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Study of solution properties of galactomannan from the seeds of *Mimosa scabrella*

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The rheological properties of the galactomannan from the seeds of a member of the Leguminosae have been studied. The sample used had a mannose/galactose ratio close to 1 and an intrinsic viscosity of 900 ml/g.

The viscosity results are characteristic of a random coil polymer with a critical concentration $c^* = 2{\cdot}6/[\eta]$ which is similar to the values found for polystyrene and polystyrenesulphonate, but higher than the value obtained for more rigid polysaccharides. The slope of the logarithmic plot of the specific viscosity measured at zero shear rate against $c[\eta]$ in the semi-dilute regime was 4·2, a value in agreement with the theoretical predictions for linear polymers interacting by purely topological entanglements. The viscoelastic behaviour was lower than that found for solutions of other galactomannans and this and the less severe dependence of the viscosity on the coil overlap parameter is probably due to lower interactions because of the high galactose content.

INTRODUCTION

The viscosity and thickening properties of galactomannan extracted from the seeds of Leguminosae have found many applications in industry such as food, paints, cosmetics, paper products, pharmaceuticals, in oil drilling muds, and others (Sandford & Baird, 1983; Clark, 1986).

Their chemical structure is a linear $(1 \rightarrow 4)$-β-linked-D-mannose backbone which is substituted by single-galactopyranosyl units as side chains. These are attached to the backbone by $(1 \rightarrow 6)$-α-linkages (Soni & Bose, 1985).

The physical properties of the gums are determined in part by the amount and distribution of galactose side chains, as well as the molecular weight and polymer concentration.

Sharman *et al.* (1978) have studied galactomannans extracted from seeds of different legumes. A general relationship between the solution properties and the molecular weight, seems to hold for the series of galactomannans studied despite differences in the mannose to galactose ratios of the polymers. More recently, rheological properties of aqueous solutions of the guar galactomannan have been studied using flow and viscoelastic measurements (Doublier & Launay, 1977, 1981; Robinson *et al.*, 1982; Launay *et al.*, 1986). The effect of concentration and molecular weight on these properties indicated the random coil nature of guar but also its tendency to form specific polymer–polymer interactions in concentrated solutions in contrast to other polysaccharides (Morris *et al.*, 1981). Nevertheless, more recent work (Richardson & Ross-Murphy, 1987) showed that the behaviour of aqueous solutions of galactomannan studied from dynamic oscillatory, steady and transient shear methods appears to be typical of an entangled network with liquid-like behaviour at low frequencies.

This paper deals with the rheological behaviour of galactomannan from the seeds of *Mimosa scabrella* (bracatinga). This species, a native tree that grows abundantly in Southern Brazil, furnished 30% of whole seeds as galactomannan. This galactomannan is characterized by a low mannose to galactose ratio. The results obtained are discussed in terms of the previous studies and of the mannose to galactose ratio.

MATERIAL AND METHODS

Galactomannans of *Mimosa scabrella* were prepared from the milled whole seeds as previously described (Ganter *et al.*, 1988); crushed seeds (30 g) were extracted with 2:1 v/v benzene–ethanol in a Soxhlet apparatus

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(14 h). The residue was then extracted with water at 4°C (800 ml) for 24 h with constant mechanical stirring. The extract was concentrated and precipitated with three volumes of ethanol. After drying under vacuum we obtained 9 g of galactomannan i.e. a yield of about 30%.

Total carbohydrate content was assayed by the phenol–sulphuric acid method (Dubois *et al.*, 1956). Relative proportions of mannose and galactose were determined by total acid hydrolysis (1 M TFA for 5 h at 100°C). The monosaccharide analyses were performed by GLC on the corresponding alditol acetates. The proportions of mannose:galactose were confirmed by methylation analysis (Hakomori, 1964), ^{13}C-NMR and HPLC (Heyraud & Salemis, 1982).

Solutions were prepared by dispersing the known weights of the dry sample in deionized water during 16 h at 25°C under magnetic stirring.

Viscosity measurements were performed with a Low Shear 30 from Contraves ($10^{-2} < \dot{\gamma} < 128\ \mathrm{s}^{-1}$) and a Carri-Med CS 50 rheometer equipped with a Rheo 1000 C system and a 4-3 software which allows direct viscosity–shear rate determination by angular speed control. The different geometries used are double cylindric cylinders ($R1$ = 20 mm, $R2$ = 20·38 mm, $R3$ = 21·96 mm, $R4$ = 22·38 mm and h = 20·55 mm) and cones (4 and 6 cm diameters, 4° cone angle). For dynamic measurements, the cone of 4 cm as diameter has been used. The shear stress can be varied depending upon the geometry used from 0·005 to 3000 N m^{-2} and then approximate shear rate from 10^{-1} to 2000 s^{-1} depending on experimental conditions. All measurements were performed at 25°C.

RESULTS AND DISCUSSION

Polymer characterization

The purified galactomannan was found to be homogeneous. Complete hydrolysis of the polysaccharide revealed the presence of D-galactose and D-mannose. The ratio of constituent sugars was determined by HPLC after hydrolysis, GLC of their alditol acetates, ^{13}C-NMR and from methylated sugar proportion. The results are reported in Table 1.

The galactomannan extracted from the seeds of *Mimosa scabrella* contains a high galactose proportion as found for galactomannans from *Lotus*, lucerne and red clover (Sharman *et al.*, 1978). The intrinsic viscosity $[\eta]$ = 900 ml g^{-1} was determined in the Newtonian regime with the Low Shear viscometer. This is a normal value for galactomannans.

Flow behaviour

Flow curves in the Newtonian plateau and their dependence on shear rate were determined for galactomannan solutions over a wide range of polymer concentration (0·09 g litre^{-1} to 50 g litre^{-1}) as illustrated in Fig. 1. The values obtained with the two viscometers used are given.

No shear rate viscosity dependence is experimentally obtained in the range of $\dot{\gamma}$ used for the lower concentrations investigated. For higher concentrations ($c >$ 3·6 g litre), the behaviour becomes shear-thinning. It was observed as would be expected that the shear rate $\dot{\gamma}_r$ corresponding to the transition from Newtonian to viscoelastic behaviour moves to lower values with increasing concentration.

The concentration dependence of the specific viscosity at zero shear rate in a logarithmic plot is shown in Fig. 2. The representation is given as a function of the overlap parameter $c[\eta]$ (a) or as a function of the modified Huggins relation (b) $c[\eta] + k'(c[\eta])^2$. Two curves were obtained; the departure from slope 1 for curve b gives a critical concentration $c^*[\eta] \sim 2{\cdot}6$. It is attributed to the transition between the dilute and semi-dilute regime. The same determination for xanthan (Milas *et al.*, 1990), welan (Campana *et al.*, 1990) and succinoglycan (Gravanis *et al.*, 1990) leads to a critical c^* concentration in the range of $[\eta]^{-1}$. Usually in the literature c^* is determined from the intersection between the two linear parts of the curve $\log \eta_{sp} = f(\log c[\eta])$. In this representation, a unique curve is usually obtained for most randomly coiled hydrocolloids and the reduced critical concentrations $c^*[\eta]$ are generally found to be in the range of 2·5–4 (Morris *et al.*, 1981; Launay *et al.*, 1986). Our determination proposed for c^* fits with these previous results.

The higher values found for $c^*[\eta]$ on these polysaccharides compared to xanthan, welan or succinoglycan can be attributed to the higher stiffness of the last ones: the persistence lengths of these three polysaccharides is higher than 30 nm, while those of the other polysaccharides described (Morris *et al.*, 1981;

Table 1. Monosaccharides obtained from *Mimosa scabrella* seed galactomannan

Monosaccharides	Method			
	GLC	HPLC	^{13}C-NMR	Methylation
Mannose	1·1	1·19	1·0	1·07
Galactose	1·0	1·0	1·0	1·0

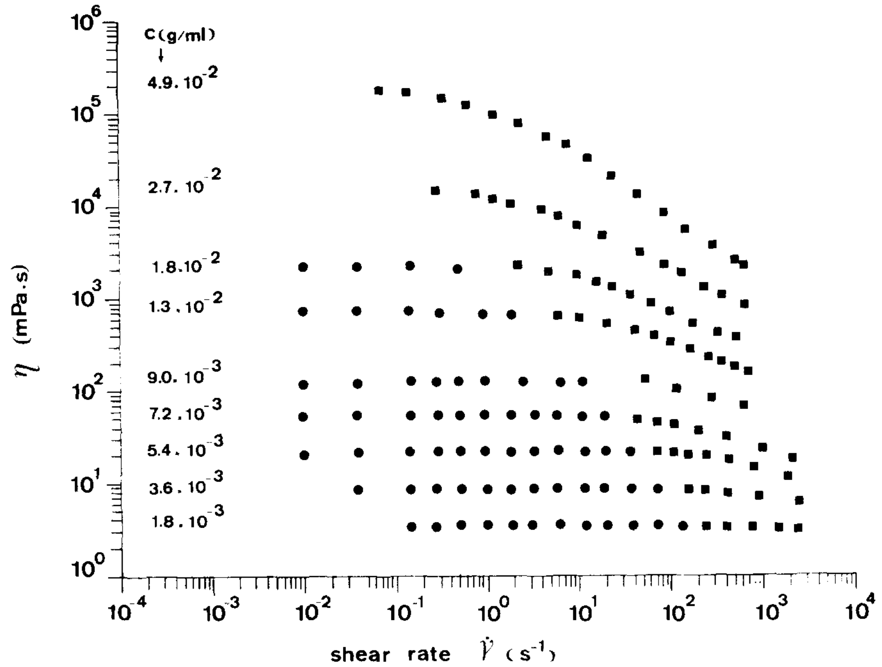

Fig. 1. Viscosity as a function of shear rate ($\dot{\gamma}$) for galactomannan in water. Concentrations expressed in g ml^{-1}. ●, Low Shear; ■, Carri-med.

Launay *et al.*, 1986) and galactomannans are known to be lower than 10 nm (Robinson *et al.*, 1982). A $c^*[\eta]$ value equal to 2·6 recently found on the flexible polymers, polystyrene and polystyrenesulphonate confirms this hypothesis (Ganter *et al.*, 1990).

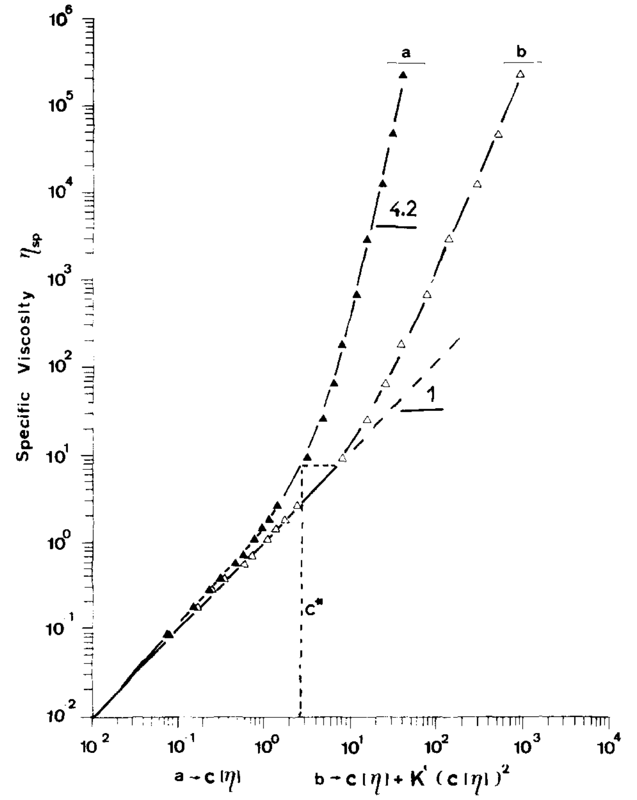

Fig. 2. Specific viscosity in the Newtonian plateau as a function of the overlap parameter. (a) $c[\eta]$ (b) $c[\eta] + k'(c[\eta])^2$.

For higher values of $c[\eta]$ (i.e. $c[\eta] > 7$) the logarithmic dependence of η_{sp} with $c[\eta]$ becomes linear with a slope of 4·2.

Then, the following relation is obtained:

$$\eta_{sp\dot{\gamma}\to 0} \sim (c[\eta])^{4\cdot 2} \sim c^{4\cdot 2}M^{3\cdot 05}$$

taking into account the Mark–Houwink parameter $a = 0{\cdot}723$ given in the literature, (Robinson *et al.*, 1982). This result is in good agreement with the dependence usually observed (Schurz, 1975)

$$\eta_{\dot{\gamma}\to 0} \sim c^4M^{3\cdot 5}$$

or with the theoretical dependence for linear polymers interacting in solution by purely topological entanglements in the absence of hydrodynamic interactions and in θ conditions (de Gennes, 1976, 1979):

$$\eta \sim M^3c^4$$

knowing that θ conditions are approached and hydrodynamic interactions decrease when polymer concentration increases.

The results found with this galactomannan species are different to other galactomannans. Previous results show a higher specific viscosity variation with polymer concentration for $c[\eta] > 7$. Consequently, the specific viscosity of galactomannan from *Mimosa scabrella* at a given polymer concentration i.e. $c[\eta] = 10$ is lower than the values obtained with other galactomannans (Table 2). This may be attributed to the higher content of galactose units reducing intermolecular interactions.

Guar galactomannan (having also a low mannose to galactose ratio) investigated previously (Robinson *et al.*, 1982) was reconsidered (Richardson & Ross-

Table 2. Specific viscosities (η_{sp}) for overlap parameter $c[\eta] = 10$; slopes, S, of logarithmic variation of η_{sp} versus $c[\eta]$ for $c[\eta] > 7$; limit slope, n, of the logarithmic variation of the viscosity versus the shear rate in the viscoelastic domain; mannose to galactose ratio, M/G, for different galactomannans. Comparison with the generalized concentration dependence found on polysaccharides (e)

	References					
	a	b		c	d	e
η_{sp} at $c[\eta] = 10$	600	6300	2200	2000	300	250
S	5·1	6·65	4·5	4·3	4·2	3·3
n	−0·79	−0·73	−0·7	0·72	(−0·65)*	−0·72
M/G	1·56	4	2	3·85	1·1	—

a, Robinson *et al.* (1982); b, Doublier & Launay (1981); c, Morris *et al.* (1981); d, this work; e, Morris *et al.* (1981).
*The brackets mean that the limit is not attained.

Murphy, 1987); in this last paper, they found a better liquid-like behaviour and a typical entangled network response. The experimental data seem to depend on the purification and preparation of solution.

A comparison of the storage and loss modulus found in these two last papers with the experimental data obtained on galactomannan from *Mimosa scabrella* are given in Fig. 3. Knowing that the intrinsic viscosity of the two galactomannans compared are similar, these results confirm the liquid-like behaviour of galactomannan from *Mimosa scabrella* even in semi-dilute solutions.

Above a critical shear rate and polymer concentration, the galactomannan solutions show a viscoelastic behaviour. The relationship between the viscosity and the shear rate can be expressed by: $\eta \sim \dot{\gamma}^n$ The values of the slope n as a function of the overlap parameter $c[\eta]$ are shown in Fig. 4. In this figure we added the values obtained by Sharman *et al.* (1978) for different sources of galactomannan. In Table 2, we reported the limit of n reached in the high $c[\eta]$ domain. Our n values, even if no limit is attained, agree quite well with those of Sharman *et al.* for $c[\eta]$ lower than 30 but are a little bit lower than the values obtained by other authors. As n values are affected by polydispersity (Graessley, 1974) and the presence of specific interactions (hyperentanglements) between chain segments in an opposite way, these results may characterize a polydispersed sample in the absence of large specific interchain interactions.

CONCLUSION

The rheological properties of galactomannan solutions from *Mimosa scabrella* show a typical behaviour of a

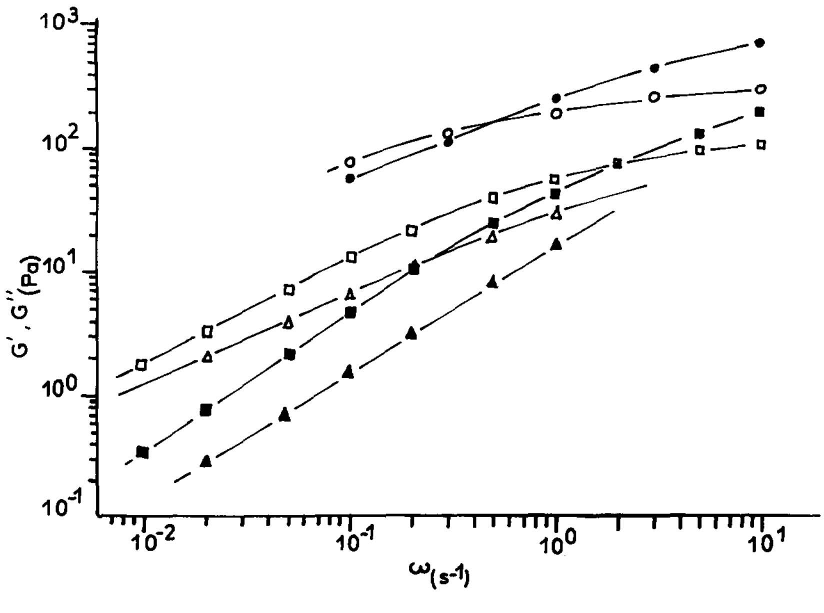

Fig. 3. Storage modulus G' (▲) and loss modulus G'' (△), at 25°C, plotted against frequency for galactomannan from *Mimosa scabrella* (c = 2·7% w/w, $[\eta]$ = 900 ml g^{-1}, $c[\eta] \sim 24$). Comparison with the results of Robinson *et al.*, 1982 (●, ○) and Richardson & Ross-Murphy, 1987 (■, □) on galactomannan Vidocrem D (c = 3% w/w, $[\eta]$ = 880 ml g^{-1}, $c[\eta] \sim 26·4$).

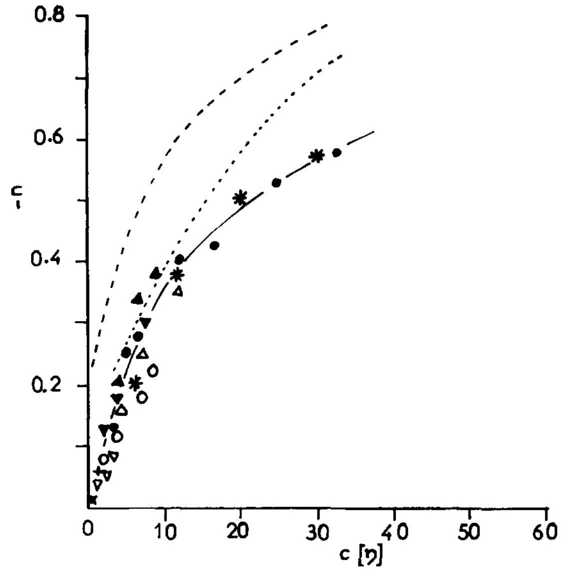

Fig. 4. Exponent $-n$ (●) of the power law $\eta \sim \dot{\gamma}^n$ in the non-Newtonian regime as a function of the polymer concentration expressed as the overlap parameter $c[\eta]$ for galactomannan from *Mimosa scabrella* in water. Comparison with galactomannans from other sources (Sharman *et al.*, 1978). ×, *Lotus* 1; +, soy bean; O, lucerne; △, carob; ▽, *Lotus* 2; ▲, *Sophora japonica*; ▼, red clover; *, guar. (.....) data from Graessley (1974) for polystyrene in toluene. (----) data from Milas *et al.* (1990) for xanthan.

liquid-like solution in contrast to most of the galactomannans described in the literature. This difference has been attributed to the high galactose content of this galactomannan species. The results obtained are characteristic of a random coil polymer with a departure from the Huggins law for coil overlap parameter $c[\eta]$ higher than 2·6, that corresponds to a critical concentration $c^* = 2{\cdot}6/[\eta]$ similar to the values found for polystyrene and polystyrenesulphonate (Ganter *et al.*, 1990), but higher than the value obtained in more rigid polysaccharides (Milas *et al.*, 1990). The slope of the logarithmic variation of the specific viscosity measured at zero shear rate with $c[\eta]$ in the semi-dilute regime attains 4·2 value in agreement with the theoretical prediction for linear polymers interacting by purely topological entanglements. The galactomannan solutions from *Mimosa scabrella* show lower viscoelastic behaviour compared to other polysaccharides and other galactomannans which is perhaps a consequence of the polydispersity index of our sample but also to lower interactions due to the high galactose content.

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