added sodium counterion

The intrinsic viscosity of λ -carrageenan in a $20 \text{ mmol/dm}^3 \text{ Na}^+$ solution is 14.7 dL/g . Values reported in the literature are 9.5 dL/g in $100 \text{ mmol/dm}^3 \text{ NaCl}$ for $M_w = 614 \text{ kDa}$ [9], and 10.8 ($M_w = 870 \text{ kDa}$), 9.60 ($M_w = 730 \text{ kDa}$), 3.40 dL/g ($M_w = 340 \text{ kDa}$) in $100 \text{ mmol/dm}^3 \text{ NaCl}$, pH 7.0 [17]. The intrinsic viscosity of λ -carrageenan without added Na^+ decreased almost 93% with added Na^+ (20 mmol/dm^3). This reduction in $[\eta]$ suggests high flexibility of λ -carrageenan chains, since otherwise, the charge screening would not have been sufficient to decrease the hydrodynamic volume. The intrinsic viscosities were not determined for concentrations higher than $20 \text{ mmol/dm}^3 \text{ Na}^+$ because the viscosity of solutions with lower polysaccharide concentrations remained practically constant, regardless of the concentration of external Na^+ . It is possible to assume that $[\eta]$ of λ -carrageenan with added Na^+ is constant regardless of the amount of sodium ion present because in a 20 mmol/dm^3 solution, the stoichiometric ratio of sulfate groups/ Na^+ is satisfied and all charges in the polysaccharide chains are screened.

The critical concentration, C^* , of λ -carrageenan with 20 mmol/dm^3 added Na^+ was 0.38%. This value is higher than that for the solutions without added Na^+ . This behavior means that more polysaccharide chains are required for overlapping to occur. This phenomenon is essentially due to the decrease in hydrodynamic volume of the strands and compaction from a highly

expanded form to a coiled one. The physical state of the systems can be depicted as follows. In the dilute and semidilute regimes, without added Na^+ carrageenan chains are extended and stiff to some extent because of electrostatic repulsion between unscreened charges. Under an applied shear rate, the chains align themselves in the flow direction and overlap to a degree dependent on the solution regime. From 0.5% λ -carrageenan, semidilute regime, the chains overlap and under the action of shear rate, they align in such a way that the shear-thinning zone becomes important. In this flow region, the rate of formation of new entanglements would be lower than the shear rate. Therefore, the chains are oriented and isolated, which results in a decrease in viscosity. When Na^+ is added to solutions with low polysaccharide concentrations, e.g., from 0.002 to 0.01%, charge screening results in a reduction in hydrodynamic volume and the viscosity drops practically to that of the solvent. For solutions with 0.08% λ -carrageenan, the polysaccharide concentration is sufficient for the viscosity not to fall to that of the solvent. In the semidilute regime, 0.5, 0.8, and 1.0% λ -carrageenan, the chains fold and viscosity decreases. Further addition of external Na^+ makes cations accumulate in the medium without significant interaction with the polysaccharide. The effect of added Na^+ on the solutions with 1.5 and 2.0% λ -carrageenan is different from the rest. From very low concentrations of added Na^+ , viscosity, and dynamic moduli increase suggesting the formation of a semiordered, rigid, and elastic structure, due to the increase in the polysaccharide concentration and counterion and the intermolecular interactions of the polysaccharide with water and with added Na^+ .

3.8. Flow models of λ -carrageenan solutions with added sodium counterion

The Carreau-Yasuda model describes better the flow curves of λ -carrageenan without added Na^+ . The same happens with added Na^+ . However, it is not always possible to obtain proper fittings because, in most cases, the zero-shear region is not observed in the semidilute regime or the shear-thinning zone in the dilute regime. **Table 4** shows the experimental values of the parameters η_0 and a . However, λ and n values do not always follow the expected trend. For instance, in solutions with 0.8% λ -carrageenan one might expect that as the concentration of added Na^+ increases the non-Newtonian behavior becomes more accentuated, and n would

$C_{\lambda C}$ (%)	Na^+ (mmol/dm ³)	η_0 (Pa·s)	λ (s)	a	n	r^2
0.5	70	0.022	0.018	1.426	0.82	0.9945
	80	0.023	0.014	1.139	0.79	0.9994
0.8	20	0.087	0.014	0.801	0.61	0.9996
	30	0.080	0.023	0.990	0.69	0.9995
	50	0.077	0.021	0.931	0.67	0.9999
	70	0.073	0.020	0.888	0.65	0.9998
1.0	20	0.166	0.030	0.847	0.61	0.9990
	30	0.159	0.009	0.643	0.42	0.9986
1.5	20	0.658	0.046	0.691	0.47	0.9997

Table 4. Parameters of the Carreau-Yasuda model for different λ -carrageenan concentrations and added Na^+ .

decrease progressively. On the other hand, the power-law model cannot be applied to the flow curves of the solutions with added Na⁺ because the concavity exhibited by most of them in the shear-thinning region does not allow only this model to describe the entire flow region.

3.9. Master curves for mechanical spectra and steady flow

The mechanical spectra and flow curves can be expressed with their corresponding master curves for a constant concentration of added Na⁺ and λ-carrageenan concentrations of 0.002–2.0%. Two empirical shift factors were determined to produce each master curve. The factor

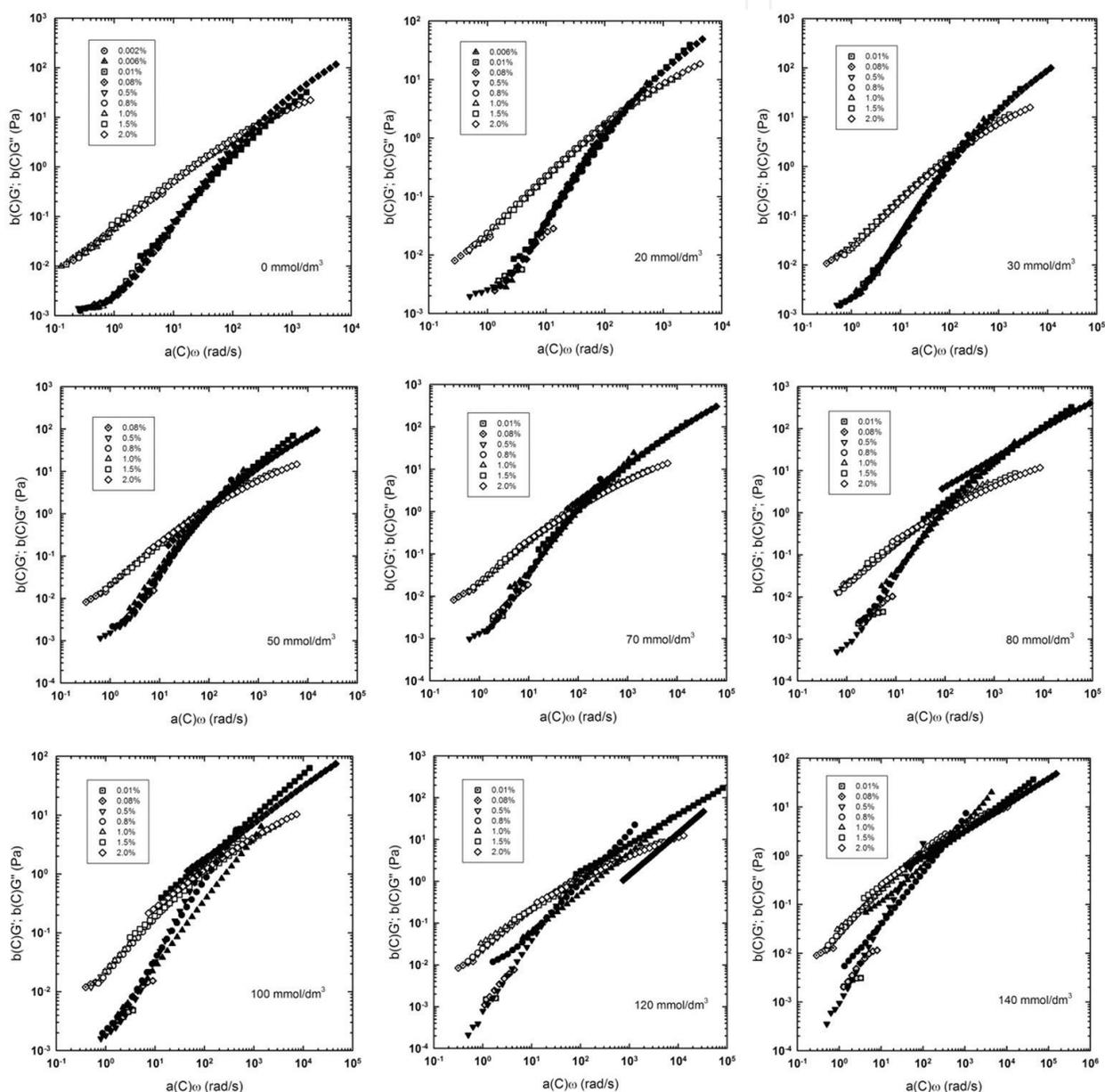


Figure 9. Master curves for the modified dynamic moduli as a function of the modified angular frequency for all λ-carrageenan solutions and different concentrations (mmol/dm³) of added Na⁺. The shift factors were determined as explained in the text. The complete range of total ionic strength is 0.024–94 mmol/dm³.

$a(C)$ modifies the x-axis, ω , or $\dot{\gamma}$, and the factor $b(C)$ the ordinate axis, $G'(\omega)$, $G''(\omega)$, or $\eta(\dot{\gamma})$. Here, (C) indicates that factors depend on polysaccharide concentration. These factors were determined by choosing 0.5% λ -carrageenan as a reference. The factors applied to the curves are the following:

$$a(C_1) = \frac{1}{n} \sum_{\omega_{\max}}^{\omega_{\min}} \frac{G'(C)}{G'(0.5\%)}; b(C_1) = \frac{G'(0.5\%) \forall \omega}{G'(C) \forall \omega} \quad (6)$$

$$a(C_2) = \frac{1}{n} \sum_{\omega_{\max}}^{\omega_{\min}} \frac{G''(C)}{G''(0.5\%)}; b(C_2) = \frac{G''(0.5\%) \forall \omega}{G''(C) \forall \omega} \quad (7)$$

The modulus G' is superposed by applying $a(C_1)$ to each frequency and $b(C_1)$ to G' . The same procedure is followed for the loss modulus using $a(C_2)$ and $b(C_2)$. In **Figure 9** the master curves of the dynamic moduli are presented. A proper overlapping of the loss moduli for concentrations of added Na^+ in the range 0–70 mmol/dm^3 is obtained along six decades of modified frequency. However, for higher added Na^+ concentrations (80–140 mmol/dm^3), the highest concentrations of polysaccharide show some deviation from the reference curve. This same behavior is observed for the storage modulus for 70 mmol/dm^3 added Na^+ . Superposition was difficult for high concentrations of added Na^+ (100–140 mmol/dm^3). The more the values of $\tan \delta = G''(\omega)/(G'(\omega))$ approach one, the more difficult is to produce a master curve for $G'(\omega)$. This behavior is only observed when the polysaccharide concentration is high (1.5 and 2.0%), but not when it is 0.5%.

The following shift factors are used to superimpose the flow curves:

$$a(C) = \frac{1}{n} \sum_{\dot{\gamma}_{\max}}^{\dot{\gamma}_{\min}} \frac{\eta(C)}{\eta(0.5 \text{ mM})}; b(C) = \frac{\eta_0(0.5 \text{ mM})}{\eta_0(C)} \quad (8)$$

As it happens with the mechanical spectra, the factor $a(C)$ modifies the shear rate and $b(C)$ the viscosity. The reference concentration was 0.5% because it was possible to observe the zero-shear and transition regions together with the shear-thinning zone. As shown in **Figure 10**, good superpositions are obtained for the flow curves from concentrations in the range of 0–70 mmol/dm^3 added Na^+ along seven decades of modified shear rate. As it happens with the master curves for $G''(\omega)$, it is hard to superimpose the flow curves for the highest polysaccharide concentrations (1.5–2.0%) with appropriately calculated shift factors along thirteen decades of modified shear rate. It was easier to superimpose the dynamic moduli and flow curves when systems were in the dilute regime; without added Na^+ , $C^* = 0.21\%$, and 20 mmol/dm^3 added Na^+ , $C^* = 0.38\%$, and low concentrations of added Na^+ . It is possible to assume that for high polysaccharide concentrations (1.5–2.0%) with added Na^+ , the dynamic moduli and viscosity increase as compared with systems without added Na^+ due to the entanglement of λ -carrageenan chains. This behavior is not observed for the reference concentration (0.5%) until concentrations higher than 100 mmol/dm^3 added Na^+ . This situation may explain the difficulty to superimpose the curves of such systems.

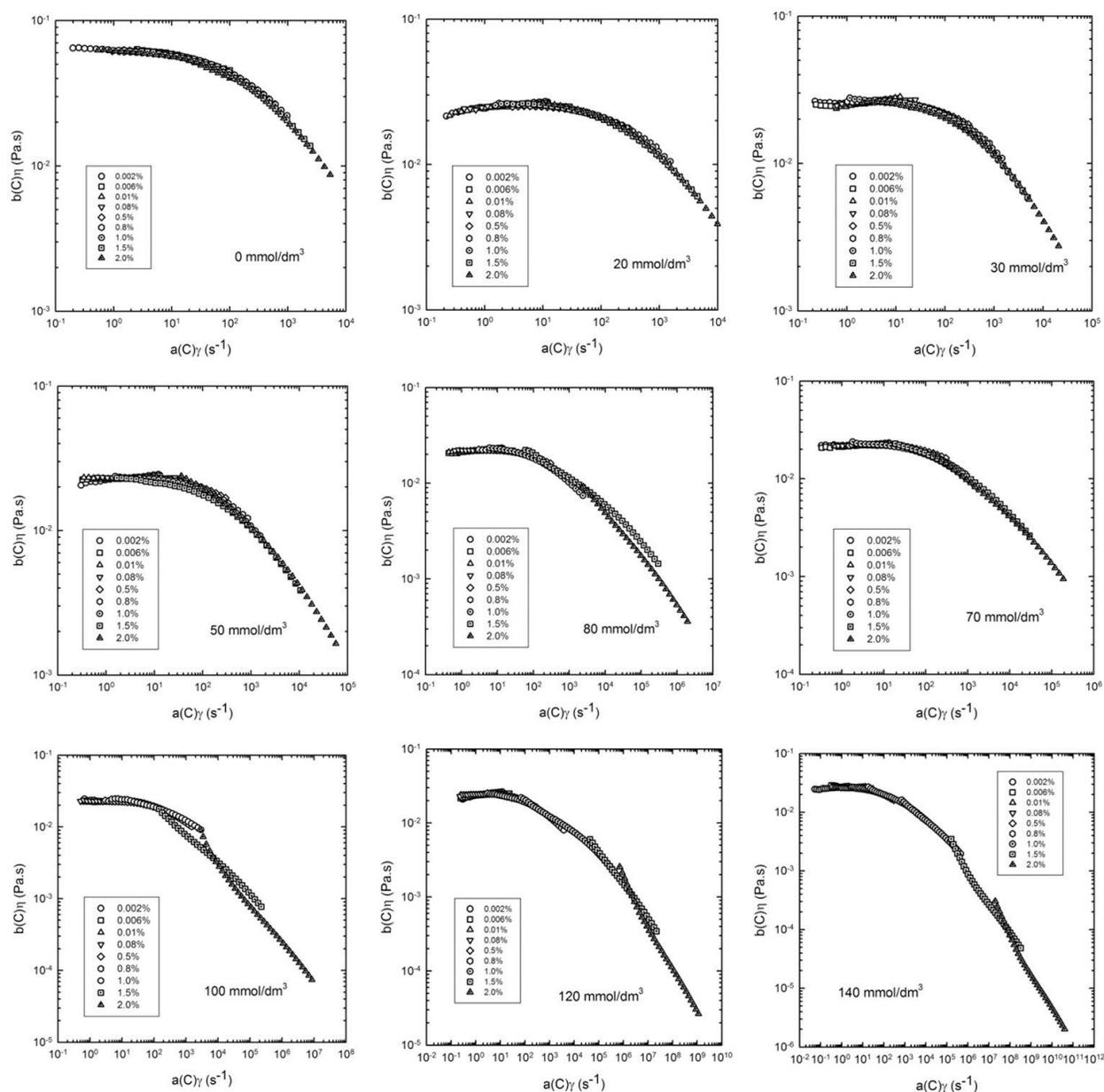


Figure 10. Master flow curves for all λ -carrageenan solutions and different concentrations (mmol/dm^3) of added Na^+ . The shift factors were determined as explained in the text. The complete range of total ionic strength is 0.024–94 mmol/dm^3 .

4. Conclusion

The results of this investigation make evident the high sensitivity of λ -carrageenan to the ionic strength of the aqueous environment, mainly given by the added Na^+ . This sensitivity is primarily attributed to the polyelectrolyte character of the polysaccharide, but hydration effects and competition for the solvent between the polyanion and sodium counterions can also play a role. The solutions of the commercial preparation of λ -carrageenan without and with added Na^+ are viscoelastic fluids with a dominant viscous behavior. However, with added Na^+ the elastic character becomes more important when the polysaccharide concentra-

tion increases. In the dilute regime, the viscous character is considerably more sensitive to the addition of Na^+ . In the semidilute regime, the opposite occurs as the addition of Na^+ affects more the elastic nature. Also, with added Na^+ , it is possible clearly to distinguish three types of behaviors of the apparent viscosity and the dynamic moduli. In the dilute regime and the low-concentration region of the semidilute regime, moduli decrease drastically when the total ionic strength increases slightly over that without added Na^+ and then remain substantially constant regardless of the increase in the total ionic strength. In the semidilute regime for moderate carrageenan concentrations, the moduli reach a minimum for intermediate total ionic strengths and then recover when the total ionic strength increases without necessarily achieve their values without added Na^+ . Finally, in the same semidilute regime but for large concentrations of polysaccharide, the moduli decrease as the total ionic strength increases slightly over that without added Na^+ and show a high recovery, which in the case of the storage moduli and the apparent viscosity significantly exceed their level without added Na^+ .

Considering all this evidence, the existence of different levels of structural organization of the polysaccharide chains together with their close interactions with them and with the solvent and the added Na^+ mainly can be postulated. Therefore, the results presented here allow the polyelectrolyte behavior of λ -carrageenan to be better understood for a significant range of polysaccharide concentrations under broad conditions of total ionic strength. These characteristics take relevance in the case of commercial preparations that under normal circumstances are used without further treatments, e.g., separation of accompanying counterions to produce a particular salt form of the polysaccharide. Such purified forms are used for more fundamental studies and would be the next step in the investigation of the flow properties of the polysaccharide.

The authors would like to acknowledge the financial support of Programa de Apoyo a la Investigación y el Posgrado (PAIP) of Facultad de Química-UNAM (Grant 5000-9098).

Author details

Andrea Rivera del Rio, Mariana Ramírez-Gilly and Alberto Tecante*

*Address all correspondence to: tecante@unam.mx

Department of Food and Biotechnology, Faculty of Chemistry, National Autonomous University of Mexico, Cd. Universitaria, CdMx, México

References

- [1] Niu TT, Dong-Sheng Z, Hai-Min C, Xiao-Jun Y. Modulation of the binding of basic fibroblast growth factor and heparanase activity by purified λ -carrageenan oligosaccharides. *Carbohydrate Polymers*. 2015;125:76–84. DOI: 10.1016/j.carbpol.2015.02.069
- [2] Chen H, Wang F, Mao H, Yan X. Degraded λ -carrageenan activates NF- κ B and AP-1 pathways in macrophages and enhances LPS-induced TNF- α secretion through

- AP-1. *Biochimica et Biophysica Acta*. 2014;1840(7):2162–2170. DOI: 10.1016/j.bbagen.2014.03.011
- [3] McHugh DJ. Carrageenan: A Guide to the Seaweed Industry. FAO Fisheries Technical Paper 441. [Internet]. 2003. Available from: <http://www.fao.org/docrep/006/y4765e/y4765e0a.html> [Accessed: 2016-05-30]
- [4] Commission of Codex Alimentarius. GSFA Online. Carrageenan (407). [Internet]. 2012. Available from: <http://www.codexalimentarius.net/gsfaonline/additives/details.html?id=49&lang=es> [Accessed: 2016-05-30]
- [5] Code of Federal Regulations. Title 21: Food and Drugs, Part 172 Food Additives Permitted for Direct Addition to Food for Human Consumption, Subpart G—Gums, Chewing Gum Bases and Related Substances. §172.620 Carrageenan [Internet]. 2013. Available from: www.wcfr.gov [Accessed: 2016-05-30].
- [6] van de Velde F, De Ruiter GA. Carrageenan. In: Steinbúchel A, Rhee SK, editors. *Polysaccharides and Polyamides in the Food Industry*. Weinheim: Wiley–Blackwell; 2005. pp. 85–111.
- [7] Eliasson A. *Carbohydrates in Food*. 2nd ed. Boca Raton: CRC Press; 2006. pp. 244–252.
- [8] De Lestang Bremond G, Quillet M, Bremond M. λ -Carrageenan in the gametophytes of *Chondrus crispus*. *Phytochemistry*. 1987;26(6):1705–1707.
- [9] Sloommaekers D, van Dijk JAPP, Varkevisser FA, Bloys van Treslong CJ, Reynaers H. Molecular characterization of κ - and λ -carrageenan by gel permeation chromatography, light scattering, sedimentation analysis and osmometry. *Biophysical Chemistry*. 1991;41:51–59.
- [10] Nosedá MD, Cerezo AS. Room temperature, low-field ^{13}C -N.M.R. spectra of degraded carrageenans: Part III. Autohydrolysis of a lambda carrageenan and of its alkali-treated derivative. *International Journal of Biological Macromolecules*. 1993;15:177–181.
- [11] Camacho MM, Martínez-Navarrete N, Chiralt A. Influence of locust bean gum/ λ -carrageenan mixtures on whipping and mechanical properties and stability of dairy creams. *Food Research International*. 1999;31:653–658.
- [12] Lizarraga MS, De Pianté D, González R, Rubiolo A, Santiago LG. Rheological behaviour of whey protein concentrate and λ -carrageenan aqueous mixtures. *Food Hydrocolloids*. 2006;20:740–748.
- [13] Bayarri S, Chuliá I, Costell E. Comparing λ -carrageenan and an inulin blend as fat replacers in carboxymethyl cellulose dairy desserts. Rheological and sensory aspects. *Food Hydrocolloids*. 2010;24:578–587.
- [14] Cross MM. Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems. *Journal of Colloid Science*. 1965;20:417–437.
- [15] Bird RB, Armstrong CR, Hassager O. *Dynamics of Polymeric Liquids*. Vol. 1 Fluid Mechanics. New York: John Wiley & Sons Inc.; 1987. 670 p.

- [16] Graessley W. The entanglement concept in polymer rheology. *Advances in Polymer Science*. 1974;16:164–179.
- [17] Almutairi FM, Adams GG, Kök MS, Lawson CJ, Gahler R, Wood S, Foster TJ, Rowe AJ. An analytical ultracentrifugation based system study on the conformation of lambda carrageenan in aqueous solution. *Carbohydrate Polymers*. 2013;97:203–209.

IntechOpen

IntechOpen