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Effect of mono and divalent salts on gelation of native, Na and deacetylated *Sterculia striata* and *Sterculia urens* polysaccharide gels

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Abstract

The effects of purification and salt addition on gelation of *Sterculia striata* and *Sterculia urens* (karaya) gels were investigated. Both gums form thermoreversible and ‘true’ gels. Melting transition temperature (T_m) of Na-polysaccharide sample was lower than that of the native gum. A gel-like mechanical spectrum is observed for two *Sterculia* gums with $G' > G''$ and little frequency dependence. The presence of acetyl groups in both gums seems to stabilize the gel. The T_m decreases and the critical gelation concentration increases after deacetylation. The addition of monovalent salts (LiCl, NaCl, KCl) to native *S. striata* polysaccharide decreases the T_m. However, the gel becomes stronger when monovalent salts are added to Na- and deacetylated gum. The gel strength of Na- *S. striata* polysaccharide in the presence of divalent salt follows the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, i.e. inversely proportional to the cationic radius. Addition of divalent salts to *S. urens* polysaccharide promotes a T_m decrease. A model for the gelation was proposed that includes ionic interactions and hydrogen bonding.

Keywords: *Sterculia striata*; *Sterculia urens*; Polysaccharide; Gelation; Salt

1. Introduction

Sterculia genus trees are well known for producing an acidic polysaccharide with a high solution viscosity and gelation characteristics, such as those observed for the gum from *Sterculia urens* (karaya gum), a commercial gum which has emulsifying, stabilizing and thickening properties (Le Cerf, Irinei, & Muller, 1990). Karaya gum is a partially acetylated polysaccharide of the substituted rhamnogalacturonoglycan (pectic) type. Treatment of the gum with dilute alkali to saponify acetate groups gives a product for which about 60% of the sugar residues are neutral (rhamnose and galactose), and 40% are acidic (galacturonic acid and glucuronic acid) (Stephen & Churms, 1995). It contains approximately 8% acetyl groups (Meer, 1980). Major structural features are illustrated in Fig. 1, showing two main regions (I and II) in the polysaccharide chain (Aspinall & Sanderson, 1970; Stephen & Churms, 1995). The general structure appears to consist of an elongated framework with a multiplicity of ionisable acidic groups interspersed with hydrophobic regions provided by the methyl groups of the ramnose units and, in the native gum, of acetyl groups (OAc) (Stephen & Churms, 1995). It contains relatively rigid ordered domains of high intramolecular attraction and more flexible less associated domains due to the order-destroying effect of bulky side chains that readily entrain water molecules. Deacetylated *Sterculia striata* polysaccharide from Brazil contains galactose (23.4%), rhamnose (28.8%), uronic acid (42.2%) and some xylose residue (5.6%). Native gum contains 10.7% acetyl groups (Brito, Silva, de Paula, & Feitosa, 2003).

Different viscosity behaviour in solutions of native and deacetylated *S. urens* and *S. striata* were observed. Deacetylated *S. urens* gum solutions exhibits a much higher relative viscosity than the native sample (Le Cerf et al., 1990) while for *S. striata* the opposite behaviour was found (Brito et al., 2003). Aged and fresh *S. urens* gums exhibit gel-like properties as evidenced by mechanical spectrum, with $G' > G''$. The fresh gum behaves as a stronger gel than the aged one (Le Cerf & Muller, 1994).

Gels are extensively used as thickening or gelling agents, texture enhancers, stabilisers in the food industry or in the pharmaceutical/cosmetic industries, in lotions, creams,

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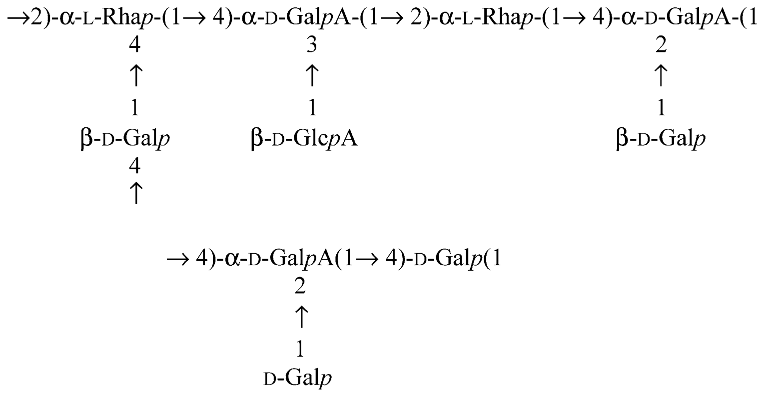

$$\begin{array}{cccc}
\rightarrow 2)\text{-}\alpha\text{-L-Rha}p\text{-}(1\rightarrow & 4)\text{-}\alpha\text{-D-Gal}p\text{A-}(1\rightarrow & 2)\text{-}\alpha\text{-L-Rha}p\text{-}(1\rightarrow & 4)\text{-}\alpha\text{-D-Gal}p\text{A-}(1 \\
4 & 3 & & 2 \\
\uparrow & \uparrow & & \uparrow \\
1 & 1 & & 1 \\
\beta\text{-D-Gal}p & \beta\text{-D-Glc}p\text{A} & & \beta\text{-D-Gal}p \\
4 & & & \\
\uparrow & & &
\end{array}$$

(I)

$$\begin{array}{c}
\rightarrow 4)\text{-}\alpha\text{-D-Gal}p\text{A}(1\rightarrow 4)\text{-D-Gal}p(1 \\
2 \\
\uparrow \\
1 \\
\text{D-Gal}p
\end{array}$$

(II)

Fig. 1. Structural elements in *Sterculia urens* gum (Aspinall & Sanderson, 1970; Stephen & Churms, 1995).

toothpaste, etc. Gel-forming polysaccharide must have a structure that allows partial but not overall association, since the later could cause precipitation or insolubility (Böhm & Kulicke, 1999). The mechanism for gelation of ionic polysaccharide could involve formation and subsequent aggregation of double helices, as in gellan (Mazen, Milas, & Rinaudo, 1999) or carrageenan (Millán, Moreno, & Nieto, 2000), or ionic interchain association mediated by divalent cations, described as the 'egg-box model', as in alginate (Grant, Morris, Rees, Smith & Thom, 1973) and low-methoxy pectin (Cardoso, Coimbra, & Lopes da Silva, 2003). More than one mechanism could also be involved as in gel formation in high-methoxy pectin, which is governed by both hydrogen bonds and hydrophobic interactions (Schmelter, Vreeker, & Klaffke, 2001).

In neutral polysaccharides, for example dextran, gels are formed by interactions of the individual polymer chain that are mediated by specific interactions between the hydroxyl groups and/or the bound water molecules (Naji et al., 2003). In schizophyllan, another neutral polysaccharide, triples helices are formed (Bot, Smorenburg, Vreeker, Páques, & Clark, 2001).

Melting temperature (T_m) is one parameter used to characterise polysaccharide gelation (Izumi, Kikuta, Sakai, & Takezawa, 1996; Lai & Lii, 1997; Oliveira, Silva, de Paula, Feitosa, & Paula, 2001; Tan, Moet, & Baer, 1983; Yoshida, Takahashi, Hatakeyama, & Hatakeyama, 1998). It corresponds to the temperature when dissociation of the junction zones in the gel network occurs (Lai & Lii, 1997). Macroscopic techniques, such as the falling ball method (FBM) and visual observation of the onset of the fluidity of the gel on heating are the most frequently used to study the initiation (melting) of flow (Izumi et al., 1996; Lai & Lii, 1997; Lai, Huang, & Lii, 1999; Oliveira et al., 2001; Takahashi, Hatakeyama, & Hatakeyama, 2000; Tan et al., 1983; Yoshida et al., 1998).

The junction zones formed in the gel network are controlled by several thermodynamic and structural parameters such as temperature, solubility, content and type of counter ion, and side chain or monosaccharide regularity on the main chain. In polysaccharides containing ironic acid residues, the counter ion characteristics strongly influence gel properties, as was observed when gel formation involves a coil-helix transition, for example in gellan (Izumi et al., 1996; Mazen et al., 1999; Tang, Tung & Zeng, 1996), or an 'egg-box' structure, for example in alginate (Draget, Steinsvag, Onsoyen, & Smidsrød, 1998; Khairou, Al-Gethami, & Hassan, 2002; Zheng, 1997) and pectin gels (Cardoso et al., 2003; Oosterveld et al., 2000; Schmelter et al., 2001). Even when gelation does not involve formation of structure ordered, as with the gum exudates from *Enterolobium contortisiliquum* (Oliveira et al., 2001), the counter ion characteristics can be important.

The degree of polysaccharide deacetylation is another important parameter in gel formation, for example in gellan (Mazen et al., 1999; Morris et al., 1996) and in pectin (Oosterveld et al., 2000).

This work reports the effect of deacetylation and salt addition on gelation properties of Brazilian *S. striata* gum in comparison with the commercial *S. urens* (karaya) gum. This study will allow new applications of this polysaccharide, which is widely found in Brazil, to be devised.

2. Materials and methods

2.1. Samples origin

Crude gum specimens from *S. striata* were collected in October 1996, from native trees at Fortaleza, Ceará, Brazil. Species was identified by Prisco Bezerra Herbarium where a voucher sample is kept. *S. urens* (karaya) gum was supplied by Sigma Co. and described as native.

2.2. Preparation of native and Na- *Sterculia* polyssacharides

Nodules free of bark from *S. striata* were selected and dissolved in distilled water at room temperature to give a 1% (w/v) solution. The solution pH was adjusted to approximately 7.0 by addition of diluted aqueous NaOH.

The clear solution was successively filtered through sintered glass (number 2 and 4) and the polysaccharide precipitated with ethanol. The polysaccharide obtained after this first procedure was denoted as native. The preparation of *S. striata* and *S. urens* Na-polysaccharide was carried out in two stages using the Rinaudo–Milas method with modifications previously described (Costa, Rodrigues, & de Paula, 1996). Initially native polysaccharide (1 g) was dissolved in distilled water (100 ml) at room temperature. The pH was adjusted to 7.0 and NaCl (1 g) was added. The polysaccharide was precipitated with ethanol, washed with acetone and dried with hot air. In order to eliminate excess of Na^+ the polymer was finally re-dissolved in distilled water and precipitated as described above.

2.3. Preparation of deacetylated polysaccharides

The Na-polysaccharides were deacetylated following the methodology described by Lee, Ashby and Day (1996).

2.4. Determination of melting temperature of gels (T_m)

The melting temperature of gels (T_m) was determined by visual observation of the onset of the fluidity of the gel on heating, as utilised for other polysaccharide gels as gellan (Izumi et al., 1996; Tan et al., 1983), red algal polysaccharide (Lai et al., 1999) and *E. contorsilliquum* gum (Oliveira et al., 2001). Different amount of 0.1 mol/l of aqueous salt solution (NaCl, KCl, LiCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$) were added to the dried gum in order to obtain the desired polysaccharide concentration. After sample swelling, the gel was heated to promote better homogeneity and cooled at room temperature (≈25 °C). T_m was determined for self-supporting gels at room temperature by heating the tube at 0.5 °C/min. Critical gelation concentration (CGC) is the minimum gum concentration that forms a self-supporting gel at room temperature.

2.5. Rheological measurements

Dynamical oscillatory was carried out in a Haake rheometer, model RS75, sensor C 60/2°, using a peltier system to control temperature. The analyses were performed for 5 g/dl aqueous solution of *S. striata* and *S. urens* Na-gums. All data were obtained in duplicate.

3. Results and discussion

3.1. Proposed model for the Sterculiaceae gelation

A suggested model of the gelation of is showed in Fig. 2, based on the model for low methoxy pectins (Voragen, Pilnik, Thibault, Axelos, & Renard, 1995) with adaptation due to structural differences. Gelation could be due to the formation of intermolecular junction zones, involving ionic interaction between homogalacturonic ('smooth') segments (from partial structure II) of different chains and calcium ions giving an 'egg-box model' (zone A), and hydrogen bonding between rhamnose segments (from partial structure I) in the hydrophobic areas (zone B). Ionic interactions could also occur between two or more galacturonic acid residues on different main chains or glucuronic acid in branched, or non-regular chain segments (zone C).

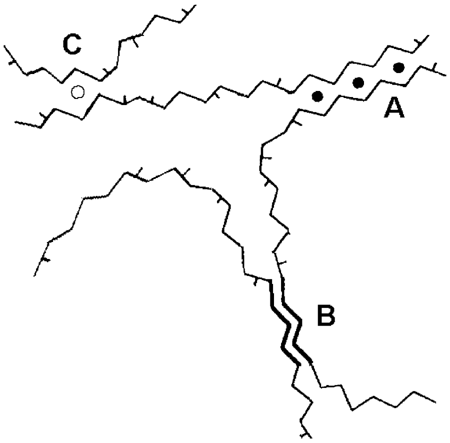

Fig. 2. Proposed model for Sterculiaceae gelation showing ordered ionic interaction between galacturonic acid residues and calcium ions (●) (zone A); hydrogen bonding between rhamnose segments (zone B) and single ionic interaction involving galacturonic and counter ions (calcium or other metal ions) (○), (zone C).

3.2. Effect of sample purification on gelation

S. striata and *S. urens* gum forms stable thermoreversible gels. The effect of the purification method on the T_m of native, Na-polysaccharide and deacetylated polysaccharides gels is showed in the phase-diagram depicted in Figs. 3 and 4 for *S. striata* and *S. urens* gum, respectively. The region below a line joining the data point indicates a gel phase, while the region above the line denotes a sol phase. High gel T_m and a low CGC was observed for native *S. striata*

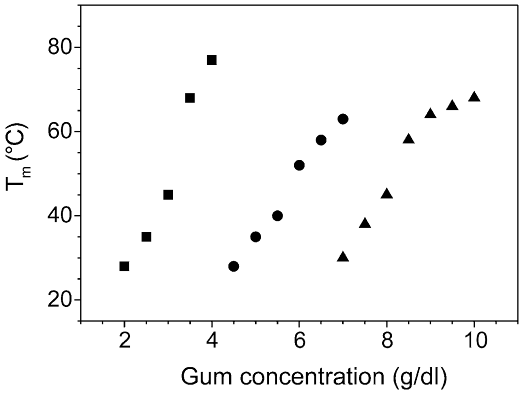

Fig. 3. Effect of purification method on melting temperature of *S. striata* gel. (■) native -polysaccharide; (●) Na-polysaccharide; (▲) deacetylated polysaccharide.

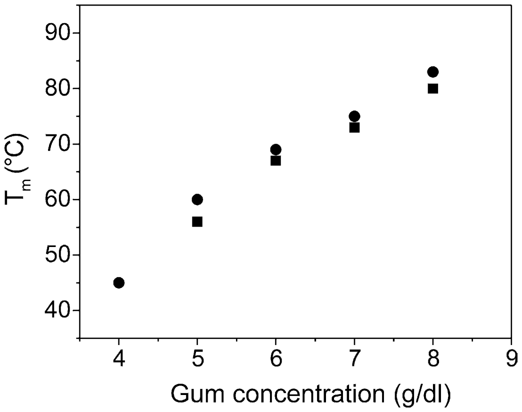

Fig. 4. Effect of purification method on melting temperature of *S. urens* gel. (■) native-polysaccharide; (●) Na-polysaccharide.

polysaccharide (Fig. 3). The values of the CGC of Na- and deacetylated *S. striata* polysaccharides were, respectively, two and threefold that of the native polysaccharide. Substitution of the majority of the counter ions present in native sample by Na^+, inhibits associations, leading to a decrease in gel strength in the case of *S. striata* gum. These results indicate that the presence of divalent ions and/or hydrogen bonds in native- *S. striata* polysaccharide enhances the stability of gel junction zones.

When the native gum is purified, divalent counter ions are substituted by sodium ions. The junction zones A and C that contributed to the gel formation in the suggested model (Fig. 2) are diminished or eliminated and the gel becomes more unstable. For *S. urens* gum (Fig. 4), only a slight T_m increase and CGC decrease were observed when the gum was purified as a Na-polysaccharide. It is likely that the commercial sample and the Na-gum are very similar in counter ion content. The native gum could be predominantly in a sodium salt form or the substitution of sodium by the multivalent originally present was only partial.

The effect of deacetylation for *S. striata* polysaccharide is also showed in Fig. 3. The lower T_m value indicates a decrease in gel strength as acetyl groups are removed from the polysaccharide. This result suggests that the acetyl groups contribute to the stability of the junction zones. It is known that deacetylated karaya is more water-soluble and assumes a more expanded and less branched conformation than native acetylated gum (Le Cerf et al., 1990). In addition to that, OAc in native gum is reported by Stephen and Churms (1995) to be part of the hydrophobic region in Sterculiaceae, suggesting that the effect of acetyl group may be more significant for the stabilization of zone B (Fig. 2). The acetyl free *S. striata* gum shows gel formation from above 7% (w/v) gum concentration, but deacetylated *S. urens* gum does not form self-supporting gel up to 20% (w/v) of gum concentration. This points to a large decrease in chain interactions due to acetyl groups removal in *S. urens* gum. The relative participation of zones A, B and C (Fig. 2) on gelation and/or different distribution of acetyl groups in two *Sterculia* gums could be an explanation for the deacetylation effects.

3.3. Comparison between Na-polysaccharide *S. striata* and *S. urens* gels

Fig. 5 shows phase diagrams for the gel in the absence of external salt. *S. urens* shows much higher T_m's than *S. striata*, over the investigated concentration range (4–7 g/dl). A higher interaction between *S. urens* polysaccharide molecules must occur, resulting in more stable junction zones. In order to confirm whether a true gel is formed for *S. striata* and *S. urens* gums a preliminary dynamic mechanical analysis was carried out with 5% Na-polysaccharide solutions. Frequency sweep results for G' and G'' of *S. urens* and *S. striata* are shown in Fig. 6. A gel-like spectrum is observed for both samples with $G' > G''$ and little frequency dependence. At 1 Hz the G'/G'' ratio for *S. urens* (7.11) is higher than that for *S. striata* (3.39) indicating that a stronger gel is formed in *S. urens,* which confirms the results shown by the T_m values (Fig. 5). The possible presence of multivalent counter ions in Na- *S. urens* gum could be the main reason for the difference in behaviour.

3.4. Effect of monovalent salt addition on the gelation of native *S. striata* gum

The effect of monovalent salt addition on T_m of native *S. striata* gum is shown in Fig. 7. The decrease in T_m indicates a decrease in gel strength. Draget et al. (1998) proposed two different effects of monovalent salt on the Ca^{2+}-induced gel state of alginate. At low salt concentration (NaCl and KCl) the added cation could promote a non-specific shielding of the long range electrostatic repulsions between the highly negatively charged polysaccharide chains, thus facilitating multivalent counter ion interchain cross-links and increasing gel strength. At high salt

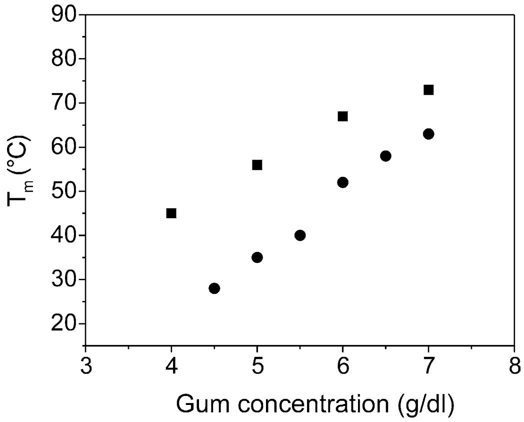

Fig. 5. Phase diagram of Na-purified polysaccharides. (●) *S. striata*; (■) *S. urens*.

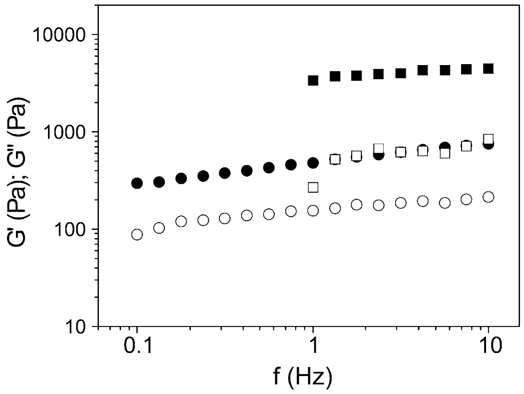

Fig. 6. G' (full) and G'' (open) versus frequency for 5% (w/v) gel of Na-polysaccharide from *S. striata* (■) and *S. urens* (●) in water at 25 °C.

concentration, the effect of the added salts starts to overshadow the original counter ion and the gel strength becomes lower. In this case, monovalent cations will compete with Ca^{2+} and ionic selectivity is observed. As the concentration of the monovalent ion added to the native *S. striata* gum was not so high (0.1 mol/l) and so the estimated $[M^+]/[M^{2+}]$ ratio (in the range of 2–3), the effect could be intermediate, with decrease in gel strength, but without ionic selectivity (order of $T_m = Li^+ \approx Na^+ \approx K^+$). The monovalent ion will compete with multivalent counter ions, screening the charge of the polymer and decreasing the cross-linking junctions between polysaccharide chains. A similar explanation was proposed by Marudova and Jilov (2003) for the effect of NaCl on low-methoxy pectin gels.

3.5. Effect of monovalent salt addition on the gelation of Na- and deacetylated S. striata gum

The addition of monovalent salts to Na-polysaccharide from *S. striata* (Fig. 8) enhances the gelling ability leading to an increase in T_m and a CGC decrease from 4.5% (without salt) to 4.0% (with added salt). The possibility of effective participation of M^+ is cross-links through polyanion-cation-water-cation-polyanion linkages between adjacent chains was suggested by Tang, et al. (1996). The authors showed that the Na-gellan gel strength depends on the monovalent cation concentration and exhibits a maximum at a particular range of cation concentration (about 15–20 $[Na^+]/[COO^-]$ ratio). The T_m increase of Na-*S. striata* gum may be explained by the increase in shielding of electrostatic repulsion, promoting the possibility of more polyanion/M^+/water/M^+/polyanion interactions. The small effect could be explained by the small $[Na^+]/[COO^-]$ ratio (≈ 2). In order T_m ($K^+ > Na^+ \approx Li^+$) in gel promotion was observed for the anionic polysaccharide (Na-gellan) (Tang et al., 1996) and also for the neutral polysaccharide (dextran) (Naji et al., 2003).

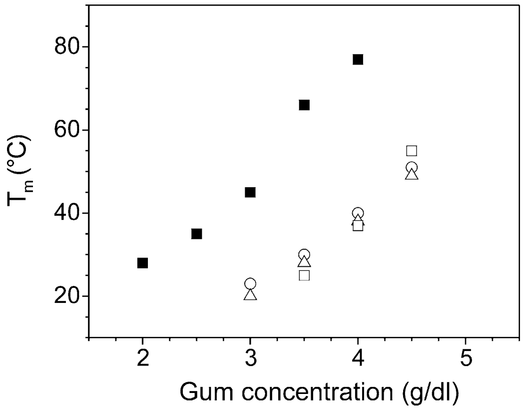

Fig. 7. Effect of monovalent salts on T_m of native *S. striata* gel. (■) without salt addition; in the presence of: (○) LiCl; (△) NaCl; (□) KCl.

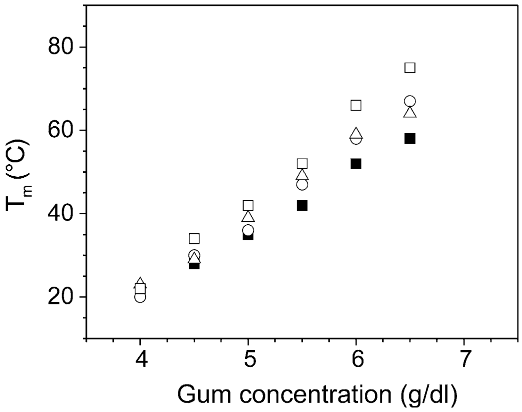

Fig. 8. Effect of monovalent salts on T_m of Na-purified *S. striata* gel. (■) without salt addition; in the presence of: (○) LiCl; (△) NaCl; (□) KCl.

Addition of monovalent salt to Na-purified *S. urens* gum shows a T_m decrease in relation to the system without salt addition, in contrast to *S. striata* (Table 1). This behaviour could be explained by the partial substitution of original multivalent counter ions by Na^+ when native gum was purified. The monovalent ion added could compete with multivalent counter ions, screening the charge on the polymer and decreasing the cross-linking junctions between the polysaccharide chains.

The effect of monovalent salt addition to deacetylated *S. striata* polysaccharide (Fig. 9) is to decrease gel strength, in contrast to that observed for Na-gum (Fig. 8). Both samples are in the Na form, and so the explanation of competition M^+/M^{2+}, as suggested for the native gum, could not be appropriate. The results suggest that acetyl groups may also

Table 1
Effect of addition of 0.1 mol/l salts on T_m for *Sterculia* Na-polysaccharide gels

Gum[a]	T_m (°C)			
	Without salt	LiCl	NaCl	KCl
S. striata	52	58	59	66
S. urens	70	39	37	38

[a] 6% (w/v) Gum concentration.

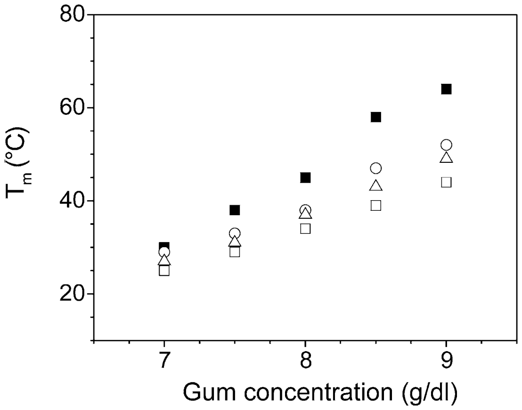

Fig. 9. Effect of monovalent salts on T_m of deacetylated *S. striata* gel. (■) without salt addition; in the presence of: (○) LiCl; (△) NaCl; (□) KCl.

be part of the hydrophilic area of *S. striata* structure and thus be significant for the stabilization of zone C (Fig. 2). The selectivity between the monovalent ions (order of T_m decrease: $K^+ > Na^+ > Li^+$) could be an indicative of a specific interaction between the deacetylated polysaccharide and the cation.

3.6. Effect of divalent salt addition on the gelation of Na- S. striata gum

Addition of multivalent salts causes a T_m increase and a small CGC decrease for *S. striata* Na-polysaccharide (Fig. 10). The results indicate the formation of a more stable gel in the presence of divalent cations in the following order of affinity: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. As the $[M^{2+}]/[Na^+]$ and $[M^{2+}]/[COO^-]$ ratios were not so high (0.7–1.0), the excess of divalent cations was not high enough to impose repulsive forces and prevent the formation of cross-links. The added divalent cations will compete with Na^+ counter ion for the anionic sites and increase junction zone and gel strength. The same multivalent ion added to native and deacetylated polysaccharide lead to a T_m decrease and CGC increase (Table 2). In these cases, the repulsion forces between the polymer molecules must prevail.

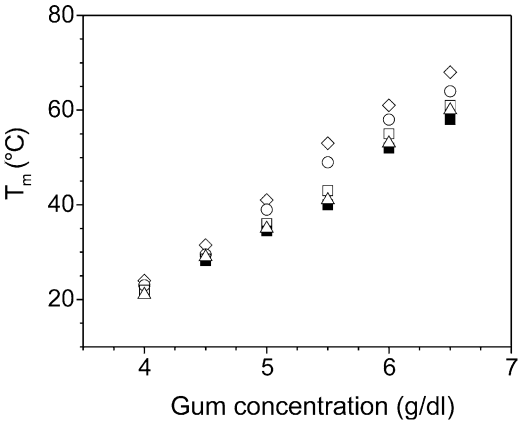

Fig. 10. Effect of divalent salts on T_m of Na-purified *S. striata* gel. (■) without salt addition; in the presence of: (◇) $MgCl_2$; (○) $CaCl_2$; (□) $SrCl_2$; (△) $BaCl_2$.

Table 2
Effect of addition of 0.1 mol/l divalent salts on melting temperature of polysaccharide *S. striata* gels

Gum	T_m (°C)				
	Without salt	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Native[a]	77	56	51	36	29
Deacetylated[b]	58	72	100	116	136

[a] 4% (w/v) Gum concentration.
[b] 8.5% (w/v) Gum concentration.

The interaction between alkaline earth counter ions and carboxylate groups is of ionic character and depends on the cationic radius. The dependence of the observed Na- *S. striata* T_m increase on the radius of the added alkaline earth cation is shown in Fig. 11. The Mg^{2+} cation, which possesses the smallest radius (53 pm) (Atkins & Jones, 1999), promotes the formation of the strongest gel. Ba^{2+} cation, with largest radius (136 pm), induces the formation of the weakest gel. The order of gel strength depends inversely on cationic radius ($Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^2$). Similar behaviour on T_m by addition of metal ion was also verified for *E. contortisilliquum* gum gel (Oliveira et al., 2001). The non-ordered structure of this gum and the fact that Ca^{2+} addition promotes alginate gelation through the 'egg-box' mechanism, but Mg^{2+} does not (Zheng, 1997), indicates that the predominant model of ionic interaction in *S. striata* gels are not of the 'egg-box' type (Zone A, Fig. 2).

3.7. Effect of divalent salt addition on the gelation of Na- S. urens

Fig. 12 shows the phase diagram of Na- *S. urens* gum in the presence of divalent ions. A decrease in T_m due to

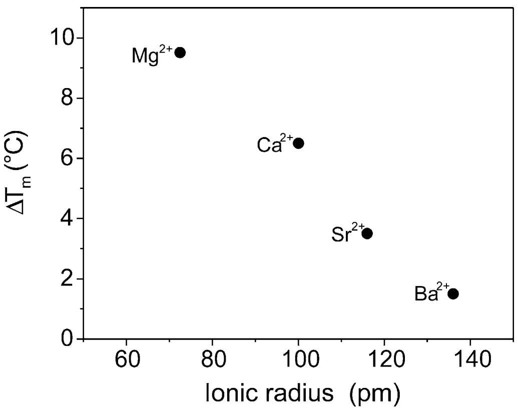

Fig. 11. Effect of ionic radius of alkaline cation on melting temperature of 6% (w/v) Na-purified *S. striata* gel.

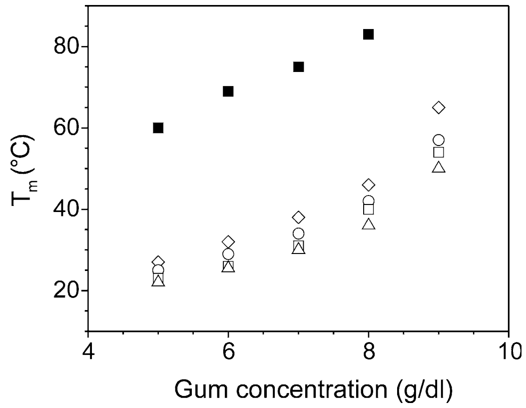

Fig. 12. Effect of divalent salts on T_m of Na-purified *S. urens* polysaccharide. (■) without salt addition; in the presence of: (◇) $MgCl_2$; (○) $CaCl_2$; (□) $SrCl_2$; (△) $BaCl_2$.

the presence of the divalent ions was observed, in contrast to the behaviour of *S. striata*. This is again indicative of the presence of multivalent counter ion in the supposed Na-*S. urens* polysaccharide. The excess of added divalent cation in relation to the total carboxylate content of the polyanion may lead to the formation of $M^{2+}(COO^-)$ bonds, instead of $M^{2+}(COO^-)_2$. The positive net charge in the polymer chains, due to the $M^{2+}(COO^-)$ groups, induces the occurrence of repulsive forces, prevents the formation of cross-links and decreases gel strength. The less pronounced effect of the cationic radius on *S. urens* gum T_m may be due to the mixture of counter ions present, those from the original material and that added.

4. Conclusions

S. striata and *S. urens* (karaya) gums form thermoreversible gels with gelation conditions (concentration and melting temperature) depending on the purification method, acetyl group content, counter ions present and salt addition. The substitution of multivalent cation by Na^+ in the purification process leads to a decrease in gel strength. Acetyl groups stabilize some junction zones necessary for gelation.

The effects of monovalent salt on gelation could be:

(1) decreasing gel strength by overshadowing the effect of the original counter ion by screening the charge of the polymer and decreasing the cross-links between the polysaccharide chains (high salt concentration and multivalent counter ion);
(2) increasing gel strength by the promotion of a non-specific shielding of the long range electrostatic repulsions between the highly negative charged polysaccharide chains, thus facilitating multivalent counter ion interchain cross-linking (low salt concentration and multivalent counter ion);
(3) increasing gel strength by augmenting the shielding of electrostatic repulsion, promoting the effective participation of the monovalent cation in cross-link through in polyanion/water/M + /water/M + / polyanion interaction (high salt concentration and monovalent counter ion).

The effects of divalent salt could be:

(1) increasing gel strength due to the substitution of monovalent counter ion by divalent cation and increasing cross-links (low salt concentration and monovalent counter ion).
(2) decreasing gel strength due to the repulsive forces between positive net charges on the polymer chains, originating from the excess of divalent cations and formation of $M^{2+}(COO^-)$ bonds, instead of the $M^{2+}(COO^-)_2$, which characterise the cross-links (any salt concentration and divalent counter ion or high salt concentration and monovalent counter ion).

The formation of intermolecular junction zones in the proposed model of the Sterculiaceae gelation includes ionic interaction and hydrogen bonding. Ionic interactions between two galacturonic acid residues of different principal chains and counter ions or two glucuronic acid residues of branching are predominantly of individual character. The ionic interaction between homogalacturonic segments of different chains and calcium ions, such as ‘egg-box model’, could also be possible, but to a smaller extent. Hydrogen bonding may occur between rhamnose segments.

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