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Thermal, conformational and rheological properties of κ -carrageenan-sodium stearyl lactylate gels and solutionsM.C. Ortiz-Tafoya^a, Agnès Rolland-Sabaté^{b,c}, Catherine Garnier^b, Josefina Valadez-García^d, Alberto Tecante^{a,*}^a Departamento de Alimentos y Biotecnología, Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, CdMx, 04510, Mexico^b UR1268, INRA, Biopolymères Interactions Assemblages, F-44316 Nantes, France^c UMR408 Sécurité et Qualité des Produits d'Origine Végétale, INRA, Université Avignon, F-84000, Avignon, France^d Departamento de Bioquímica, Facultad de Medicina, Universidad Nacional Autónoma de México, Ciudad Universitaria, CdMx, 04510, Mexico

A B S T R A C T

Polysaccharide-surfactant blends are widely used in foods. However, their possible mutual interactions have not been extensively studied. The purpose of this work was to examine how the anionic surfactant sodium stearyl lactylate (SSL) affects different properties of κ -carrageenan solutions and gels. Rheometry, differential scanning calorimetry, asymmetrical flow field-flow fractionation coupled with multiangle laser light scattering, among others, were used to determine the flow and viscoelastic behavior, thermal transitions, and conformation changes, respectively. Interference caused by SSL is postulated as the primary factor to explain the variations in the conformation of κ -carrageenan in gels and solutions. However, electrostatic repulsions between κ -carrageenan and SSL can also be involved. These latter interactions are more important for high SSL concentrations (13 mmol dm⁻³) without addition of KCl, because of the higher net negative charge density of the system. SSL significantly modifies the properties of κ -carrageenan in aqueous media.

Keywords:

Carrageenan
DSC
Rheology
Surfactant
Sodium stearyl lactylate

1. Introduction

Polysaccharides and surfactants are used in dairy, meat and bakery products, among others, to stabilize emulsions and foams. Interactions between surfactants, proteins, and polysaccharides are of paramount importance in food and non-food applications. Research has primarily focused on mixtures of proteins and surfactants and to a lesser extent on blends of polysaccharides and non-food surfactants. Mixtures of chitosan with nonionic and anionic surfactants have been amply studied. Interactions between chitosan and nonionic surfactants like sorbitan monolaurate, sorbitan monooleate, sorbitan trioleate, octaethyleneglycol and mono *n*-dodecyl ether are weak and depend on the chitosan-surfactant concentration and chain length of surfactant (Chiappisi & Gradzielski, 2015; Grant, Cho, & Allen, 2006). Interactions between chitosan and anionic sulfated surfactants like sodium dodecyl sulfate, sodium lauryl ether sulfate, and sodium taurocholate are governed by hydrophobic interactions, although electrostatic interactions can also be present. Hydrogen bonds between chitosan and fatty acids can also exist, but hydrophobic interactions are more significant in the final behavior of these mixtures because of the contribution of the hydrocarbon chain of the acids. The degree of ionization of chitosan and fatty

acids changes with pH, and therefore these interactions are also pH dependent (Chiappisi & Gradzielski, 2015).

Mixtures of carrageenans with different surfactants have been studied to a lesser extent. κ , ι , and λ carrageenans mixed with cationic surfactants like N-dodecyl pyridinium chloride, N-cetylpyridinium chloride, and dodecyl ammonium chloride have been investigated. The type of carrageenan and surfactant concentration determine the behavior of the polysaccharide-surfactant complexes (Kogej, 2008), but it is mainly governed by electrostatic repulsions between oppositely charged species (Vinceković, Katona, Bujan, & Sovilj, 2011). However, the role of the physical characteristics of the polysaccharides in general, like molar mass, the degree of branching, charge density, the rigidity of the chain, and polar group and chain length of surfactants, should be examined. It is also essential to know the impact of the sol-gel-sol transition temperatures and the sensitivity of the polysaccharide to mono or divalent ions. All this knowledge would facilitate the development of new and more stable products and create the conditions for the components to express their functionalities (Bouyer, Mekhloufi, Rosilio, Grossiord, & Agnely, 2012).

κ -carrageenan is a sulfated D-galactan polysaccharide. Its primary structure consists of a repeating disaccharide of alternate (1 → 3)

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β - D-galactose-4-sulfate and (1 \rightarrow 4) α -3,6-anhydro-D-galactose. It is used in the food industry as a stabilizer and gelling agent. Its gels are stiff, brittle, exhibit syneresis and thermal hysteresis. Gelation occurs when hot solutions are cooled and involves a coil-helix transition followed by helix aggregation (De Ruiter & Rudolph, 1997). The coil to double helix transition is the key step for gelation to occur. Moreover, gelation is very sensitive to salts and can be controlled by the presence of specific cations like K^+ , Cs^+ , and Rb^+ , since they increase the double helix stability and mediate helix-helix aggregation. Double helix aggregation occurs at a critical temperature, and its value depends on concentration and type of cation present (Rochas & Rinaudo, 1984).

Sodium stearoyl lactylate (SSL) is an anionic surfactant synthesized from fatty acids and lactic acid in the presence of sodium (Boutte & Skogerson, 2004). It is formed by a hydrophilic charged head coming from ionic lactic acid and a long hydrophobic hydrocarbon tail from stearic acid (Grigoriev, Leser, Michel, & Miller, 2007). Commercial SSL is mainly a mixture of 50% stearoyl-1-lactylate (SSL1), 20% stearoyl-2-lactylate (SSL2), and 5% stearoyl-3-lactylate (SSL3) (Boutte & Skogerson, 2004). SSL is widely used in the food industry as an emulsifier in meat products, and as a whipping agent and softener in bakery products (Zinoviadou, Moschakis, Kiosseoglou, & Biliaderis, 2011). All the components of SSL exhibit different interfacial activities; as an example, the larger hydrophilic head group of SSL2 makes it less surface active than SSL1 (Grigoriev, Leser, Michel, & Miller, 2006).

The goal of this work was to determine how SSL, a surfactant applied for food use, affects the conformation and physicochemical properties of κ -carrageenan. The information obtained will serve to understand the behavior of polysaccharide-surfactant mixtures to use it in the development of more complex systems.

2. Materials and methods

Food-grade κ -carrageenan (Ingredients Solutions, USA) was used without further purification. Its molar mass (see Section 2.4) was 308 366 g mol⁻¹. Its potassium, sodium, calcium and magnesium contents determined by atomic absorption spectroscopy were 62 100, 21 513, 1301 and 5.2 ppm, respectively. KCl (Merck, Mexico) and NaCl (AppliChem, Germany) were reagent grade. Food-grade sodium stearoyl lactylate (SSL, CAS: 25383-99-7; EC: 246-929-7; Palsgaard, Denmark) was used with potassium, sodium, calcium and magnesium contents of 1230, 21 710, 118 and 1.4 ppm, respectively; and a measured critical micellar concentration (CMC) of 0.893 mmol dm⁻³. Deionized water was used in all experiments.

2.1. Preparation of κ -carrageenan solutions and gels

κ -carrageenan was dispersed in deionized water under stirring for 30 min at room temperature. After complete dispersion, the surfactant was added to obtain concentrations of 0–1.0% (g/100 g), and the mixture was stirred for 15 min more. Next, the mixture was heated to 92 °C for 10 min. The hot solutions were cooled to 50 °C. Evaporative losses were compensated by the addition of deionized water. In systems with KCl, the salt was added when the temperature reached 92 °C. In this case, gels were formed on cooling.

2.2. Differential scanning calorimetry (DSC)

The thermal transitions of 0.5% κ -carrageenan gels and solutions were determined using a microcalorimeter (μ DSC 7 Evo, Setaram, France). A mass of 600 \pm 10 mg of sample was weighed into a Hastelloy cell. The reference cell contained an equivalent mass of sample solvent. Both cells were equilibrated for 30 min and then heated from 5 to 80 °C, held at 80 °C for 10 min, cooled at 5 °C, and kept at this temperature for 10 min, in three heating-cooling cycles. The heating and cooling rates were 0.8 °C min⁻¹. Melting and gelation temperatures and enthalpies were determined with commercial software (OriginPro

9.1, OriginLab Corporation, USA). Enthalpies were expressed in J g⁻¹ of dry matter.

2.3. Zeta potential

Zeta potentials of κ -carrageenan solutions and their blends with SSL were measured at 20 °C with a Zeta Meter 3.0+ (Zeta-Meter, Inc., USA) equipped with a microprocessor unit. κ -carrageenan solutions were diluted to 0.1% (w/w). Blends with surfactant were diluted to 0.01% (w/w) SSL. pH was measured at 20 °C with a potentiometer (Thermo Scientific Orion, model 420A, Cole-Parmer, USA). The sample was placed in a cell, and electrophoretic mobility of charged particles was measured by tracking their displacement in an electric field with a stereoscopic microscope. Zeta potential (mV) was calculated by the microprocessor unit. Average values obtained by tracking at least twenty different particles are reported.

2.4. Asymmetrical flow field-flow fractionation coupled with multiangle laser light scattering (AF4-MALLS)

Molar mass, size, and conformation were analyzed by AF4-MALLS. The AF4 channel flow, cross flow, sample injection and focus flow were controlled with a Wyatt Eclipse AF4 flow chassis (Wyatt Technology Corporation, Santa Barbara, USA), a pump and an autosampler (ThermoFisher Scientific; Waltham, MA, USA). The sample was introduced at 25 °C into a 275 mm long trapezoidal channel equipped with a spacer of 350 μ m thickness and a regenerated cellulose membrane with a nominal cut-off of 10 kDa (Millipore, Bedford, MA, USA). The on-line detectors included a MALLS unit (Dawn[®] HELEOS[™]) fitted with a K5 flow cell and a He-Ne laser (λ = 658 nm), and a refractometer (Optilab T-rEX) operating at the same wavelength (Wyatt Technology Corporation). κ -carrageenan concentrations were 0.15 and 0.05% for samples without and with SSL, respectively. All samples were filtered through a 0.45 μ m membrane (Millipore) before injection. Injection volumes were 65 and 100 μ L of κ -carrageenan solutions or mixtures with the surfactant, respectively. The carrier, 100 mmol dm⁻³ NaCl (Millipore), was filtered through a 0.1 μ m membrane (Millipore) and eluted initially at 1 mL min⁻¹ in the channel. κ -carrageenan samples were eluted following a procedure adapted from Bourgoin, Zablackis, & Poli (2008). The cross-flow was set to 0.8 mL min⁻¹ and the sample was injected at 0.20 mL min⁻¹ for 300 s. After injection, the sample was left to relax and focus on 120 s. The carrier flow was set to 1 mL min⁻¹ for elution, and the cross flow decreased from 0.8 mL min⁻¹ to 0.05 mL min⁻¹ for 40 min, maintained at this value for 3 min, and finally kept at 0 mL min⁻¹ for 2 min. Elution recovery rates were calculated from the ratio of the mass eluted from the channel, given by the integration of the differential refractive index signal, and the injected mass. The latter was obtained from the exact concentration in the injected samples determined by desiccation of 5 g of sample at 100 °C for 24 h.

The number-average molar mass, \overline{M}_n , the weight-average molar mass, \overline{M}_w , the dispersity, $\overline{M}_w/\overline{M}_n$, and the z-average radius of gyration (nm), \overline{R}_G , were obtained with ASTRA[®] software (Wyatt Technology Corporation; version 6.1.2.84 for PC) as previously described for other polysaccharides (Rolland-Sabaté, Colonna, Mendez-Montealvo, & Planchot, 2007; Rolland-Sabaté, Guilois, Jaillais, & Colonna, 2011). The refractive index increment, dn/dc, for glucans was 0.146 mL g⁻¹. The molar mass and radius of gyration of the *i*th slice, M_i , and $R_{G,i}$, respectively, were obtained for each slice of the chromatogram peak using the Berry extrapolation with a first order polynomial fit of the light scattered to zero angle.

2.5. Atomic force microscopy (AFM)

κ -carrageenan gels and its mixtures with 0.5 and 1.0% SSL were prepared as described in 2.1. Before cooling, they were diluted with hot

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(85 °C) deionized water to a final concentration of 20 µg mL⁻¹. A 0.04% (w/w) SSL solution was prepared in water at 55 °C under mechanical stirring and was not diluted. Aliquots of 5 µL of each sample were deposited on mica (diameter 20 mm), then onto a magnetic disc, dried at room temperature and relative humidity for at least 30 min, and observed. Each sample was scanned over an area of 10 µm² at a rate of 1 Hz and 256 lines in an Innova Scanning Probe microscope (Veeco Instruments Inc., USA) equipped with a Nanodrive 8.02 controller. The tapping mode was employed using a scanning probe (RTESPA-CP; Bruker, USA) with a constant force and a resonance frequency of 40 N m⁻¹ and 300 kHz, respectively. Imaging was made at room conditions. AFM data were processed with the Nanoscope Analysis 1.40 software (Bruker, USA) and edited with the Gwyddion 2.49 software (Czech Republic).

2.6. Rheometry

Rheological properties were determined using a rotational rheometer (ARES-RFS III, TA Instruments, USA). Flow curves of κ-carrageenan solutions without KCl were obtained from 0.01–100 s⁻¹ at 25 °C in a cone-plate fixture, 50 mm in diameter, cone angle 2.3° (0.04 rad) and 40.6 µm gap. Viscoelastic properties of gels with KCl and solutions were determined under low-amplitude oscillatory shear from 0.1–100 rad s⁻¹ at 25 °C using serrated parallel plates, 25 mm in diameter, 3 mm gap. The zone of linear viscoelasticity was established from strain sweeps at 6.28 rad s⁻¹. Solutions were stored at 4 °C at least 18 h before the rheological measurements. The dependence of the dynamic moduli G' and G'' with angular frequency, ω, was determined by power-law relationships of the type G' ∝ ω^α and G'' ∝ ω^β.

2.7. Statistical analysis

All measurements were made in triplicate. A one-way ANOVA was done with commercial software (Microsoft® Office Excel® 2007, 12.0.6750.5000). Differences between treatment means were obtained by Fisher's least significant difference (LSD) procedure, using Eq. (1).

$$LSD = t \sqrt{\frac{2MS_E}{n}} \quad (1)$$

In this equation, t is the Student's t-distribution percentile based on the error degrees of freedom at α = 0.05 level of significance, n is the number of scores in each treatment sample, and MS_E is the mean squared error for the ANOVA.

3. Results and discussion

3.1. DSC thermal behavior

3.1.1. Gelation and melting in the presence of SSL and KCl

DSC experiments allowed obtaining the transition temperatures, melting enthalpy, ΔH_m, and the absolute value of gelation enthalpy, |ΔH_g|, of κ-carrageenan chains in the presence and absence of potassium ions. All these parameters decreased with the increase in SSL concentration as shown in Fig. 1.

The transition temperatures (T_m = 39.8 °C; T_g = 28.0 °C), and enthalpies (ΔH_m = 36.1 J g⁻¹; ΔH_g = 33.9 J g⁻¹) of κ-carrageenan gels were similar to those previously reported (Núñez-Santiago & Tecante, 2007). The melting and gelation enthalpies were similar, showing that comparable energy was required for double helix aggregation and melting of the aggregates. Thermal hysteresis, i.e., T_m > T_g, similar to that observed by Gekko, Mugishima, & Koga (1987) was present. They observed a difference of 10 °C between melting and gelation transitions in mixtures of κ-carrageenan with 25 mmol dm⁻³ KCl. This result was attributed to the cooperative nature of gelation, i.e., the formation of the first helix facilitates the development of new helices. Thermal

hysteresis has been associated with helices aggregation above a total ionic concentration, C*, of 7 mmol dm⁻³. Below this concentration, this effect is not observed because only a coil-helix transition takes place (Núñez-Santiago & Tecante, 2007).

The addition of SSL decreased the transition temperatures of gels as shown in Fig. 1a. However, melting exhibited three different zones; 1, 2, and 3, for concentration ranges of 0–5.3, 5.3–11, and 11–27 mmol dm⁻³, respectively. The gelation temperatures had a single-slope linear decrease for 0–27 mmol dm⁻³ SSL. The linear correlations are given by Eqs. (2)–(5) with C_{SSL} units as shown in Fig. 1, the slope in °C dm³ mol⁻¹, and the ordinate in °C.

Melting

$$\text{Zone1 } T_{m1} = -443C_{SSL} + 39.8 \quad r=0.9834 \quad (2)$$

$$\text{Zone2 } T_{m2} = -174C_{SSL} + 38.5 \quad r=0.9941 \quad (3)$$

$$\text{Zone3 } T_{m3} = -93.5C_{SSL} + 37.4 \quad r=0.9547 \quad (4)$$

Gelling

$$\text{Zone1 } T_{g1} = -123C_{SSL} + 28.0 \quad r=0.9989 \quad (5)$$

The rate of decline of transition enthalpies was linear but depended on the range of surfactant concentration. ΔH_m decreased seven times faster in the range of 0–5.3 mmol dm⁻³ (Zone 1) than in the range of 5.3–27 mmol dm⁻³ (Zone 2) (Fig. 1b). On the other hand, |ΔH_g| dropped three times faster in Zone 1 than in Zone 2. The linear relationships between transition enthalpy and surfactant concentration are given by Eqs. (6)–(9) with C_{SSL} in mmol dm⁻³, the slope in J dm³ g⁻¹ mol⁻¹, and the ordinate in J g⁻¹.

Melting

$$\text{Zone1 } \Delta H = -3291C_{SSL} + 35.5 \quad r=0.9940 \quad (6)$$

$$\text{Zone2 } \Delta H = -453C_{SSL} + 20.2 \quad r=0.9735 \quad (7)$$

Gelling

$$\text{Zone1 } \Delta H = -1987C_{SSL} + 34.1 \quad r=0.9903 \quad (8)$$

$$\text{Zone2 } \Delta H = -663C_{SSL} + 25.9 \quad r=0.9763 \quad (9)$$

These variations show that the surfactant had a significant impact on the melting process, and the behavior shown in Fig. 1a and b can be interpreted as the result of a lower degree of association between κ-carrageenan molecules. This action suggests the existence of a less dense aggregation leading to the destabilization of the κ-carrageenan gel network.

The melting process is noticeably affected by the surfactant, and significant changes occur below 5.3 mmol dm⁻³. The differences between melting and gelation temperatures can be explained by the aggregation of double helices. It is evident that gelation in the presence of KCl is less affected by SSL, perhaps due to the cooperative nature of carrageenan gelation but also to the mobility of the SSL molecules at the gelation temperature which improves the formation of the network. Besides, the addition of surfactant decreases progressively the thermal hysteresis which means less aggregation of helices. It has been shown that the gradual addition of glycerol, erythritol, xylitol, sorbitol, maltitol and carbohydrates like ribose, xylose, mannose, galactose, fructose, maltose and sucrose to κ-carrageenan and 25 mmol dm⁻³ KCl, increased gelation temperatures but decreased the absolute values of ΔH_g (Gekko et al., 1987). The authors attributed this unusual behavior to polymer-solvent interactions because in general, absolute values of ΔH_g increase with the increment in KCl and other salts concentration. Changes in polymer-solvent interactions modify electrostatic, hydrophobic and hydrogen bond interactions of the κ-carrageenan network, and therefore its physicochemical properties (Gekko et al., 1987).

3.1.2. Behavior in the presence of SSL without KCl

The thermal behavior of κ-carrageenan, without added KCl, in the

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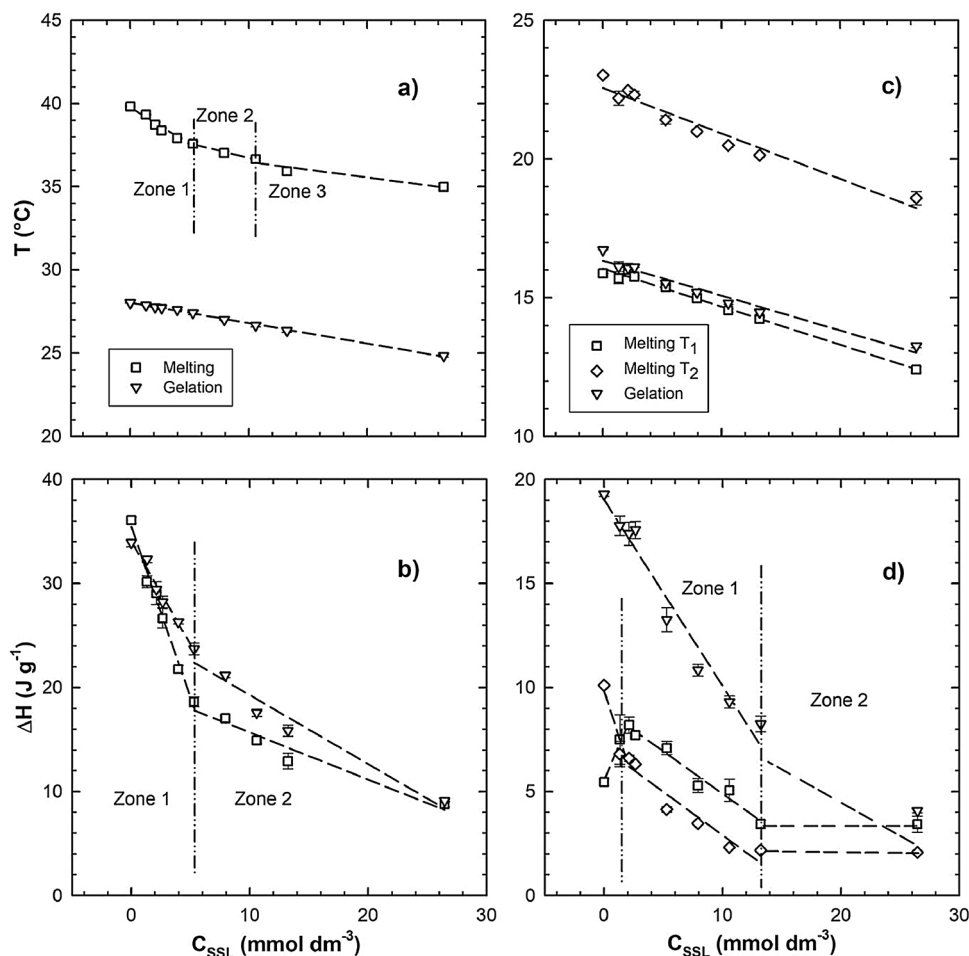


Fig. 1. Variation with SSL concentration of transition temperatures and enthalpies of 0.5% (w/w) κ -carrageenan gels with 13 mmol dm^{-3} KCl, (a), (b), respectively, and without KCl, (c), (d), respectively. Melting (squares and diamonds), gelation (inverted triangles).

presence of SSL was similar to that of gels. There was a reduction in transition temperatures and enthalpies as in gels as shown in Fig. 1c and d, respectively. However, two transition peaks, (not shown), were observed on melting, in all the mixtures. The first peak, designated here as Melting T_1 , can be attributed to disaggregation of double helices and the second, Melting T_2 , to the unwinding of double helices to separate coils. Double helices exist as aggregates when the ionic concentration, C_T , of K^+ counterions is higher than the critical concentration C^* . For κ -carrageenan, $C^* = 7.1 \text{ mmol dm}^{-3}$ (Rochas & Rinaudo, 1984). C_T for the solutions analyzed here was calculated from the concentration of K^+ ions, obtained by atomic absorption, in the samples of κ -carrageenan and SSL. The values are between 14.35 and $14.67 \text{ mmol dm}^{-3}$ without SSL and with the maximum SSL concentration, respectively, due to the intrinsic potassium content of the samples. On the other hand, for an ionic concentration of 5 mmol dm^{-3} KCl, the amount of helical dimmers and single helices was estimated to be 35 and 65%, respectively (Rochas and Landry, 1987). Considering our atomic absorption data, the ionic concentration in a 0.5% (w/w) κ -carrageenan solution is $7.9 \text{ mmol dm}^{-3} K^+$. These facts mean that in all the κ -carrageenan solutions, aggregates and double helices can coexist.

The presence of these conformations, i.e., double helices and their aggregates, explains the two transitions on heating. Moreover, as indicated in Section 2, the commercial sample of κ -carrageenan used in this work was not purified. The appearance of two transition peaks could also be due to the possible presence of ι -carrageenan as a minor component. However, NMR analysis (data not shown) showed 93% κ -carrageenan and 7% ι -carrageenan in the sample. Therefore, the contribution of ι -carrageenan was considered marginal, since in the

solutions its concentration is lower than 0.04%.

The effect of SSL concentration on the transition temperatures followed the same general trend for melting and gelation. In the entire concentration range, 0 – 27 mol dm^{-3} , there was a single-slope decrease. The corresponding equations with the same units as (2–5) are:

$$\text{Melting } T_1 \quad T_{m1} = -137C_{SSL} + 16.0 \quad r=0.9938 \quad (10)$$

$$\text{Melting } T_2 \quad T_{m2} = -164C_{SSL} + 22.6 \quad r=0.9740 \quad (11)$$

$$\text{Gelling} \quad T_g = -125C_{SSL} + 16.3 \quad r=0.9808 \quad (12)$$

The addition of SSL had a more significant effect on gelation because ΔH_g decreased twice faster than each ΔH_m . Changes in the enthalpies of gelation and melting transitions did not occur over the same SSL concentration range; 0 – 13 mmol dm^{-3} for gelation, 2.1 – 13 mmol dm^{-3} for melting (Fig. 1d, Zone 1 and before). Below 2.1 mmol dm^{-3} , Fig. 1d, before zone 1, the behavior of enthalpy for both melting processes was different. For Melting T_1 , enthalpy increased, but for Melting T_2 there was a reduction. Eqs. (13)–(15) show the relationships between enthalpy and SSL concentration with the same units as in Eqs. (6)–(9):

$$\text{Melting } T_1 \quad \Delta H = -407C_{SSL} + 9.0 \quad r=0.9849 \quad (13)$$

$$\text{Melting } T_2 \quad \Delta H = -417C_{SSL} + 7.1 \quad r=0.9612 \quad (14)$$

$$\text{Gelling} \quad \Delta H = -896C_{SSL} + 19.3 \quad r=0.9831 \quad (15)$$

From all these results, modification of the conformation of κ -carrageenan in gels and solutions by SSL is evident regardless of the

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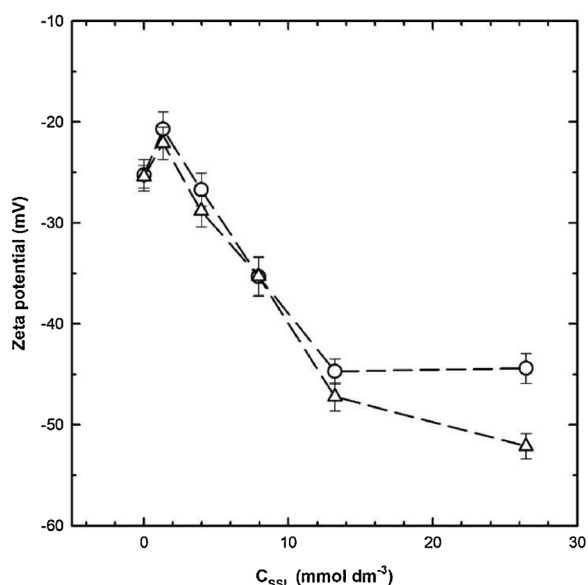


Fig. 2. Variation of the zeta potential of 0.5% (w/w) κ -carrageenan solutions with different SSL concentrations at 20 °C, without KCl (triangles) and with 13 mmol dm⁻³ KCl (circles).

differences in thermal behavior between these systems. In this way, the SSL changes the spatial arrangement of κ -carrageenan. This phenomenon can be explained by the occurrence of hindrance caused by SSL in both systems. The aggregation of κ -carrageenan double helices is hindered by SSL, which explains the decrease of the melting enthalpy; but, over a specific surfactant concentration, surfactant molecules can aggregate causing a drop of melting enthalpy to a lesser extent than below such level.

Another possibility to explain the behavior of κ -carrageenan in the presence of SSL is the existence of electrostatic repulsion between both components as they are negatively charged. This effect occurs in solutions and gels because negative charges are not entirely screened by the positive charges of the counterions (Fig. 2).

Negative charges are in excess, either with or without KCl, and the addition of SSL increases the negative charge density. However, this behavior tends to be stable for high SSL concentrations (13 mmol dm⁻³), probably due to aggregation of SSL molecules into micelle-like structures. The overall negative charge density is higher without KCl than with the salt, because of the screening effect of potassium ions. The combination of hindrance and electrostatic repulsion could explain the behavior differences between solutions and gels. In both systems, a decrease of enthalpies and transition temperatures occurs. However, in the solutions, the decline is continuous throughout the range of concentrations, while in the gels it happens above 5.3 mmol dm⁻³ SSL.

3.2. Size, molar mass and conformation in solution

Table 1 shows the size, molar mass, and dispersity of κ -carrageenan and its mixtures with SSL, using NaCl as an eluant. The molar mass of 3.08·10⁵ g mol⁻¹ found for κ -carrageenan without surfactant agrees

Table 1

Elution recovery, weight average molar mass (\overline{M}_w), z-average radius of gyration (\overline{R}_G), dispersity ($\overline{M}_w/\overline{M}_n$), and Flory exponent (ν) of κ -carrageenan solutions obtained by AF4-MALLS.

κ -carrageenan (%)	SSL (%)	Elution recovery (%)	$\overline{M}_w \cdot 10^{-5}$ (g mol ⁻¹)	\overline{R}_G (nm)	$\overline{M}_w/\overline{M}_n$	ν
0.15	0.0	83	3.08 ± 0.16	56 ± 2.1	1.4 ± 0.01	0.60 ± 0.02
0.05	0.004	89	4.64 ± 0.13	75 ± 4.4	1.3 ± 0.18	0.50 ± 0.02
0.05	0.017	67	12.92 ± 1.03	157 ± 20.3	2.9 ± 0.74	0.48 ± 0.02

with those reported on other samples in 100 mmol dm⁻³ NaCl (Wittgren, Borgström, Piculell, & Wahlund, 1998; Bourgoïn et al., 2008). The molar mass and the radius of gyration increase clearly with SSL concentration. These results suggest that a change in the aggregation state of κ -carrageenan macromolecules occurs, as they appear more prominent in the mixtures with SSL, especially for the highest surfactant concentration.

This phenomenon is probably due to polymer-surfactant interactions. These data show the same general trend than the one observed in separate mixtures of bovine serum albumin (BSA) with sodium dodecyl sulfate (SDS), dodecyl trimethylammonium bromide (DTAB) and polyoxyethylene 8 lauryl ether (C12E8), which are anionic, cationic and nonionic surfactants, respectively. That is to say, the increase in the hydrodynamic radius of BSA compared to the hydrodynamic radii of the BSA-surfactants complexes, when the surfactant concentration increased. Such behavior has been attributed to cooperative binding of surfactants, which means that binding of one ligand enhances the affinity of the protein for subsequent ligands (Valstar, Almgren, Brown & Vasilescu, 2000). Light scattering has also been used to study the behavior of individual blends of a capsular anionic bacterial polysaccharide with the cationic surfactants benzyl dimethyl-*n*-hexadecyl ammonium chloride (BDHAC), cetyltrimethylammonium bromide (CTAB), cetyl pyridinium chloride (CPC) and dodecyl pyridinium chloride (DPC). The variation of the hydrodynamic radius with surfactant concentration exhibited a maximum. This behavior was attributed to aggregation derived from polysaccharide-surfactant complexation by electrostatic attraction between both components. Beyond the maximum, the decrease in hydrodynamic radius was explained by coiling up of the polysaccharide resulting from its charge neutralization (Dasgupta, Nath, Manna, Mitra, & Panda, 2014).

The dispersities of κ -carrageenan without surfactant and with 0.004% SSL were similar (≈ 1.4). However, for the maximum SSL level, a higher dispersity was obtained, indicating a broader size distribution, also shown in the cumulative molar mass distribution (Fig. 3), which highlights a considerable proportion of high molar masses in the solution with 0.017% SSL.

This result could be due to macromolecule association caused by polymer-surfactant interactions. It is also in line with the lower elution recovery observed for κ -carrageenan with the maximum SSL level (67% instead of 83 and 89% for κ -carrageenan without SSL and with the minimum SSL level, respectively), which could correspond to the retention of the major macromolecular structures in the AF4 channel.

Table 1 also includes values of the Flory exponent (ν), calculated by linear regression of the log-log plot of R_{Gi} versus M_i , according to $R_{Gi} = K M_i^\nu$, where K is a constant. For a swollen linear polymer, ν is around 3/5. The exponent is used to determine whether the polymer is in a suitable solvent. In such case, polymer-solvent interactions are more favorable than polymer-polymer interactions (Rubinstein & Colby, 2003). In κ -carrageenan solutions without SSL, polysaccharide chains are in a suitable solvent ($\nu = 0.60$). The addition of surfactant decreased the value of ν to about 0.50 for both conditions. For this value of the Flory exponent, theta conditions exist, i.e., the polysaccharide is on the border between good and poor solvent. In the theta state, the solvent has a minimal solvation effect on the polymer molecules, i.e., the polymer is becoming insoluble (Su, 2013).

These results suggest a change in polymer-solvent interactions

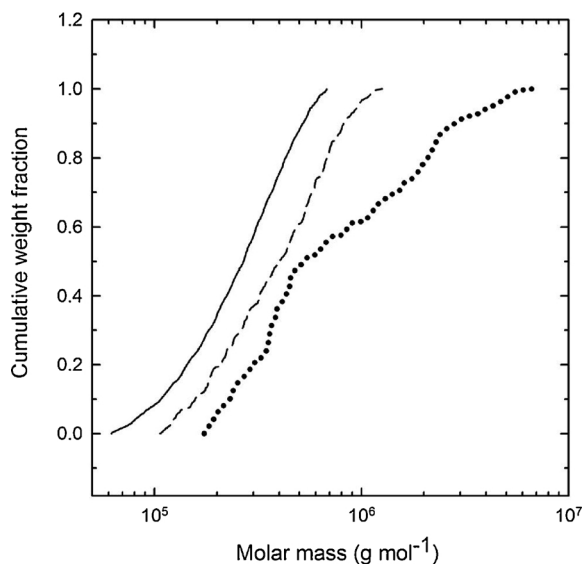


Fig. 3. Cumulative molar mass distributions obtained by AF4-MALLS of 0.5% (w/w) κ -carrageenan solutions without SSL (continuous line), with 0.004 and 0.017% SSL (dashed and dotted line, respectively).

probably due to electrostatic interactions between κ -carrageenan and SSL, which can cause compaction of polymer chains and therefore a modification in their conformation.

3.3. Rheological behavior

3.3.1. Gels

Frequency sweeps for κ -carrageenan gels with different SSL concentrations are shown in Fig. 4a. The slopes of G' and G'' were found to increase with SSL concentration; $\alpha = 0.032$ - 0.078 with $r > 0.9669$, and $\beta = 0.125$ - 0.167 with $r > 0.9109$, respectively. This variation means that both dynamic moduli were more frequency dependent as SSL concentration increased. Therefore, the presence of SSL intensified the viscous character of κ -carrageenan gels, showing a less organized network. This effect is also evidenced by the disappearance of the plateau in G' at low frequency for the highest SSL concentration.

Also, the elastic character of the gels decreased, i.e., the loss angle, δ , increased from 3.7 to 8.4° for 27 mmol dm^{-3} SSL. These features can be observed in Fig. 4b. For concentrations below 4 mmol dm^{-3} , G' at 1 rad s^{-1} decreased as SSL concentration increased. Above this concentration, changes were not significant. G'' exhibited the same behavior for κ -carrageenan without SSL and with 1.3 mmol dm^{-3} . However, for 13 and 27 mmol dm^{-3} SSL, G'' increased with the frequency which means an accentuation of the viscous behavior of the systems.

3.3.2. Solutions

The κ -carrageenan solutions exhibited a typical macromolecular behavior (Fig. 5a), i.e., G'' was greater than G' and both moduli were highly dependent on frequency (Doublier, Garnier & Cuvelier, 2016). As in the gels, G' and G'' decreased as SSL concentration increased, but for the highest level, 27 mmol dm^{-3} , both moduli increased. The evolution of the apparent viscosity of κ -carrageenan solutions, Fig. 6a, was like that of the dynamic moduli. All solutions exhibited shear-thinning behavior, i.e., the apparent viscosity decreased as shear rate increased. It is well known that the viscosity of polyelectrolyte solutions decreases with the increment of salt concentration because there is a compaction of the polymer chain due to the screening of the electrostatic repulsions between charges along the chain by the counterions (Wyatt, Gunther, & Liberatore, 2011). This effect explains the reduction of the apparent viscosity with the increment of SSL concentration in agreement with the light scattering results. Increases in G' , G'' and η for the κ -carrageenan

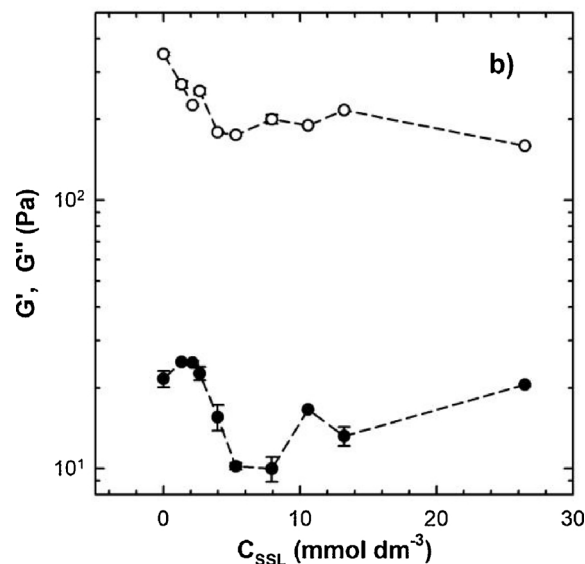
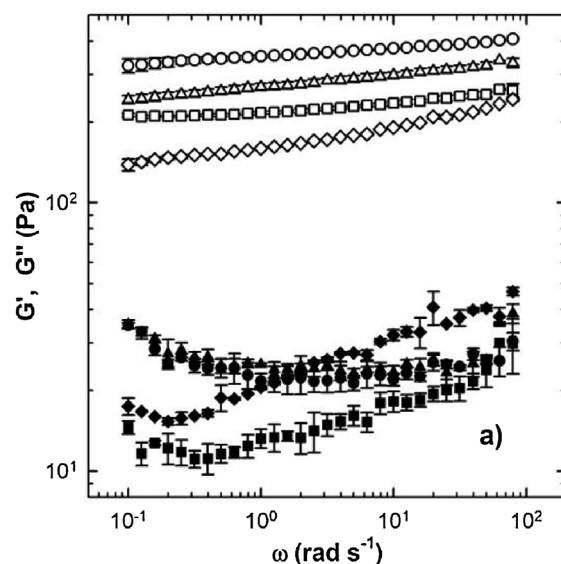


Fig. 4. a) Variation of G' (open symbols) and G'' (filled symbols) with angular frequency (ω) of 0.5% (w/w) κ -carrageenan gels with 13 mmol dm^{-3} KCl, and without SSL (circles), 1.3 mmol dm^{-3} (triangles), 13 mmol dm^{-3} (squares), and 27 mmol dm^{-3} (diamonds) at 25°C ; b) Variation of G' and G'' with SSL concentration at $\omega = 1 \text{ rad s}^{-1}$ and 25°C .

solution with 27 mmol dm^{-3} SSL are due to the surfactant concentration. Indeed, the viscosity of the SSL solution with the same concentration is $282 \text{ mPa}\cdot\text{s}$ at 25°C and $\dot{\gamma} = 1 \text{ s}^{-1}$, although κ -carrageenan had a lower viscosity from $51 \text{ mPa}\cdot\text{s}$.

The rheological results coincide with thermal effects, since the addition of SSL to κ -carrageenan gels and solutions modifies the polysaccharide behavior. The presence of at least two zones with different responses is observed with both techniques. Thus, two effects are proposed for these differences. In the first zone, electrostatic repulsions would predominate, while in the second zone hindrance caused by SSL micellization could also be present.

3.4. Microstructure of gels

The AFM microstructures of SSL, κ -carrageenan gels and its mixtures are shown in Fig. 7. Spherical vesicles can be observed in the SSL solution (Fig. 5a). These structures are similar but smaller than those observed by differential interference contrast light microscopy in 0.1% SSL (Bezeldgues, Serieye, Crosset-Perrotin & Leser, 2008). The lower

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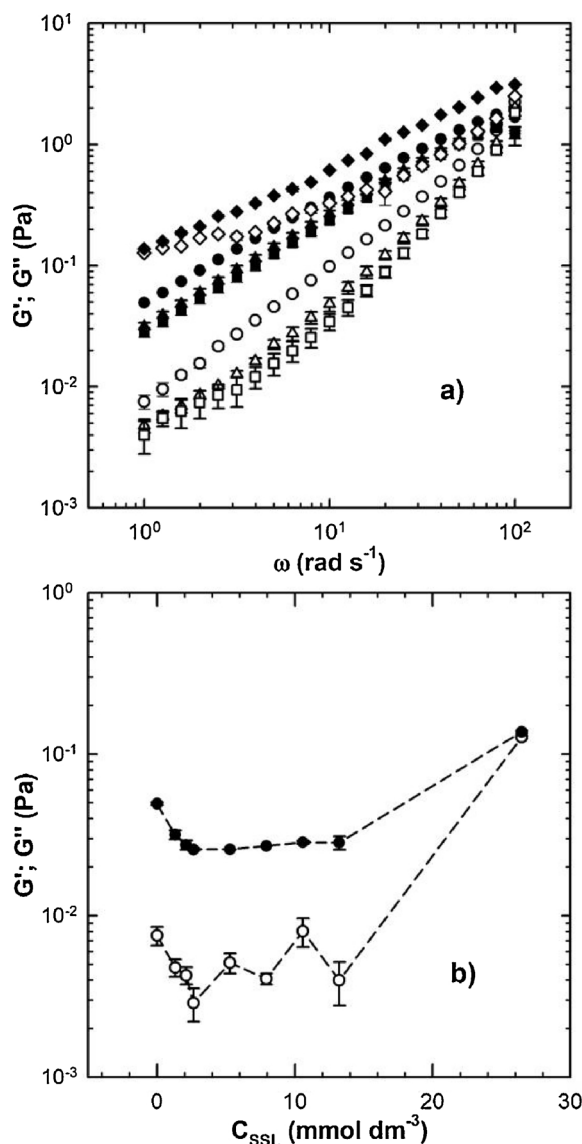


Fig. 5. a) Variation of G' (open symbols) and G'' (filled symbols) with frequency of 0.5% (w/w) κ -carrageenan solutions without SSL (circles), 1.3 mmol dm^{-3} SSL (triangles), 13 mmol dm^{-3} SSL (squares), and 27 mmol dm^{-3} SSL (diamonds) at 25°C , and b) Variation of G' and G'' with SSL concentration at $\omega = 1 \text{ rad s}^{-1}$ and 25°C .

surfactant concentration used in our study could explain the differences. The black areas in the image are air holes left by water evaporated before the observations. This phenomenon also explains the proximity between the structures. The fibrous structure of κ -carrageenan with 13 mmol dm^{-3} KCl is shown in Fig. 7b. This salt concentration causes incipient side-by-side aggregation like that observed in κ -carrageenan solutions without KCl, but with a higher κ -carrageenan concentration ($25 \text{ }\mu\text{g mL}^{-1}$) (Sokolova et al., 2013). Despite this difference, a network was formed, and gelation occurred, which is consistent with the rheological data shown in 3.3.1. The addition of SSL leads to segregation between both components (Fig. 7c), may be caused by the electrostatic repulsions. A higher SSL concentration (Fig. 7d) originated structures resembling to those obtained without surfactant. However, areas with segregation were still observed. It is evident that the addition of SSL to κ -carrageenan modifies its space arrangement, since surfactant alters the formation of the κ -carrageenan network. SSL concentration is a crucial factor for these modifications to occur, and the interactions between SSL and κ -carrageenan depend on the amount

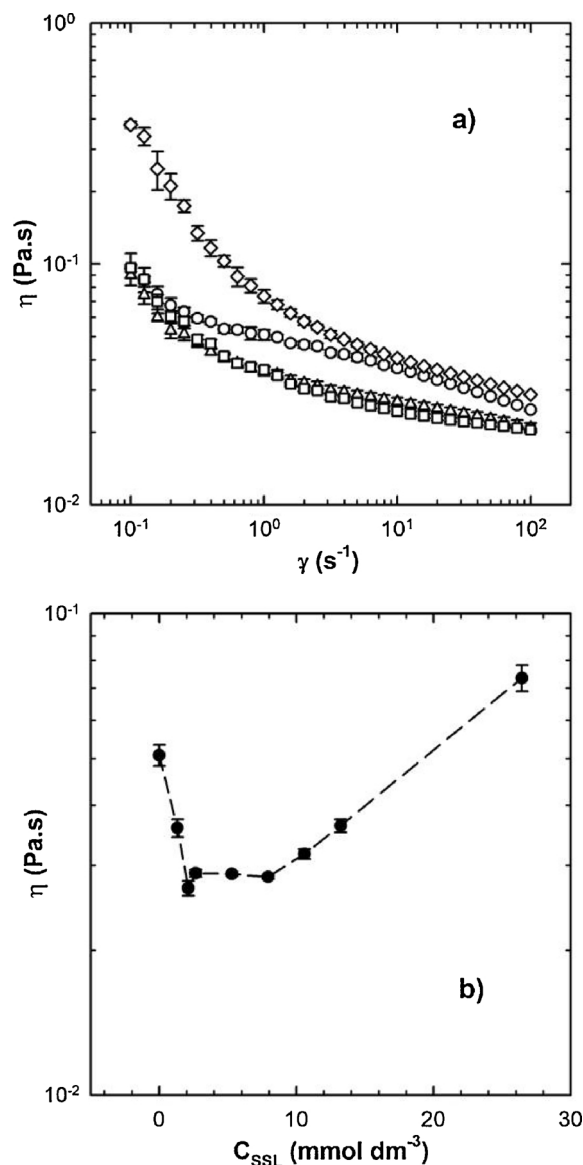


Fig. 6. a) Viscosity flow curves of 0.5% (w/w) κ -carrageenan solutions without SSL (circles), 1.3 mmol dm^{-3} SSL (triangles), 13 mmol dm^{-3} SSL (squares) and 27 mmol dm^{-3} SSL (diamonds) at 25°C , and b) Variation of viscosity with SSL concentration at $\dot{\gamma} = 1 \text{ s}^{-1}$ and 25°C .

of SSL. When SSL concentration in the mixture was 13 mmol dm^{-3} , a noticeable segregation occurred. However, when the level increased to 27 mmol dm^{-3} , this phenomenon was reduced. This behavior agrees with the thermal and rheological behaviors. On the other hand, the cationic surfactant cetyl(trimethyl) ammonium bromide (CTAB) gives rise to a denser cross-linking of the double helices leading to a denser κ -carrageenan network. The interaction between CTAB and κ -carrageenan stabilizes the helices of the polysaccharide even in the absence of K^+ ions (Kolesov et al., 2008). The behavior of κ -carrageenan with SSL and CTAB is different because the former is negatively charged, while the latter has positive charges.

4. Conclusions

The addition of SSL to κ -carrageenan gels and solutions modified the conformation of the polysaccharide. The mixtures presented widespread but more compact conformations than the polysaccharide without surfactant. This alteration is due to hindrance of SSL molecules on κ -carrageenan chains and changes in polysaccharide-solvent

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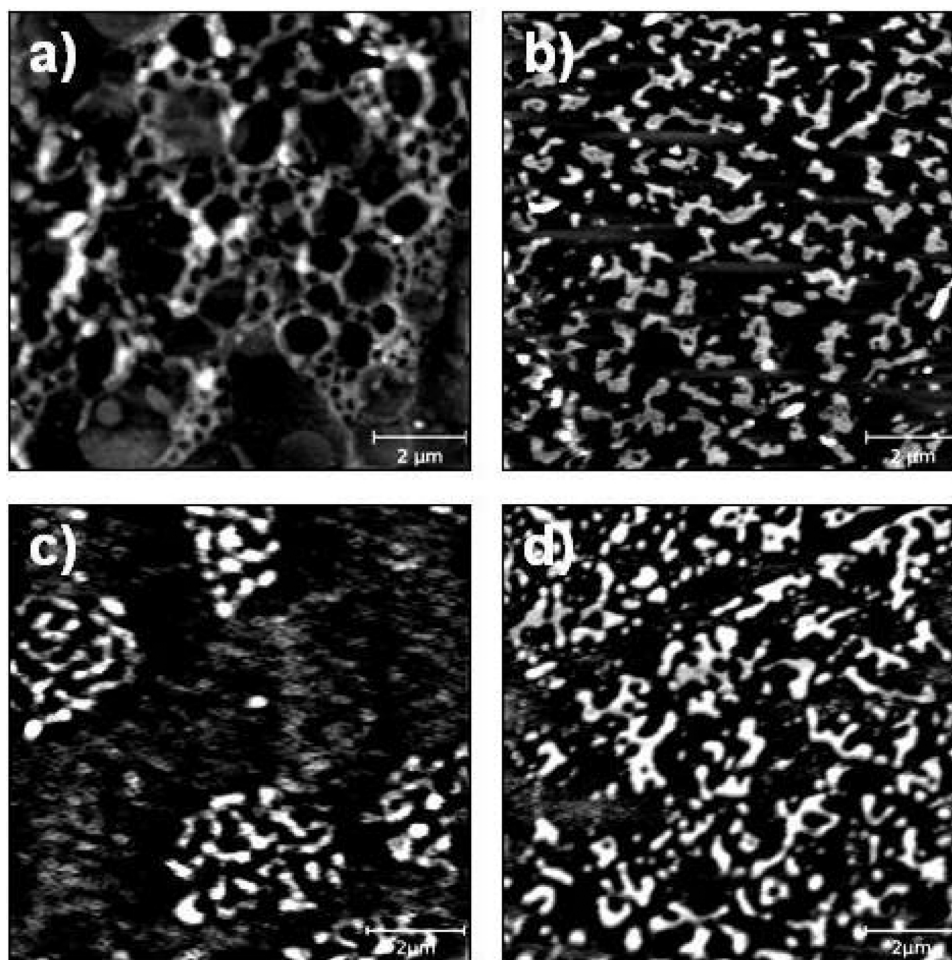


Fig. 7. AFM height profiles of a) 1.1 mmol dm⁻³ SSL solution; 0.5% κ-carrageenan solutions: b) with 13 mmol dm⁻³ KCl, c) with 13 mmol dm⁻³ SSL, and d) with 27 mmol dm⁻³ SSL. All κ-carrageenan solutions were diluted to 20 μg mL⁻¹ before cooling. Size 10 × 10 μm.

interactions caused by electrostatic interactions between both components, which affect the thermal, rheological and conformational parameters. In general, a destabilization of κ-carrageenan conformation is suggested. This phenomenon explains the results obtained in this work.

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