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Composition and rheological properties of *Albizia lebbeck* gum exudate

R.C.M. de Paula[a], S.A. Santana[b], J.F. Rodrigues[a]

[a]*Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, CP 12.200, CEP 60455-760, Fortaleza, Ceará, Brazil*
[b]*Departamento de Química, Universidade Federal do Maranhão, Campus Universitário do Bacanga, CEP 65080-040, São Luís, Ma, Brazil*

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Abstract

The composition, structure and rheological properties of *Albizia lebbeck* gum from Brazilian plants were investigated. The content of galactose, arabinose and uronic acid is similar to those from Venezuelan and African gums. Mannose, present in gum from other origins, was not identified in Brazilian polysaccharide. ^{13}C NMR spectra of intact and Smith-degraded polysaccharide allowed the chemical shift assignment to be made. The main chain is composed of galactan core $(1 \rightarrow 3)$ linked with approximately 33% of substitution at C-6. GPC indicated a major polysaccharide fraction of M_{pk} 2.4×10^6 g/mol and two other minor fractions of M_{pk} 3.6×10^5 and 4.5×10^4 g/mol. The whole gum is a low viscosity polysaccharide with an apparent flow activation energy of 16.6 and 17.2 kJ mol^{-1}, for solutions of 2 and 3% (w/v) concentration, respectively. These values are characteristic of branched systems with little intra- and intermolecular interactions. NaCl, $CaCl_2$ and $AlCl_3$ affected reduced and intrinsic viscosities and Huggins constant of gum solution in different manners. The effect, due to the affinity between *A. lebbeck* polysaccharide and metal ions, follows the order: $Al^{3+} > Ca^{2+} > Na^{+}$.

Keywords: *Albizia lebbeck*; Gum; Polysaccharide; Rheology

1. Introduction

Albizia lebbeck is a tree from leguminosea family originally from Africa and wide spread in Asia and in the American continent as an ornamental tree. In China, it has been used as a folk medicine for treating psychological disorders, insomnia and warts (Kan, 1979). Other native medicine uses include insecticidal and anthelmintic (Allen & Allen, 1981). Saponins, tanins and xanthones have been extracted from the bark and associated with the medicinal properties (Chiu & Chang, 1992; Ma, Hsiiao, Chen & Hsu, 1997).

The gum exudate has been reported as a substitute for arabic gum (US National Academy of Science, 1979). The presence of tannins and high proportion of aluminium and heavy metals indicates that the gum could not be used as a food additive (Anderson & Morrison, 1990). Composition of *A. lebbeck* gum from Venezuela and Africa was determined by Martinez, Leon de Pinto, Alvarez, González de Troconis, Ocando and Rivas (1995) and by Anderson and Morrison (1990), respectively. Venezuelan species are constituted of galactose, arabinose, mannose, glucuronic acid and 4-*O*-methyl-glucuronic acid. The African gum was reported to be similar, except for the presence of rhamnose that was not detected in the Venezuelan polysaccharide. Polysaccharide gums find wide application because of their rheological properties. The increase of the use of *Albizia* spp in agroforestry, and in projects to regenerate arid zones, may lead to an increase of the availability of *Albizia* gum in future. This work is concerned with viscosity properties of *A. lebbeck* gum from Brazil. As some variations in composition were found between species from different geographic locations, the composition and structural features are also discussed.

2. Experimental

2.1. Origin and purification

Crude gum specimens from *A. lebbeck* were collected in April 1996, from the native tree at Fortaleza, Ceará, Brazil. It was purified as Na salts using the method reported by Milas and Rinaudo (1991) with some modifications as previously described (Costa, Rodrigues & Paula, 1996).

2.2. Sugar composition

Purified gum solution 5% (w/v) in 0.5 M sulphuric acid was heated for 18 h at 100°C. After cooling, the solution was neutralized with $BaCO_3$. The mixture was filtered and the solution passed through an Amberlite IR-120 H^+ resin exchange column and then concentrated. Thin layer chromatography (TLC) was carried out in silica gel plates

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Table 1
Comparison of analytical data for *A. lebbeck* gum from different origins

Constituent sugar[a] (%)	Gum from Brazil	Venezuela[b]	Africa[c]
Uronic acid	10.5 ± 0.5	14.0–15.0	9
Galactose	52 ± 1	49–52	55
Arabinose	36 ± 0.8	29–32	21
Rhamnose	< 2	nd[d]	9
Mannose	nd[d]	3–4	6

[a] Corrected for moisture.
[b] Anderson and Morrison (1990).
[c] Martinez et al. (1995).
[d] nd—not detected.

with *n*-butanol/pyridine/water (10:3:3 by volume) as solvent. The chromatogram was developed with orcinol–sulphuric acid reagent.

High performance liquid chromatography (HPLC) was carried out with Shimadzu equipment with a differential refractometer as detector. A Spherex-NH_2 column was used with acetonitrile: water (8:2 v/v) as solvent at room temperature. The total content of uronic acid was determined as Na salt by conductimetric titration with 0.012 M HCl as described by Rodrigues, de Paula and Costa (1993).

2.3. Molar mass distribution

The peak molar masses (M_{pk}) were estimated by gel permeation chromatography (GPC) with Shimadzu equipment at room temperature using an Ultrahydrogel linear column and 0.1 M $NaNO_3$ as solvent. A differential refractometer was used as detector and the elution volume corrected to the internal marker of ethylene glycol at 11.25 cm^3. The GPC was calibrated with dextran and fractions of *Anadenanthera macrocarpa* and *Anacardium occidentale* gums. These gums are branched acidic heteropolyssacharide, which are constituted predominantly by galactose and arabinose as neutral monossacharides, and glucuronic acid (ca 6%) (de Paula & Rodrigues, 1995; Silva, Rodrigues & de Paula, 1998). The fractions of the gums were previously characterized by light scattering (de Paula, Budd & Rodrigues, 1997; de Paula, Heatley & Budd, 1998).

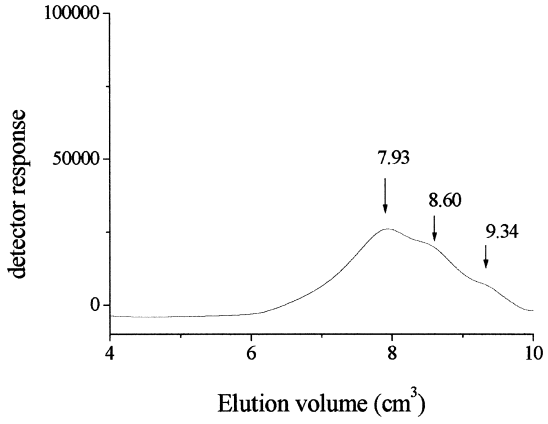

Fig. 1. GPC curve for *A. lebbeck* polysaccharide.

2.4. Nuclear magnetic resonance (NMR) spectroscopy

^{13}C NMR spectra of 10% w/v solutions in D_2O at room temperature were recorded in a Bruker advance DRX 500 spectrometer. Chemical shifts are given in values relative to internal acetone at 31.07 ppm. DEPT spectra were recorded in order to determine the multiplicity of carbons peaks; the acquisition time and delay time was 1.0 s. The ($CH–CH_3$) and CH_2 sub-spectra were obtained by addition and subtraction of DEPT spectra obtained with final ^1H pulse flip angles of 45 and 135°, respectively.

2.5. Viscosity measurement

The measurements were performed in an Ubbelohde viscometer with a flow time for water of 300 s at 25.0°C. All solutions were prepared by mixing with magnetic stirring during 30 min at room temperature (25–28°C). The intrinsic viscosity determination was made in the presence of different salts while maintaining the same ionic strength: 1.0 M NaCl; 0.334 M $CaCl_2$ and 0.170 M $AlCl_3$. Solutions of 2% gum were prepared at different salt concentrations (1×10^{-4} to 5×10^{-3} M) by addition of small aliquots of NaCl, $CaCl_2$ and $AlCl_3$.solutions. The temperature was 25.0 ± 0.1°C in all experiments. The effect of temperature was investigated for aqueous solutions of gum at different concentrations (1, 2 and 3% w/v) by heating from 10 to 70°C at a rate of 1°C/min. Measurements during cooling (70–10°C) were also made. All flow times were averages of at least five replicates.

3. Results and discussion

3.1. Structural characterization

3.1.1. Composition

Analysis of *A. lebbeck* gum hydrolysates by TLC chromatography indicate the presence of galactose ($R_f = 0.48$), arabinose ($R_f = 0.56$), glucuronic acid ($R_f = 0.05$). Rhamnose was detected by HPLC using an amino column, as was also observed in the African species of the gum (Anderson & Morrison, 1990). Mannose found in both African and Venezuelan species has not been identified in Brazilian *A. lebbeck* gum.

Table 1 shows the analytical data for Brazilian *A. lebbeck* gum and results from previous work for comparison. The ratio of the two major monosaccharides, galactose/arabinose are 2.4/1.0, is close to the African species (2.6/1.0) (Anderson & Morrison, 1990), but higher than the sample from Venezuela (1.5–1.8/1.0) (Martinez et al., 1995). The glucuronic acid and ash content (10.5 and 6.0%,

Table 2
GPC data for *A. lebbeck* exudate gum

Peak maximum	M_{pk} (g/mol)	
	Gum fractions[a] calibration	Dextran calibration
7.93	2.4×10^6	3.6×10^5
8.60	3.6×10^5	5.4×10^4
9.34	4.5×10^4	6.4×10^3

[a] *A. macrocarpa* and *A. occidentale* gums.

respectively) are similar to that of the African samples (9.0 and 6.0%).

3.1.2. Molar mass distribution

GPC chromatogram of *A. lebbeck* gum is shown in Fig. 1. A wide polydispersity was observed for the polysaccharide with a major peak at 7.93 cm^3 (peak 1) and two shoulders at 8.60 and 9.34 cm^3 (peaks 2 and 3, respectively). Multimodal chromatograms have been reported for other exudate gum polysaccharides as *Acacia senegal* (Vandevelde & Fenyo, 1985), *A. occidentale* (de Paula & Rodrigues, 1995; de Paula et al., 1998) and *A. macrocarpa* gum (de Paula et al., 1997).

As the exudate gum generally is a highly branched polysaccharide, dextran is not an appropriated standard because the molar mass values may be underestimated. *A. occidentale* gum peak molar mass using dextran as standard (de Paula & Rodrigues, 1995) is much lower than the one obtained using fraction of the same gum previously characterized by light scattering (de Paula et al., 1998).

In order to estimate the peak molar mass for *A. lebbeck* gum, fractions of exudate polysaccharide, previously characterized by light scattering, have been used for GPC calibration. Data of M_{pk} with dextran GPC calibration can also be seen in Table 2 for comparison. As already discussed, the peak molar mass using exudate gum fractions for GPC calibration gives much higher M_{pk} values.

3.1.3. ^{13}C NMR of the exudate polysaccharide

^{13}C NMR spectrum of intact *A. lebbeck* gum from Brazil is complex (Fig. 2). The signals of spectra from native and Smith-degraded gums were assigned on the basis of literature data from related compounds from (Bock & Pedersen, 1983; Defaye & Wong, 1986; Leon de Pinto, 1991). The spectrum of intact gum shows a small peak at 177.8 ppm attributed to carbonyl groups from glucuronic acid residues. In the anomeric region (90–110 ppm) three major peaks were observed. Two are single lines (100.4 and 108.8 ppm) due to the presence of anomeric carbons from β-arabinopyranose and α-arabinofuranose, respectively. The overlapping group of peaks (104.5–105.0 ppm) were inferred as β-galactopyranose (1 → 3) linked and β-glucuronic acid.

The 4-O-methyl derivative of glucuronic acid from Venezuelan *A. lebbeck* gum was identified by ^{13}C NMR as the peak at 59.85 ppm, attributed to methylene carbon from methoxyl group (Martinez et al., 1995). In order to verify if this constituent was also present in the Brazilian *A. lebbeck* gum, the DEPT technique was used. Fig. 3a shows the ($CH–CH_3$) sub-spectrum of Brazilian *A. lebbeck* gum. No methyl resonances were observed at chemical shift range of 57–62 ppm indicating that 4-*O*-methyl glucuronic acid is absent in the structure of the polysaccharide from Brazil.

The CH_2 sub-spectrum can be used to observe oxygen substitution on primary carbons of polysaccharide and also to estimate the amount of oxygen-substituted carbons in the chain (de Paula et al., 1998). The CH_2 peaks from primary monosaccharide units occur at 61–63 ppm. The O-substitution of carbon in monosaccharide units generally induces a 6 to 11 ppm downfield displacement of the substituted carbon concomitant with a smaller upfield shift for the signals of the adjacent carbons (Defaye & Wong, 1986).

CH_2 sub-spectrum (Fig. 3b) of the gum shows two groups of CH_2 peaks. The first group of peaks centered at 62.0 ppm is attributed to CH_2 from primary carbons groups (CH_2OH) from galactose and arabinose residues. The peak at 68.4 ppm is due to 6-O-substitution of galactose residue. 6-O-substitution of galactose residue was also observed in *A. lebbeck* gum from Venezuela using methylation analysis

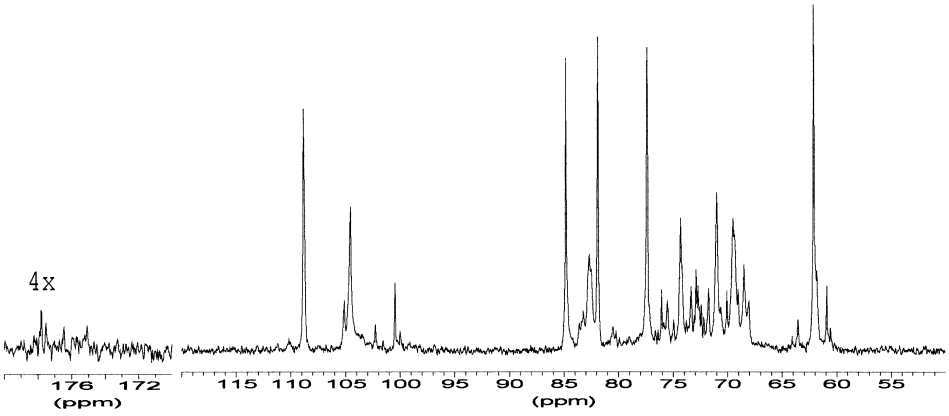

Fig. 2. ^{13}C NMR spectrum of intact *A. lebbeck* polysaccharide.

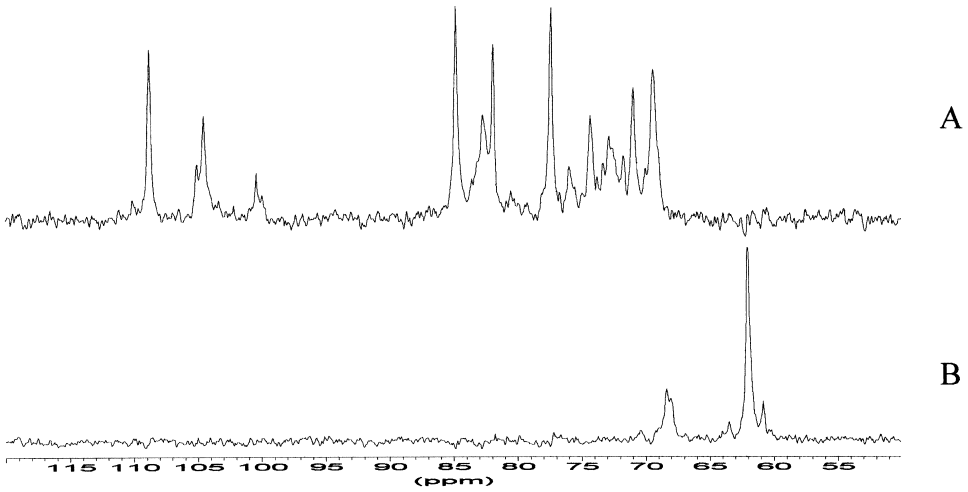

Fig. 3. Sub-spectrum of *A lebbeck* polysaccharide using DEPT technique: (a) ($CH + CH_3$); (b) CH_2 sub-spectrum.

(Martinez et al., 1995). Taking into account that only galactose may be 6-O-substituted, is possible to estimate the amount of this residue from the relative intensities of the 6-O-substituted peak and the CH_2OH peak. The ratio of substitution is one third, so about 33% of galactose residues are 6-O-substituted.

Smith-degraded *A. lebbeck* gum (Fig. 4a) gives a much simpler spectrum than that for intact gum (Fig. 2). Almost all (1 → 3) linked α-arabinofuranose and → 1) β-arabinopyranose have been eliminated. The six major peaks present at 104.6, 70.9, 82.7, 69.1, 75.4 and 61.6 ppm were consistent with the carbons assignment for C-1 to C-6, respectively, for β-galactopyranose chain. The CH_2 sub-spectrum of Smith-degraded gum (Fig. 4b) shows only one peak indicating that the (1 → 6) linked galactose units have been eliminated.

The comparison of the ^{13}C NMR spectra of intact and Smith-degraded *A. lebbeck* gum and correlation with literature data, enable the chemical shift assignments in Table 3 to be made.

3.2. Rheological properties

3.2.1. General aspects

Albizia gum is a low-viscosity polysaccharide, comparable in many aspects to gum arabic and cashew gum. The absolute viscosity of 1% aqueous solutions of these gums at 25°C are 1.2 mPa s (*Albizia* gum), 1.8 mPa s (gum arabic)

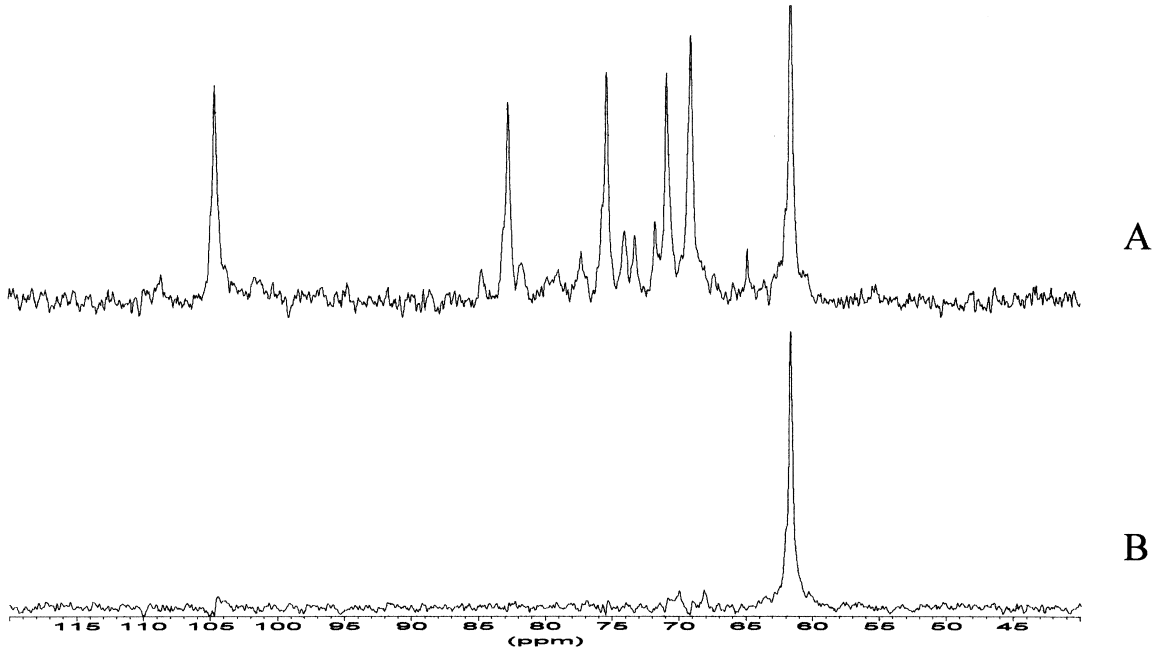

Fig. 4. (a) ^{13}C NMR spectrum of Smith-degraded *A. lebbeck* polysaccharide; (b) CH_2 sub-spectrum.

Table 3
^{13}C NMR chemical shifts for *A. lebbeck* polysaccharide

Unit	Chemical shift (ppm)						Reference
	C-1	C-2	C-3	C-4	C-5	C-6	
β-Galp							
(1 → 3) linked	104.6	70.9	82.7	69.1	75.4	61.6	Defaye and Wong (1986)
(1 → 6) linked	105.1	70.9	73.3	69.5	74.9	68.4	Martinez et al. (1995)
α-Araf	108.8	81.9	77.3	84.8	62.1		Bock and Pedersen (1983)
β-Arap	100.2	69.5	77.3	84.8	63.6		Martinez et al. (1995)
β-GlcA	104.5	74.3	76.0	72.8	75.5	177.7	Leon de Pinto (1991) Bock and Pedersen (1983)

and 1.0 mPa s (cashew gum). Other industrial polysaccharide gums like methyl cellulose, CMC HV, karaya, locust bean and tragacanth have viscosity values in the range of 1100–3400 mPa s at the same concentration (Meer, 1980). The effect of concentration on the viscosity of *A. lebbeck* gum is larger than that on *A. occidentale* gum. A 3% solution of *Albizia* gum has an absolute viscosity 83% higher than that of a 1% solution. In *Anacardium* gum the increment is only 20% (de Paula & Rodrigues, 1995).

Intrinsic viscosity in NaCl 1 M of *A. lebbeck* gum, $[\eta] = 0.23$ dl/g, is much lower than those obtained from Africa ($[\eta] = 1.42$ dl/g) (Anderson & Morrison, 1990) and Venezuela ($[\eta] = 0.38$–0.65 dl/g) (Martinez et al., 1995) species. As the uronic acid content is similar for all samples, the differences in intrinsic viscosity might be due to higher molar mass and/or to a lower degree of chain branching in polysaccharides from other regions.

The critical concentration, $C_c^{\#}$, which characterize the limit of the dilute regime, could be estimated from the average $C_c^{\#}[\eta]$ value for a random coil polysaccharide proposed by Morris, Cuther, Ross-Murphy, Rees and Price (1981), as equal to 4. Taking the $[\eta]$ value of 0.23 dl/g in 1 M NaCl, the $C_c^{\#}$ is 17 g/dl. Thus, *Albizia* gum behaves as in diluted regime up to concentrations of 17%. Even using the $C_c^{\#}[\eta]$ value for stiff polysaccharides, near 1 (Milas, Rinaudo, Knipper & Schuppiser, 1990), the critical concentration is 4%. Therefore, all measurements were performed in a very dilute regime (concentration less than 3%).

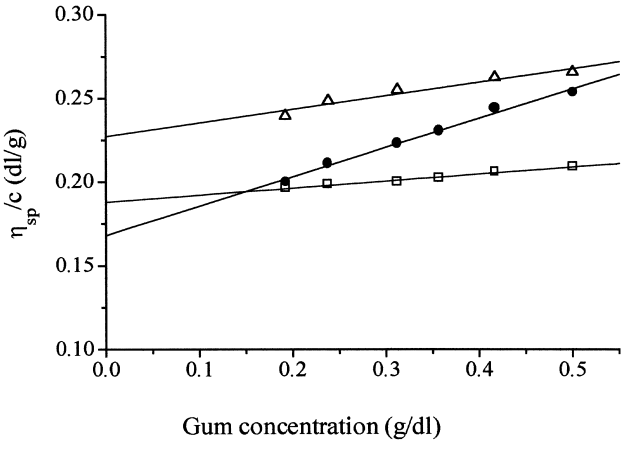

Fig. 5. Effect of salts on the reduced viscosity of *A. lebbeck* polysaccharide in presence of: (△) 1 M NaCl; (□) 0.334 M $CaCl_2$; (●) 0.170 M $AlCl_3$.

3.2.2. Effect of salts

Exudate gums are acid polysaccharides containing various metal ions as neutralized cations. The nature and content of these constituents depend on the composition of the soil upon the trees grew. The major cations of *A. lebbeck* gum from Africa or Venezuela are K^+, Na^+, Ca^{2+} and Mg^{2+}, which corresponds to more than 99% of the cationic composition (Anderson & Morrison, 1990; Martinez et al., 1995). Cationic composititon of Brazilian gum was not determined. The crude *A.occidentale* gum, containing K^+, Na^+, Ca^{2+} and Mg^{2+}, are transformed to 94.7% of Na salt, after the same purification procedure adopted to *Albizia* gum (Costa et al., 1996). So, this gum is assumed to be predominantly a Na salt.

As the exudate gum behaves as a polyeletrolyte, the solution viscosity is affected by the presence of added salt. If no intermolecular interaction occurs the viscosity of the dilute gum solution decreases due the screening of charge and contraction of the macromolecule in the presence of counter-ion. In more concentrated solution, the presence of multivalents ions may promote interaction between chains and an increase in viscosity.

The effect of Na^+, Ca^{2+} and Al^{3+} on the reduced viscosity of *A. lebbek* gum solution was investigated at same ionic strength ($I = 1$). The smallest value of the intrinsic viscosity (Fig. 5) observed in the presence of aluminium ion reflects the intense chain contraction. In the presence of sodium ions, the polysaccharide molecule (at infinite dilution) has the least contracted conformation. Calcium ions induce an intermediate contraction.

As the gum concentration increases, the effect of the interaction between polysaccharide molecules over the reduced viscosity becomes predominant. These changes in interaction are reflected in changes in the Huggins viscosity slope parameter, k_H. Usual value of k_H range between 0.33 and 0.80 (Elias, 1997). The Huggins constants of 1.6, 1.9 and 6.2, calculated for gum in presence of NaCl, $CaCl_2$ and $AlCl_3$, respectively, indicate a strong interaction between macromolecules, specially in the case of aluminium ions. The order of interaction may be ascribed to the higher

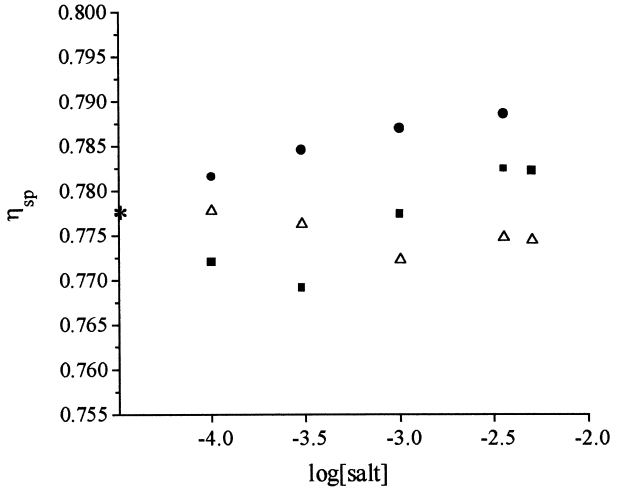

Fig. 6. Effect of salt concentration on the specific viscosity of 2% *A. lebbeck* polysaccharide solution in presence of: (△) NaCl; (■) $CaCl_2$; (●) $AlCl_3$. The point on the *y*-axis indicates the specific viscosity in absence of salt.

intermolecular crosslinking effect of Al^{3+} than that of Ca^{2+}. Sodium is not a crosslinking agent. Similar order of interaction has been observed with cashew nut gum (de Paula & Rodrigues, 1995).

Fig. 6 shows the specific viscosity of gum solution (2%) at different salt concentrations. The contribution of the shielding and crosslinking effects can be seen. At Al^{3+} concentration higher than 10^{-4} M, the crosslinking contribution prevails, as indicated by the viscosity increases. For calcium ions, there is a minimum salt concentration (3×10^{-4} g/dl) in order to make the intermolecular interaction predominant. At calcium concentration smaller than that, the screening effect prevails and a decrease of viscosity is observed due to the chain contraction. For sodium ions, only the shielding effect occurs. The chain contracts and viscosity decreases. The value of specific viscosity in absence of salt is 0.778. Those results are similar to that obtained for *A. occidentale* at the same range of salt and gum concentration (de Paula & Rodrigues, 1995).

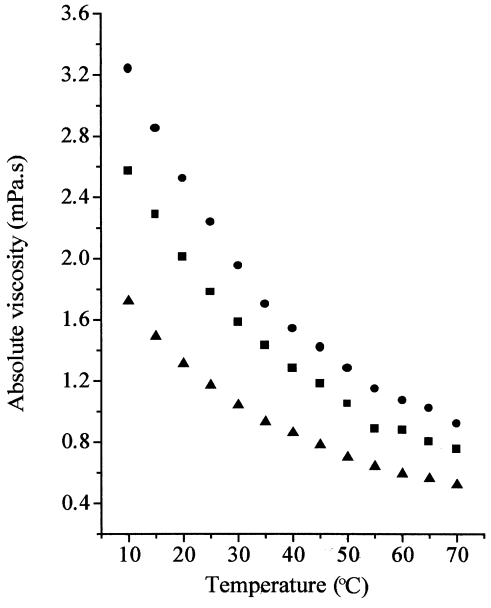

Fig. 7. Effect of temperature on the absolute viscosity of *A. lebbeck* polysaccharide aqueous solutions at concentration: (▲) 1%; (■) 2%; (●) 3%.

Both experiments suggest that the affinity between *A. lebbeck* gum and counter-ions depends on the charge/ionic radii ratios. Smaller ions with higher charge possess a stronger affinity with the chains. As the charge/ionic radii ratios are 0.058, 0.020, and 0.009 for Al^{3+}, Ca^{2+} and Na^{+} respectively, the order of interaction of *A. lebbeck* gum solution and metal ions are: $Al^{3+} > Ca^{2+} > Na^{+}$. Rendelman (1978) proposed that the affinity of metal ions with carbohydrate containing carboxylate groups follows the same order. The affinity order for karaya (Meer, 1980) and *A. occidentale* gum (de Paula & Rodrigues 1995) is also $Al^{3+} > Ca^{2+} > Na^{+}$, in agreement with the result found for *A. lebbeck* gum.

3.2.3. Effect of temperature

The effect of temperature on the viscosity of *A. lebbeck* gum solutions was investigated at a temperature range of 10–70°C (Fig. 7). A decrease of viscosity was observed for the solution at different gum concentrations. In order to verify if degradation or conformational transitions occurs during heating, the viscosity of the 2% gum solution was measured during cooling (Fig. 7). As for *A. occidentale* gum (de Paula & Rodrigues, 1995) and *A. macrocarpa* (Silva et al., 1998) no differences in viscosity were obtained, suggesting that neither degradation nor conformational transition has occured during heating.

The absence of a conformational transition was confirmed by applying the Arrehenius–Frenkel–Eyring equation (Vinogradov & Malkin, 1980) to the η versus T^{-1} data. For all gum solution concentration a linear curve was obtained for a plot of $\ln \eta$ vs. T^{-1} indicating a no order–disorder transition. From the slope of the lines, it was possible to calculate the apparent activation energy of flow (E_{at}) of 15.9, 16.6; 17.2 kJ mol^{-1} for 1, 2, 3% *A. lebbeck* gum solutions, respectively. These values were comparable with 2% solution of other branched polysaccharides, like arabic gum (15 kJ mol^{-1}, Varfolomeeva, Grinberg & Toistogusov, 1980), *A. occidentale* gum (16.2 kJ mol^{-1}, de Paula & Rodrigues, 1995) and *A. macrocarpa* gum (16.8 kJ mol^{-1}, Silva et al., 1998). Low activation energy of flow indicates few inter- and intra-interactions between polysaccharide chains in the concentration range investigated. Linear polymers strongly bonded by intra- and intermolecular interaction exhibit high value of E_{at}. Sodium carboxymethylcellulose in a 4% solution, for example, has E_{at} value of 27 kJ mol^{-1} (Narayan & Ramasubramanian, 1982), much higher than those observed for branched polysaccharide.

Structural and rheological data for arabinogalactan gums are presented in Table 4. The intrinsic viscosities in NaCl

Table 4
Structural and rheological data for some arabinogalactan gums

Gum	Uronic acid (%)	E_{at}[a] (kJ mol^{-1})	η_{abs}[b] 1% sol. (mPa s)	[η] (dl/g) in		
				NaCl[c]	$CaCl_2$[d]	$AlCl_3$[e]
A. occidentale	6.3	16.2	1.0	0.088	0.078	0.073
A. macrocarpa	7.0	16.8	1.1	0.108	–	–
A. lebbeck	10.5	16.6	1.2	0.223 ± 0.08	0.184 ± 0.03	0.168 ± 0.02
A. senegal	12.5[f]	15.0	1.8	0.243[f]	–	–

[a] Apparent activation energy of flow for 2% gum concentration.
[b] In water.
[c] 1.0 M.
[d] 0.334 M.
[e] 0.170 M.
[f] Average value (Vandevelde & Fenyo, 1985).

solution seem to be directly dependent on uronic acid content. There is no clear relationship between the activation energy of flow and that parameter. The degree of branching and multivalent cations content could be more important factors than the uronic acid percentage.

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