Reversible Gel Formation Induced by Ion Complexation. 1. Borax–Galactomannan Interactions

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ABSTRACT: The cross-linking mechanism involved in the formation of reversible gels in galactomannan–borax systems has been investigated. We studied interactions between borate ion and guaran or (hydroxypropyl)guaran. Borate ions can form several types of complexes with the various hydroxyl groups of the sugar units. To elucidate the structure of the involved complexes, glycoside compounds were used as models. Evidence of the existence of five-membered and six-membered ring monodiol- and didiol–borate complexes has been obtained by ^{11}B NMR studies. Complex formation constants were determined at four temperatures from ^{11}B NMR spectra. In addition the thermodynamic functions ΔH and ΔS are reported. For guaran and (hydroxypropyl)guaran it was possible to detect monodiol–borate complexes whose formation constant was calculated from dialysis experiments.

Introduction

Polymeric chains containing complexing groups can be linked by metal ions or Lewis acids. For instance, water-soluble polymers, such as partially hydrolyzed polyacrylamide or polysaccharides, are gelled by ions and are widely used in petroleum industry.[1] A large number of chemical elements including chromium,[2] titanium,[3] zirconium, antimony, and boron[4] have been used as cross-linking agents. Each ion imposes its own conditions (concentration range, pH, ionic strength, oxidation state, ...) for optimum cross-link formation. However, the cross-linking mechanism is rarely well established, and the gel properties depend strongly on the nature of the binding ions and on the number of induced temporary links.

The present work deals with the formation of weak reversible gels of galactomannans by complexation reactions with borate. Galactomannans are among the most commonly used polymers in industrial practice and their structure is relatively well-known.[5-8] The use of the borate ion is particularly appealing because the induced cross-links are very labile and the systems are easily brought to thermal equilibrium. In this paper, we present results concerning the cross-linking mechanism. We study galactomannan and glycoside interactions with borate by ^{11}B NMR and equilibrium dialysis techniques. The results give us a good understanding of the complexation reactions involved and enable us to control the number of cross-links induced at various conditions, which allows further studies of phase diagrams and rheological properties.

Experimental Section

Materials. (Hydroxylpropyl)guar and guar gums were kindly provided by Etudes et Fabrications Dowell Schlumberger. (Hydroxypropyl)guar is just a derivative of guar in which some of the hydroxyl groups on sugar units have been substituted by hydroxypropyl groups upon ether formation. The molar substitution of our sample is 0.48. These materials were purified by dissolution in cold water (deionized water, Milli-Q system of Millipore), centrifugation (2 hours at 20000*g*), and precipitation in ethanol. The dried and ground product was then redissolved in cold water and centrifugated. This sample preparation leads to low mannose to galactose ratios:[9] 1.2 for (hydroxypropyl)guaran and 1.3 for guaran (determined by acid hydrolysis[10] followed by thin-layer chromatography[11] and spectrophotometric titration[12]). The weight-average molar weights, estimated by light scattering (Fica photometer with a 6328-Å He–Ne laser as a light source, were found to be around 2.8×10^6 for (hydroxypropyl)guaran and 4.5×10^6 for guaran. Absolute concentrations of polymers in water were determined by total organic carbon analysis (DC 80, Dohrmann/Xertex). Galactomannans are actually polysaccharides, which consist in a linear chain of (1→4) β-D linked mannopyranosyl residues with 1–6 substituted α-D-galactopyranosyl groups.[5] Methyl α-D-galactopyranoside and methyl α-D-mannopyranoside are interesting models of galactomannan sugar units and allow a study of the various diol sites available for borate complexation (see Figures 1–3). These glycosides, borax ($Na_2B_4O_7{\cdot}10H_2O$), and other chemicals are of analytical grade and commercially available.

^{11}B NMR. All NMR spectra were recorded with a Bruker WP 250 spectrometer at 80.25 MHz by using 10-mm-o.d. sample NMR tubes. Boron-11 chemical shifts were referenced to external $BF_3O{\cdot}(C_2H_5)_2$. The samples (5 mL) were prepared by dissolving the appropriate amounts of borax, sugar, and NaCl in deionized water (Milli-Q system of Millipore) and D_2O. The pH was adjusted with NaOH. Peak assignments were made by a preliminary study of linear diols,[13] which yielded results in very good agreement with those of Van Duin et al.[14] The association constants were calculated from the measure of the relative area of each signal. The association constants reported in Table I are mean values determined over a range of total borate (0.01–0.02 M) and sugar (0.1–0.3 M) concentrations. Errors associated with the constants are ±5% for determinations in basic conditions, ±10% for determinations in borax buffered conditions.

Dialysis Experiments. The equilibrium dialysis technique has been often used by biochemists for the study of metal–protein complexes.[15] In this technique, a vessel is divided into two compartments by a membrane that is impermeable to the polymer molecules but fully permeable to the smaller ions. If the polymer is confined to one compartment and if it binds some of the ions, then at equilibrium the total concentration of ions in the polymer side will exceed that in the free-ion side. The difference between these two concentrations is a measure of the concentration of bound ions. Some asymmetry in the distribution of the ions may exist because of the Donnan effect, but adding a passive electrolyte reduces it to negligible proportions.

In this study dialysis bags were prepared from carefully washed cellulose sausage casing and filled with a known volume of a borax solution. The bag was then immersed in a glass-stoppered tube that contained the same volume of a predialyzed guaran solution. Equilibrium was reached, after 8 days at 23 °C. The free borate concentration $|B^-|$ was then determined by a hydrochloric acid titration. A control run, with a 1 M NaCl solution without polymer outside the bag, was performed in order to take into account the amount of borax bound to the bag. Free borate was titrated inside and outside the bag. The amount of borate bound to the bag was assumed to be equal to the difference between the initial borate concentration and the total borate concentration determined by titrations after equilibrium. In the presence of polymer, the concentration of formed complex was then calculated from the difference between the total amount of borate and the free borate in 1 M NaCl solution. The polymer concentrations used were low (0.1% and 0.2%), so that only monodiol-type complexes were formed. The monodiol–borate complex formation constant was then directly calculated:

$$K_1 = \frac{|\text{complexed borate}|}{|\text{free borate}|\cdot|\text{free galactomannan sugar unit}|} \quad \text{(I)}$$

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Table I
Association Constants and Thermodynamic Functions for Glycoside-Borate Complexes

		association constants						thermodyn fcns[c]	
			T, K						
compd	complex	K_i	283[a]	296[a]	296[b]	315[a]	335[a]	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}
MαDGP	$BP^-\alpha,\beta$	K_1, L mol^{-1}	12.5	10.2	12.1	9.6	7.1	−7.8	−6.8
	$B(P^-\alpha,\beta)_2^-$	K_2, L^2 mol^{-2}	22.6	17.3	20.5	12	9	−14	−23
	$BP^-\alpha,\gamma$	K_1, L mol^{-1}	8.1	7.1	5.9	6.1	4.2	−9.5	−16
	$B(P\alpha,\gamma)_2^-$	K_2, L^2 mol^{-2}			8.7				
MαDMP	$BP^-\alpha,\beta$	K_1, L mol^{-1}	15	12.4	10.9	11.8	8.9	−7	−2.2
	$B(P\alpha,\beta)_2^-$	K_2, L^2 mol^{-2}	27	21.4	23.6	19.2	12.9	−10	−8.2
	$BP^-\alpha,\gamma$	K_1, L mol^{-1}	2.4	1.9	2.4	3.5	1.8		

[a] pH 11. [b] Borax-buffered conditions. [c] Calculated from the relations $\ln K = -\Delta G/RT$ and $\Delta G = \Delta H - T\Delta S$.

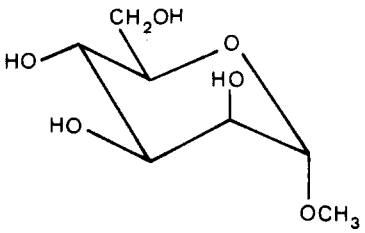


Figure 1. Methyl α-D-mannopyranoside (MαDMP).

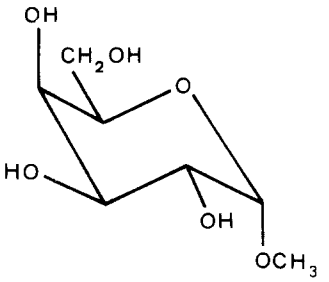


Figure 2. Methyl α-D-galactopyranoside (MαDGP).

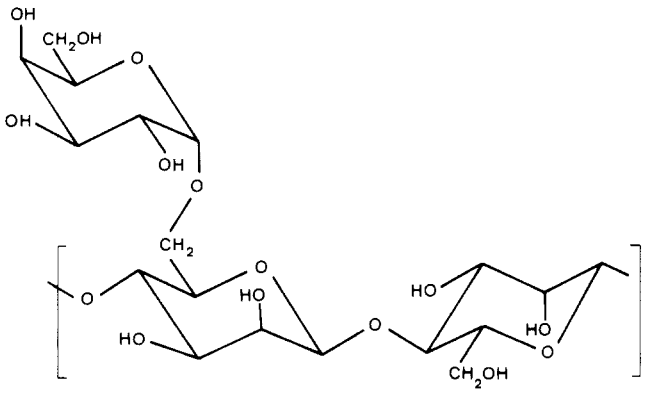


Figure 3. Typical structure unit of guaran.

In some cases (not too viscous polymer solutions), the total amount of borate ion (free plus complexed) was determined by titration of solution outside the bag and the free borate concentration was measured by titration of the inside solution. The difference of these two concentrations represents the complexed borate ion concentration. K_1 values obtained by this procedure are in good agreement with those determined as explained above.

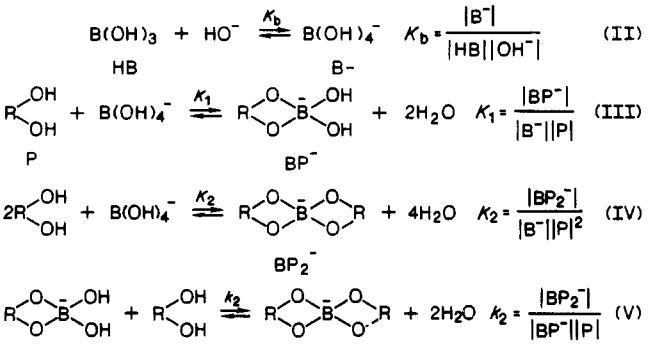
Results and Discussion

The formation of complexes between borate and simple polyols is well-known and numerous studies have been carried out on interactions of simple polyols with borate ions.[14,16-22]

The dissociation of boric acid and the successive reactions involved in the diol–borate complexation are displayed in Scheme I.

Borax Solutions. ^{11}B NMR spectra of a borax solution show a pH-dependent average signal due to the rapid exchange of boric acid (δ 18.4) and borate (δ 0.6). In the concentration range investigated (0.01–0.03 M), monomeric species largely prevail[23,24] and no polyborate ion was observed.

Scheme I



Borax or sodium tetraborate ($Na_2B_4O_7$, is a good buffer, and at low concentrations, it is totally dissociated into equal quantities of both monomeric species:

$$B_4O_7^{2-} + 7H_2O \rightleftarrows 2B(OH)_3 + 2B(OH)_4^- \quad \text{(VI)}$$

No boric acid–diol complex has been detected. So adding a diol to the borax solution lowers the pH, since borate ions are taken up by complex formation and equilibrium II is displaced. Figure 4 shows that when borate ions are complexed, the signal relative to the rapid acid–base exchange (II) is shifted downfield. We assumed therefore that in borax buffered conditions, the boric acid concentration remains unchanged during complexation.

Methyl α-D-Galactopyranoside- and Methyl α-D-Mannopyranoside–Borate Interactions. Ring sizes of glycoside models, methyl α-D-galactopyranoside (MαDGP) and methyl α,D-mannopyranoside (MαDMP), are fixed so that for each of these glycosides, only two kinds of monodiol–borate complexes were observed: one five-membered ring complex corresponding to the α,β-diol site (Figure 5) and one six-membered ring complex corresponding to the α,γ-diol site (Figure 6). Spectra in Figures 4 and 7 show that MαDGP also forms two kinds of di-diol–borate complexes, five-membered rings and six-membered rings, while with MαDMP no signal relative to diester of α,γ-type is observed. This difference may be attributed to the relative positions of OH-4 and OH-6: syn for MαDGP and anti for MαDMP. No signal relative to any mixed five- and six-membered ring diester was clearly observed, but this type of dicomplex has already been detected with some polyols.[18] Figure 8 shows the variation of the chemical shifts, with pH. No boric acid–diol type complex is observed. Signals relative to complexes only appear at pH higher than 7.5, i.e., when borate ions are present in solution. This is fully consistent with the observed influence of the pH on rheological properties of

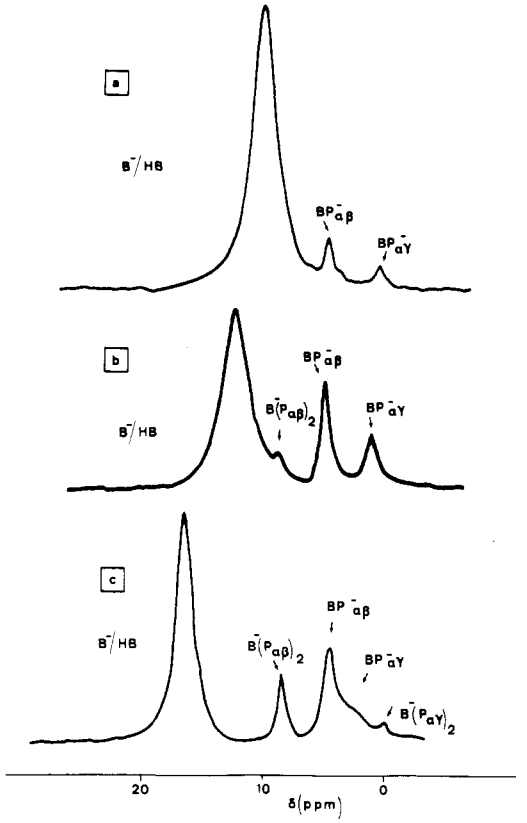


Figure 4. ^{11}B NMR spectra of borax $|B^-|_0 = 1.12 \times 10^{-2}$ M and methyl α-D-galactopyranoside at different concentrations in water (T = 23 °C). (a) |MαDMG| = 10^{-2} M, pH 9.15; (b) |MαDMG| = 10^{-1} M, pH 8.92; (c) |MαDMG| = 0.25 M, pH 8.28. When the concentration of polyol added to the borax solution increases, more complexes are formed, so that the concentration of free borate ions decreases. The acid–base equilibria (eq II) is displaced which lowers the pH and shifts downfield the signal relative to the acid–base exchange.

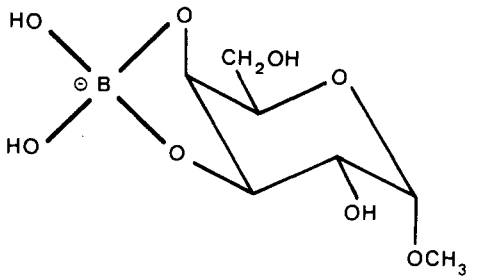


Figure 5. MαDGP–borate complex (α,β-diol–borate complex: BP⁻α,β).

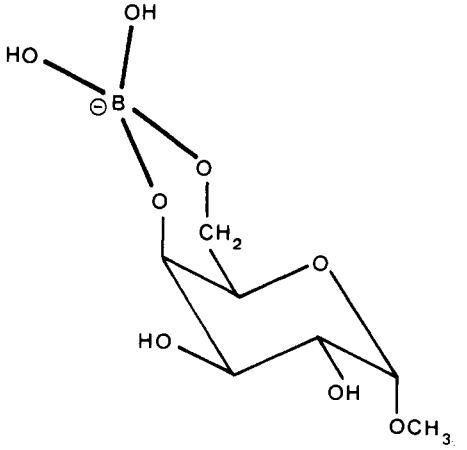


Figure 6. MαDGP–borate complex (α,γ-diol–borate complex: BP⁻ α,γ).

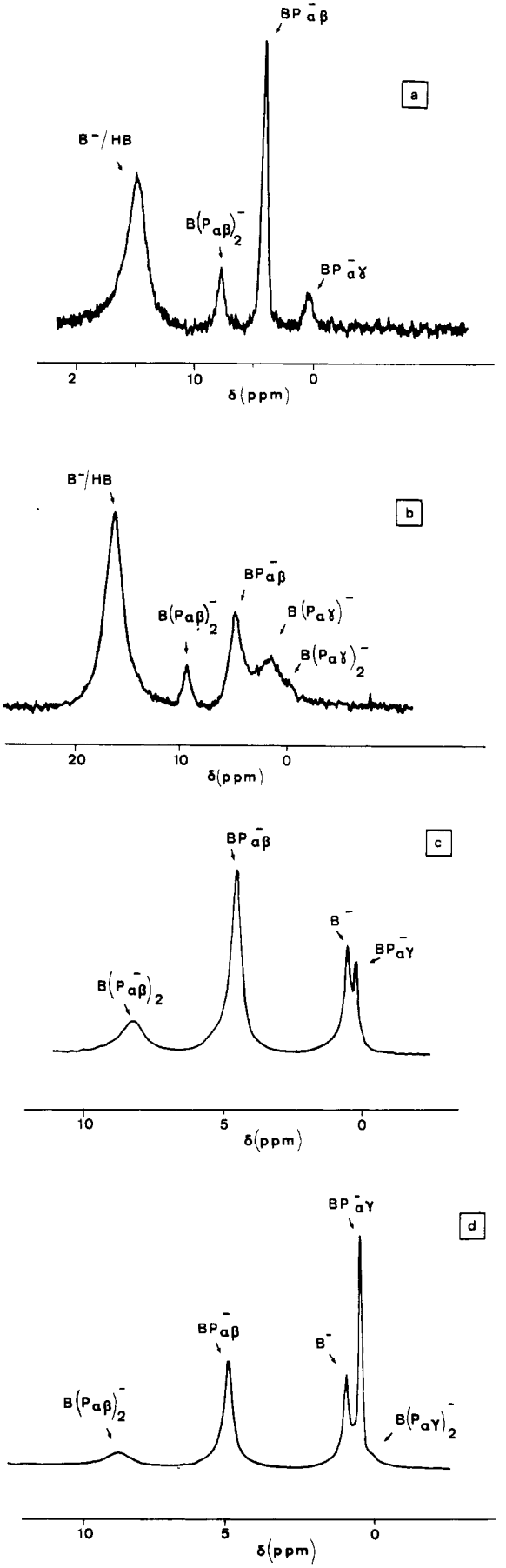


Figure 7. ^{11}B NMR spectra in 1 M NaCl and T = 23 °C. Concentration of borax, 2.5 g/L; concentration of glycoside, 0.2 M. (a) MαDMP in borax buffered conditions; (b) MαDGP in borax buffered conditions; (c) MαDMP at pH 11; (d) MαDGP at pH 11.

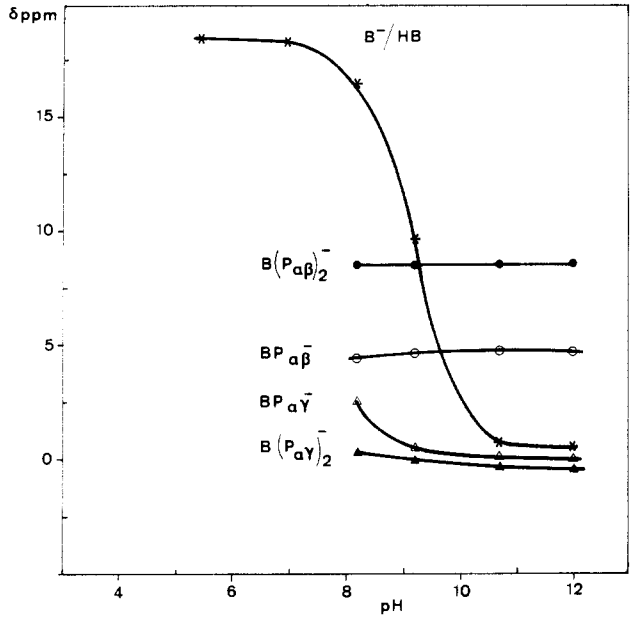


Figure 8. ^{11}B NMR data: boric acid (2.6×10^{-3} M) and MαDGP (0.2 M) in aqueous solution at different pH values.

Table II
^{11}B NMR Chemical Shifts for Borate Diol Complexes in Aqueous Solution[a]

compound	diol site	δ_{BP^-}	$\delta_{BP_2^-}$
(hydroxypropyl)guaran	α,β	4.6	
	α,γ	0.4	
guaran	α,β	4.7	
	α,γ	0.4	
MαDGP	α,β	4.6	8.5
	α,γ	0.4	0.0
MαDMP	α,β	4.5	8.1
	α,γ	0.5	

[a] At 23 °C and pH 9.

galactomannan–borax systems:[4] no gelling or thickening effect appears when the pH is lower than 7.5. Besides, only the peaks assigned to the exchange between boric acid and borate ion and to the α,γ-diol–borate complexes were significantly shifted with pH. It seems that the latter complexes are less stable than α,β-diol–borate complexes and undergo faster exchange rate with their conjugated acid form.

The amount of complex formed between borate ion and the two glycosides in a 1 M NaCl solution was measured from ^{11}B NMR spectra at four temperatures in alkaline conditions (pH 11) and at 296 K in borax buffered conditions,[25] allowing determination of the association constants, K, and thermodynamic functions (see Table I). The smaller constants observed for the α,γ-diol site may be explained by the greater loss of rotational freedom when complexation occurs, with an additional contribution of the anti position in the case of MαDMP. The values calculated for ΔH and ΔS of borate diester formation are very close to those reported for galactarate.[14]

(Hydroxypropyl)guaran- and Guaran–Borate Interactions. In order to observe chemical shifts corresponding to the various complexes, we prepared samples with galactomannan concentrations of at least 10 g/L—i.e., 6.2×10^{-2} mol/L of sugar units—so that the guaran- or (hydroxypropyl)guaran–borate systems studied were gels. In such conditions it was not possible to detect a peak assignable to a didiol complex. But the ^{11}B NMR spectra of these systems show unambiguously two peaks, corresponding to the two kinds of monodiol–borate complexes

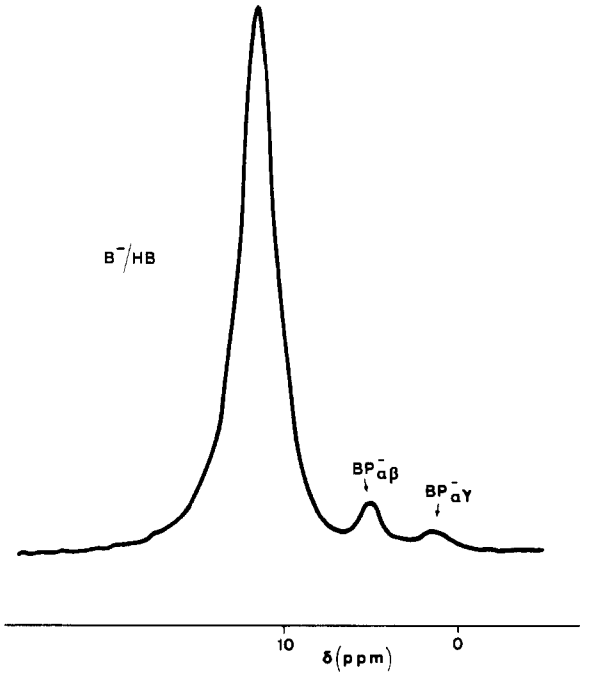


Figure 9. ^{11}B NMR spectra of (hydroxypropyl)guaran (18.7 g/L) and borax (2.15 g/L) in 1 M NaCl.

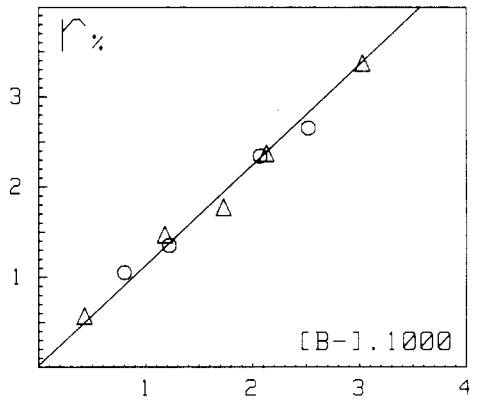


Figure 10. Binding isotherm (T = 23 °C) of borate to guaran. r is the percentage of sugar units complexed. $[B^-]$ is the titrated free borate concentration: (○) C_{guaran} = 1030 mg/L; (△) C_{guaran} = 2060 mg/L.

(see Table II and Figure 9). Nevertheless, no accurate determination of the formation constants can be expected from these spectra at low complex concentrations. In addition, in pure water, the evolution of the ^{11}B NMR glactomannan–borax spectra with the polymer concentration shows a leveling-off with the number of charged diol–borate complexes formed on the galactomannan chain. This behavior can be understood if we consider the electrostatic repulsion between the negatively charged complexes. Studies on the very similar poly(vinyl alcohol)–borate systems in dilute solutions[26] or in gels[27] by different techniques point out the same polyelectrolyte behavior of the complexed polymer chain. Moreover, it was possible to measure the number of complexes formed in 1 M NaCl by dialysis experiments. Figure 10 shows the binding isotherm of borate to guaran at 23 °C. These results allowed the determination of the value of the formation constant K_1, taking into account both α,γ-diol and α,β-diol sites. This constant K_1 may be compared with the model complexation constants calculated for guaran on the basis of moles of sugar unit per liter and taking into account only the α,β-diol site for MαDMP and both α,γ- and α,β-diol sites for MαDGP (see Table III).

Table III
Comparison of Formation Constants Obtained from ^{11}B NMR Data for Models and from Dialysis Experiments for Guaran[a]

compound	diol site	K_1	$k_2 = K_2/K_1$
MαDMP	α,β	10.9	2.2
MαDGP	α,β + α,γ	18	1.6
guaran	α,β + α,γ	11.4	

[a] T = 23 °C, 1 M NaCl, borax-buffered conditions.

The monodiol–borate complex formation constant measured for guaran is in the range of the values determined for the two models. Foster from ionophoretic studies,[21] Malcolm et al.[22] from refractive index and optical rotation measurements, and Gorin et al.[28] from proton magnetic resonance spectra showed that methyl β-D-mannopyranoside does not form borate complexes as readily as methyl α-D-mannopyranoside, because of the steric hindrance of the glycosidic methoxyl group. In the case of guaran in which linkages between mannopyranoside units are of type β, the galactose side units are the most likely points of monocomplex formation. This proposition is not in contradiction with Figure 9, which shows that the relative amounts of five- and six-membered ring complexes formed with guaran are close to those observed with MαDMG–borate complexes. It also agrees well with the formation constants of the monodiol–borate complexes. Consequently the ability of galactomannans to complex borate ions may be expected to decrease when their mannose to galactose ratio is higher.

Conclusion

This study shows that, except for polyelectrolyte effects, guaran and (hydroxypropyl)guaran seem to behave as glycoside models (especially methyl α-D-galactopyranoside) toward borate complexation: Five- and six-membered ring monodiol–borate complexes are formed. Formation constants K_1 are of the same order of magnitude. Complexes are more readily formed on galactose units. Majority of the cross-links are likely five-membered ring didiol–borate complexes. The diol–borate complexation is an exothermic reaction.

These results may provide useful information for understanding phase diagrams and rheological properties of galactomannan–borax systems.

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Note Added in Proof. After this work was completed we received a preprint by C. Gey, O. Noble, S. Perez, and F. Taravel, who studied the complexation reactions of glycoside models with borate ions at pH 12 and T = 295 K. Their results are in agreement with ours.

Registry No. Borax, 1303-96-4; galactomannan, 11078-30-1; guaran, 9000-30-0; (hydroxypropyl)guaran, 39421-75-5.

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