J. Braz. Chem. Soc., Vol. 11, No. 3, 224-231, 2000.
Printed in Brazil

0103 - 5053 $6.00+0.00

Article

Evaluation of the Complexes of Galactomannan of *Leucaena leucocephala* and Co^{2+}, Mn^{2+} , Ni^{2+} and Zn^{2+}.

Ana Lucia R. Mercê**, Erika Fernandes, Antonio S. Mangrich and Maria Rita Sierakowski

Departamento de Química, Centro Politécnico, Universidade Federal do Paraná, C.P. 19081, 81531-990, Curitiba - PR, Brazil

As constantes de complexação em solução aquosa para soluções de galactomanana da *Leucaena leucocephala* e íons metálicos Co^{2+}, Mn^{2+}, Ni^{2+} e Zn^{2+} foram obtidas por titulações potenciométricas. Os valores obtidos mostraram que o íon metálico Ni^{2+} é o ácido de Lewis que se complexa melhor com os grupos -OH, bases de Lewis, dos açúcares monoméricos do biopolímero e o Zn^{2+}, o ácido de Lewis que se complexa mais fracamente. A maior percentagem das espécies complexadas destes equilíbrios se concentraram no pH=7,0, existindo porém quantidades significativas em valores de pH tanto na região ácida quanto básica.

Os complexos sólidos isolados das soluções aquosas foram estudados por TG-DSC e espectroscopia de EPR. As curvas de comportamento térmico mostraram que para os complexos ML de menores valores de log K (Zn^{2+} e Mn^{2+}) as temperaturas de degradação final são maiores quando comparadas à do biopolímero. Os espectros de EPR confirmaram a complexação entre os íons metálicos e os sítios básicos do polissacarídeo, grupamentos hidroxilas desprotonados $-O^-$, e mostraram a dependência da natureza do íon metálico na distância em que se encontram complexados dentro da estrutura do biopolímero.

A habilidade da galactomanana em complexar íons metálicos variados em sua estrutura entrincada, a resistência que esses complexos exibiram frente a altas temperaturas e a faixa larga de pH em que as espécies complexadas mostraram-se presentes abrem novas perspectivas de utilização destes materiais em processos industriais onde essas propriedades são desejáveis, em bioremediação de rejeitos aquosos e na química de solos, como fertilizantes "slow-release".

The binding constants for the complexed species formed in aqueous solution between galactomannan of *Leucaena leucocephala* and the metal ions Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} were determined by potentiometric titrations. The calculated values showed Ni^{2+} as the best Lewis acid towards the Lewis base -OH groups of the sugar monomers, with Zn^{2+} being the poorest. For all systems, a higher percentage of the complexed species was present near pH=7.0, although complexed species existed over a wide range of acidic and basic pH values.

The isolated solid complexes were studied by TG-DSC thermal analysis and by EPR spectroscopy. The thermal profiles obtained showed higher thermal resistance to final degradation than the biopolymer alone for the complexed species ML having the smallest log K values. The EPR spectra confirmed the complexation of the metal ions *via* the Lewis base deprotonated hydroxyl groups (-O) and showed that the distances between metal ions in the complexed biopolymer structure depend on the nature of the metal ion.

The ability of galactomannans to complex a variety of metal ions in their web like structure and the resistance to high temperatures and a wide range of pH values of these complexes open new perspectives in possible industrial uses whenever these properties are required, such as in bioremediation of waste waters and in the application of slow-release fertilizers.

Keywords: potentiometric titrations, EPR spectroscopy, TG-DSC, metal complexes

Introduction

Galactomannans are mainly found in the endosperm of seeds from the Leguminosae family. They consist mainly of mannose and galactose in different ratios with the ratio varying with different species, crops, portions or fractions. They are used either in their native states or as derivatives. Their properties depend on their chemical structure, such as chain length, availability of *cis*-OH groups, steric hindrance and substituents. Any additional crosslinking *via* hydrogen bonds or *via* any other chemical reaction means less solubility, so an increase in substitution in the main chain of the polysaccharide leads to higher solubility. Galactomannans play an important role as improving agents in processes where the aqueous system has to be thickened or where hydrophilic materials need to be coated, depressed or suspended [1].

*e-mail: anamerce@quimica.ufpr.br

Galactomannans from seeds of Leguminosae are alternative sources for other polysaccharides employed in industry such as guar gum[2] and locust bean gum[3], since they have the same sugar composition. The variation in the degree of substitution and the ability of complexing metal ions may lead to different chemical properties.

Equilibrium studies of some metal ions and monosaccharides (aldoses e ketoses) and oligosaccharides were recently reviewed being the mathematical model used to calculate the binding constants only suitable for simple molecules rather than polysaccharides[4].

In this work the complexing ability of a galactomannan (mannose to galactose ratio of 2.6:1) was investigated with respect to the metal ions Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}. Also, investigated was the complexed species with the metal ion Cu^{2+} [5]. These metal ions have roles in the environment, in the chemistry of soils and in everyday human life[6-11].

The knowledge of the binding constants and their speciation as functions of pH values[12] can contribute to the development of applications, such as the use of galactomannan in the elimination of metal ions during the flocculation step of contaminated water treatment, and especially in those cases where those solid complexes can be used as slow-release fertilizers [8-10].

Potentiometric titration was used to evaluate the binding constants of the complexes in aqueous solutions and electron paramagnetic resonance spectroscopy (EPR) and thermal analysis by thermogravimetry - differential scanning calorimetry (TG-DSC), were used to investigate some structural aspects of the complexed species between the biopolymer and the metal ions in the solid state.

Experimental

Materials

All chemicals used were of analytical-reagent grade and were used as received. Freshly boiled distilled de-ionised water and grade A glassware were used in preparation of all solutions. The galactomannan used was extracted from seeds of *Leucaena leucocephala* (Leu), as described elsewhere[5]. The identity and proportion of monosaccharides were determined by analysis of their alditol acetate derivatives[13,14].

The final solution of the polysaccharide used in the potentiometric titrations was 1g L^{-1}. The molecular weight of either one of the two galactomannan monomers was used to provide the number of mols of the solution. Any monomeric sugar portion of the biopolymer is referred as the ligand (L) throughout this work.

The metal ion (referred throughout this work as M) aqueous solutions were made from the appropriate mass of nitrate salts for Co(II), Ni(II) and Zn(II) (Carlo Erba - Brazil) and from a Titrisol^{TM} solution (Merck - Brazil) for Mn(II). All the three nitrate solutions were standardized using methodology from the literature [15].

A carbonate free solution of 0.1 mol L^{-1} KOH was prepared from pellets (Merck - Brazil) and standardized by titration with potassium acid phthalate (Carlo Erba - Brazil). KNO_3 (Merck - Germany) was used as supporting electrolyte to maintain the ionic strength (μ) at 0.100 mol L^{-1}.

Methods

The alditol acetates derived from the biopolymers studied were analyzed by GLC-MS with a model 3300 Varian equipped with an OV-225 capilary column (0.25mm id x 30m) linked to a Finnigan Trap model 419 mass spectrometer unit at 70 e.V. Injections were carried out at 50ºC and the column was then heated (4.0ºC min^{-1}) to 220ºC.

All potentiometric titrations were carried out using an Orion (USA) model 420-A research grade pH meter with an Orion (Switzerland) model 91-61 glass electrode and a double junction Ag/AgCl reference electrode Orion (USA) model 90-02, stored in distilled water for short period of times, and in its filling solution (10% KNO_3 - Merck - Germany) for longer period of times. The standard procedure to standardize the pH meter followed strictly the procedures described in literature [16], where the slope was set by several trial titrations of standard HCl (Merck - Brazil) $5x10^{-3}$ mol L^{-1} [μ = 0.100 mol L^{-1} (KNO_3)] and KOH 0.1 mol L^{-1} up to the third pH decimal digit until the experimental values fitted the calculated ones by $\leq$ 0.005 pH units in buffer and at low pH values, and $\leq$ 0.015 pH units at high pH values [16]. The pH studied range was from 2.000 to 11.000. The standardization at low pH was made with a standard HCl solution, around 5 x 10^{-3} mol L^{-1} [μ = 0.100mol L^{-1} (KNO_3)] whenever a new experiment was to be performed.

All titrations were made in triplicate under a stream of purified N_2 (White-Martins, Brazil) using three aqueous solutions, the first one of pyrogallol (Merck-Germany) in KOH, the second of KOH 1 mol L^{-1}, and the third of KOH 0.1 mol L^{-1}. The temperature was maintained at 25.0 ± 0.1ºC (MQBTC 99-20, Microquímica - Brazil).

A Sigma Techware Digitrate manual piston buret was used to deliver the 0.1 mol L^{-1}, 0.02 ± 0.01 mL KOH CO_2 - free solution.

The solid complexes of the biopolymers and the metal ions were obtained as described earlier [5] and were submitted to the analytical techniques described below.

The electronic paramagnetic resonance (EPR) first derivative spectra of solid native and complexed polysaccharides of powdered samples were recorded using quartz

tubes at room controlled temperature of 25ºC in a Bruker EPR ESP 300 E spectrometer, 9.7 Ghz, 100KHz field modulation, Germany.

The simultaneous Thermogravimetry - Differential Scanning Calorimetry (TG - DSC) analyses were recorded in a Netzsch simultaneous Thermal Analyzer STA 409 EP, under air, from 21 to 520ºC, 2ºC min^{-1}, using opened cylindrical aluminum opened sample pans, 4mm diameter, 2mm high.

Computations

The mathematical model that best described the results for the formation of the equilibrium complexes was the one where one hydroxyl group of each complexing sugar unit was depleted of its proton, generating a basic site. The protonation constant for the biopolymer was taken from the literature for the monomer galactose (using UV-Vis spectroscopy[20]), as in the following equations.

$$^{-}O\text{-}L + H^{+} \rightleftharpoons HO\text{-}L \qquad \log K_{a1} = 12.6 \qquad (1), \text{ or}$$

$$L + H \rightleftharpoons HL \qquad \log K_{a1} = 12.6 \qquad (1')$$

The hydrolysis constants for the metal ions reported by Baes and Mesmer[21] were fully used in the calculations. The dissociation constant of water (pK_w) at 25.0ºC and μ = 0.100 mol L^{-1} used was 13.78[16] . All these constants were kept fixed during refinement of the binding constants of the metal ions and the biopolymer with the aid of the Best7 program [16]. This mathematical model was adjusted in Best7 in order to represent the formation of the complexed species as in the equations below:

$$L\text{-}O^{-} + M^{2+} \rightleftharpoons MOL^{+} \qquad (2), \text{ or}$$

$$L + M \rightleftharpoons ML \qquad (2')$$

$$L\text{-}O^{-} + MOL^{+} \rightleftharpoons LOMOL \qquad (3), \text{ or}$$

$$L + ML \rightleftharpoons ML_2 \qquad (3')$$

where M=metal ions Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} and L= monomer sugar unit of galactomannan, either mannose or galactose.

The species distribution was calculated with the program SPE[16] that uses as input data the output data of the Best7 program. The species considered in the equilibria were those which are most likely to be formed and also for which the other analytical techniques employed in this work showed some consistency. These species were ML, ML_2, M_2L, M_2L_2, M_2L_4, ML_3 and their protonated counterparts.

All other mathematical aspects of the microcomputer programs employed are described elsewhere [5,16,22] .

Results and Discussion

The potentiometric equilibrium profiles of 0.4 mmole of galactomannan from *L. leucocephala* (Leu) in the absence of Mn^{2+} (10 points) and in the presence of 0.4 mmole (15 points) and 0.2 mmole of Mn^{2+} (11 points) are depicted in Figure 1. The curve of the galactomannan alone starts at pH 4.5, followed by a small break until pH 6.0 and continues until precipitation near pH 9.0. In the alditol acetate assay the presence of galacturonic acid was detected in this galactomannan and it is this acid that imparts the shape of the buffer around pH values of 8.0 and causes the early precipitation in the system. The curves with Mn^{2+} show a displacement in the x axis ending in pH values near 7.0 due to formation of insoluble products. As a result of the ability of Mn^{2+} to form external sphere complexes, mainly with water, the initial pH of those titrations done in the presence of Mn^{2+} started at slightly higher values than was the case for the profile of the biopolymer alone. The profiles obtained for Co^{2+} presented almost the same features as for Mn^{2+}.

In Figure 2 the same profile of galactomannan (0.4 mmole, 10 points) alone is depicted along with those obtained with Ni^{2+} (0.4 mmol, 8 points; 0.2 mmol, 15 points). The titration ratio of galactomannan to metal ion of 2:1 was delayed to such a pH value that enabled the formation and detection of ML_2 species.

In Figure 3 the biopolymer and Zn^{2+} (0.4 mmol, 12 points; 0.13 mmol, 19 points) profiles are shown. Those profiles presented small breaks with the metal ion and started at lower pH values than the polysaccharide alone. The metal ion Zn^{2+} was chosen in the ratio of 1:3 rather than 1:2 with the galactomannan because both the shape of the profile and the calculations with this titration were more elucidative.

Figures 4 and 5 show the distribution species diagram of 0.4 mmol of galactomannan and 0.2 mmol of Ni^{2+} and 0.13 mmol of Zn^{2+}, the total concentration of metal ion set at 100%. For both metal ions the highest concentration of the complexed species occurs in the pH range of 5.0 to 9.0, unlike the case with Co^{2+} and Mn^{2+}, for which the only species detected (ML) predominates between pH values of 4.0 and 6.0.

Figures 6 and 7 present the thermal analysis of galactomannan and Mn^{2+} and Ni^{2+}, respectively. The DSC profile of the biopolymer alone (Leu) shows no thermal effect before 290ºC, when there is an exothermic break of chains (Figures 6 and 7 - number 1) associated with a great loss of mass (shown by the TG curve), followed by a conformational change near 390ºC (Figures 6 and 7 - number 2) and a final oxidative process near 445ºC (Figures 6 and 7 - number 3). The DSC profile of galactomannan and Mn^{2+} (Figure 6 - number 1) shows an endothermic

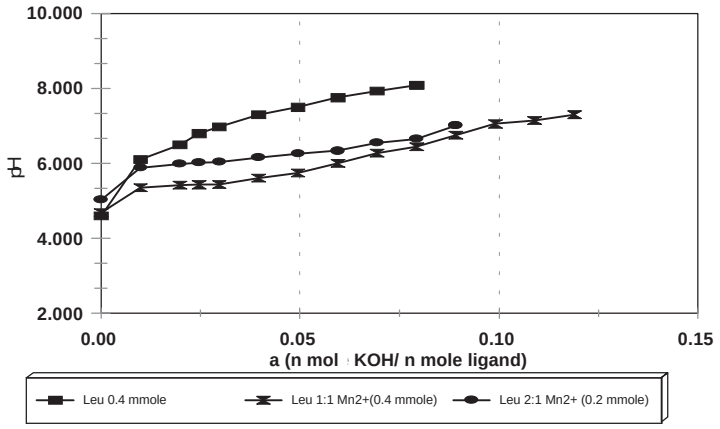

Figure 1. Potentiometric pH profile of a solution of 0.4 mmol of galactomannan from *L. leucocephala* and 0.4 and 0.2 mmol of Mn^{2+}. T=25ºC, μ=0.100mol L^{-1} (KNO_3).

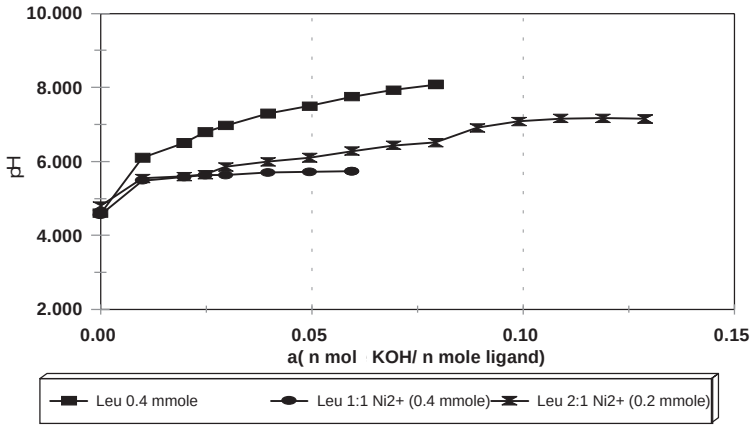

Figure 2. Potentiometric pH profile of a solution of 0.4 mmol of galactomannan from *L. leucocephala* and 0.4 and 0.2 mmol of Ni^{2+}. T=25ºC, μ=0.100 mol L^{-1} (KNO_3)

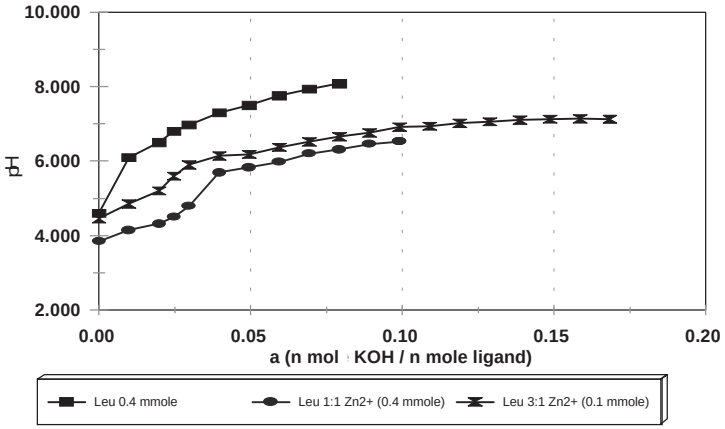

Figure 3. Potentiometric pH profile of a solution of 0.4 mmol of galactomannan from *L. leucocephala* and 0.4 and 0.13 mmol of Zn^{2+}. T=25ºC, μ=0.100 mol L^{-1} (KNO_3)

process, indicative of the formation of either a crystalline or a phase change in this temperature range, which contrasts with the exothermic process presented by the galactomannan alone. The second thermal event (Figure 6 - number 2) remains quite the same for both the complexed and non complexed galactomannan, but the final oxidative process happens at a higher temperature for the complexed material (470ºC).

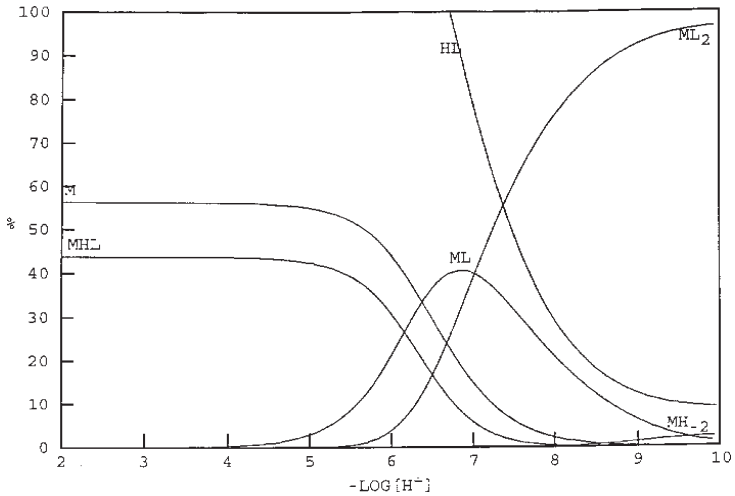

Figure 4. Species distributions of 0.4 mmole solution of galactomannan (L) with 0.2 mmol Ni^{2+} (M) at pH values from 2.0 to 10.0. % is the percentage of a species present, with the metal concentration set at 100%.

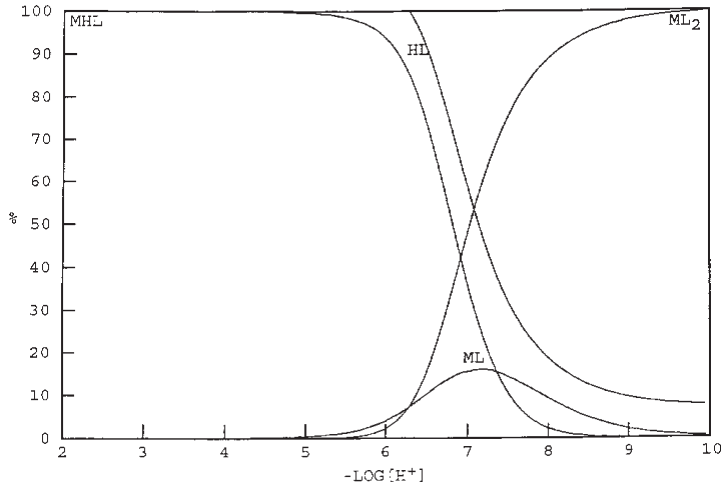

Figure 5. Species distributions of 0.4 mmole solution of galactomannan (L) with 0.13 mmol Zn^{2+} (M) at pH values from 2.0 to 10.0. % is the percentage of a species present, with the metal concentration set at 100%.

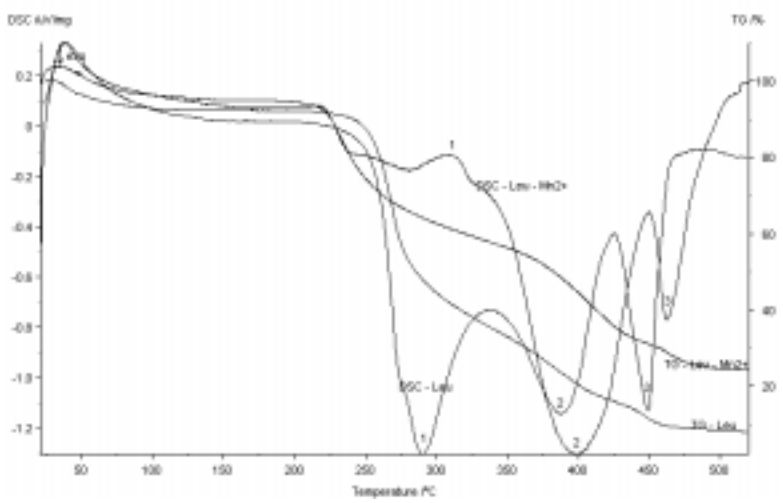

Figure 6. Thermal profile - TG - DSC - of the solid products extracted from an aqueous solution of pH = 8.0 - 9.0, 10 mol galactomannan to 1 mol of Mn^{2+}.

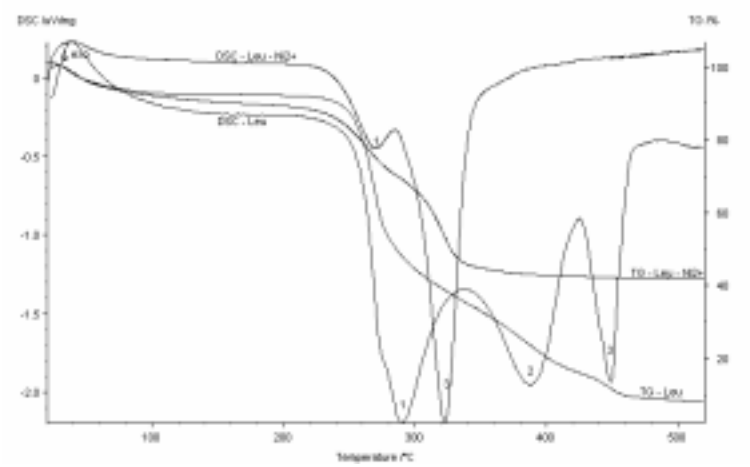

Figure 7. Thermal profile - TG - DSC - of the solid products extracted from an aqueous solution of pH = 8.0 - 9.0, 10 mol galactomannan to 1 mol of Ni^{2+}.

The DSC profile of Leu and Ni^{2+} (Figure 7 - number 1) showed a smaller break of chains (the TG curve shows a smaller mass loss) and the final oxidative process comes at 325ºC, much sooner than for the galactomannan alone (Figures 6 and 7 - number 3).

For the galactomannan - Co^{2+} complexes all thermal events disappeared but the final oxidative one, which occurred around 395ºC. For the galactomannan - Zn^{2+} complexes there was a small endothermic process around 300ºC and the final oxidative one near 450ºC. For Leu and Cu^{2+} (for other results refer to reference 5) the final oxidative process happened very soon after a break of chains, at 240ºC.

All the TG curves for the complexes showed a great mass of metallic oxide residues which were not completely vaporized at the end temperature of the assay (520ºC).

Figures 8 and 9 present the EPR spectra of galactomannan complexes with Co^{2+} and Mn^{2+}, respectively.

In the EPR spectrum of Leu complexed to Co^{2+} (Figure 8) g values of 8.10 and 2.006 were found, the latter being due to free radicals of the organic matter. Another g value of 2.49 of axial complexes of Co^{2+} presented a ΔH_{pp} = 1200G corresponding to interactions of metal to metal, showing that those metal ions, although complexed inside the galactomannan, are close enough to interact with each other in the web structure of the polysaccharide.

In Figure 9 (the EPR spectrum of Leu and Mn^{2+}), amplifying the range between 300 to 4000G of the spectrum, six sequenced peaks typical of Mn^{2+} spectra can be seen, with g=2.00 and A=100G, corresponding to Mn^{2+} external sphere complexes.

The other EPR spectra showed a g value of 2.24 with Ni^{2+} (corresponding to some Ni^{3+}) typical of complexes interacting with hard basic sites through O^{-}. To overcome the drawback of Zn^{2+} being an EPR silent metal ion, taking a look at the parameters that have changed when the polysaccharide is not complexed[5], there is a g = 2.006, indicative of free radical formation, and a ΔH_{pp} = 23G, indicating that Zn^{2+} ions are interacting with those free radicals formed.

The solid complexes obtained with Mn^{2+} and with Zn^{2+} were more resistant to heat degradation than the biopolymer alone, although presenting the lowest binding constants for ML species. This can be attributed to the occluded water molecules in the web structure of the biopolymer, which are not present in great quantities when a strong bond is formed between metal ions and the -OH basic sites. Those water molecules somehow give the biopolymer resistance to heat.

It was not the aim of this work to completely purify the galactomannan extracted since it was intended to reproduce industrial process conditions. The EPR spectroscopy was able to detect some of those impurities originating from other organic matters (other polysaccharides as well from the peels of the seeds) extracted along with the main polysaccharide. Those impurities were in such concentrations that they influenced the end of the potentiometric titrations and the presented buffer (in smaller pH values than expected), but it was still possible to quantify the binding constants for the complexed species.

The values of the logarithms of the binding constants followed the ascending order Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} [5] , showing the progressive affinity of those metal ions and the ligand basic site -OH.

The species diagrams showed that the majority of the complexed species occur at physiological pH values. The existence of a great percentage of those complexed species in some acidic and some basic aqueous solutions and their resistance to degradation in the solid state may allow their use in industrial processes which may require such resistance of pH values and temperatures.

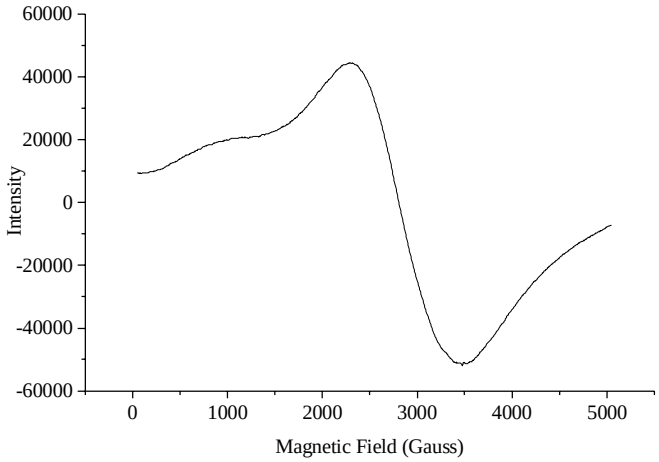

Figure 8. EPR spectrum of the solid products of Leu and Co^{2+}.

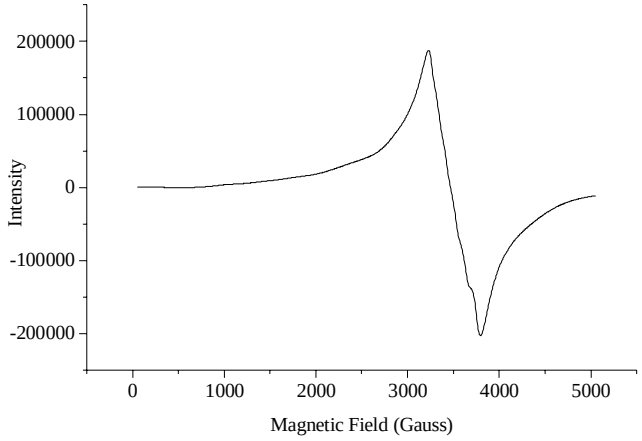

Figure 9. EPR spectrum of the solid products of Leu and Mn^{2+}.

Table 1. Logarithms for the binding constants of the complexes of Leu and Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}. T=25ºC and μ=0.100 mol L^{-1} (KNO_3).

log K - Leucaena leucocephala	Co^{2+}	Mn^{2+}	Ni^{2+}	Zn^{2+}
[ML]/[M].[L]	10.4 ± 0.1	9.9 0.4	13.1 ± 0.2	9.0 ± 0.4
[MHL]/[ML].[H]	not detected	not detected	7.4 ± 0.2	6.2 ± 0.4
$[ML_2]$/[ML].[L]	not detected	not detected	9.3 ± 0.2	8.7 ± 0.4

Table 2. EPR spectra parameters of metal complexes of Leu (refer to Figures 8 and 9).

EPR parameters L. leucocephala	g	A(G)	g	ΔHpp	g_{free} radical
Co^{2+}complexes	8.10	n.d	2.49	1200	2.006
Mn^{2+}complexes	2.00	100	n.d.	n.d.	n.d.
Ni^{2+}complexes	2.24	n.d.	n.d.	n.d.	n.d.
Zn^{2+} complexes (indirect determination)	n.d.	n.d.	n.d.	23	2.006

n.d. not determined

Conclusions

The ability of galactomannans to complex a large variety of metal ions give them potential as alternative materials for chitosan[9-11] for instance in the use of bioremediation of aqueous wastes.

The potentiometric studies, by providing the values for the binding constants for the complexes as well as the

values of pH at which they are formed and destroyed, shed new light on the possible use of these complexes in the soil as slow-release fertilizers [23-25] providing both macro and micro nutrients as the mineralization of the organic matter happens.

Structural alterations induced by chelation process is said to change the thermal behaviour of the complexes when compared to the native biopolymer [26]. The thermal patterns of the complexes with the different metal ions suggest they can be used where one needs some resistance to heat.

Judging by some of the EPR parameters found, the metal ions were not simply trapped by the biopolymer when it precipitated out from the aqueous solutions, as a great interaction between the metal ions and the deprotonated -OH groups of the polysaccharide was found.

Further studies involving derivatization and formation of blends of different biopolymers and their complexation with different metal ions are being carried out.

Acknowledgements

We thank the sponsorship of FINEP and UFPR, and CNPq for fellowship, and Dr. David Alexander Mitchell for the most helpful suggestion in the translation of this manuscript.

References

1. Bayerlein, F. In *Plant Polymeric Carbohydrates* Meuser, F., Manners, D. J. and W. Seibel eds., pp. The Royal Society of Chemistry, UK 1993, 190.
2. Varma, A. J.; Kokane, S. P.; Pathak, G.; Pradhan, S. D. *Carbohydr. Pol.* **1997**, *32*, 111.
3. Silva, J. A. L.; Gonçalves, M. P. *Food Hydrocoll.* **1990**, *4*, 277.
4. Verchère, J. -F.; Chapelle, S.; Xin, F.; Crans, D. C. *Prog. Inorg. Chem.* **1998**, *47*, 837.
5. Mercê, A. L. R.; Lombardi, S. C.; Mangrich, A. S.; Reicher, F.; Szpoganicz, B.; Sierakowski, M. R. *Carbohydr. Pol.* **1998**, *35*, 13.
6. Fraústo da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of The Elements. The Inorganic Chemistry of Life*, Clarendon Press, Oxford, 1997.
7. Sposito, G. *The Chemistry of Soils*, Oxford University Press, N.Y, 1989.
8. Masri, M. S.; Reuter, F. W.; Friedman, M. *J. Appl. Polym. Sci.* **1974**, *18*, 675.
9. Maruca, R.; Suder, B. J.; Wightman, J. P. *J. Appl. Polym. Sci.* **1982**, *27*, 4827.
10. Eiden, C. A.; Jewell, C. A.; Wightman, J. P. *J. Appl. Polym. Sci.* **1980**, *25*, 1587.
11. Bryan, N. D.; Hesketh, N.; Livens, F. R.; Tipping, E.; Jones, M. N. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 95.
12. Domard, A. *Int. J. Bio. Macromol.* **1987,** *9*, 98.
13. Wolfrom, M. L.; Thompson, A. *Methods Carbohydr. Chem. New York* **1963**, *2*, 211.
14. Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. *Carbohydr. Res.* **1983**, *113*, 291.
15. Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*, Methuen & Co Ltda, UK 1969, 244, 248, 264.
16. Martell, A. E.; Motekaitis, R. J. *The Determination and Use of Stability Constants*, VCH, New York 1992.
17. Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solutions*, Plenum Press, New York **1996**, 205.
18. Etcheverry, S. B.; Williams, P. A. M.; Baran, E. *J. Carbohydr. Res.* **1997**, *302*, 131.
19. Ciardelli, F.; Tsuchida, E.; Wöhrle, D. eds., *Macromolecule - Metal Complexes.* Springer, Berlin 1995.
20. Martell, A. E.; Smith, R. M. *NIST Critical Stability Constants of Metal Complexes*, version 4.0, NIST Database 46, Gaithersburg, MD, USA1997,and references cited therein.
21. Baes Jr., C. F.; Mesmer, R. E. *The Hydrolysis of Cations*, John-Wiley and Sons, New York 1976.
22. Mercê, A. L. R.; Szpoganicz, B.; Dutra, R. C.; Khan, M. A.; Than, X. D.; Bouet, G. *J. Inorg. Biochem.* **1998**, *71*, 87.
23. Mercê, A. L. R.; Mangrich, A. S.; Szpoganicz, B.; Levy, N. M.; Felcman, J. *J. Braz. Chem. Soc.* **1996**, *7*, 239.
24. Mercê, A. L. R.; Mangrich, A. S.; Szpoganicz, B.; Levy, N.M.; Felcman, J. *J. Braz. Chem. Soc.* **1996**, *7*, 97.
25. Mercê, A. L. R.; Lombardi, S. C.; Mangrich, A. S.; Levy, N. M.; Szpoganicz, B. *J. Braz. Chem. Soc.* **1998**, *9*, 231.
26. Sreenivasan, K. *Polymer. Degrad. Stab.* **1996**, *52*, 85.

Received: March 16, 1999