Interaction energy of various metals with 4-o-methylglucuronoxylans and hexenuronoxylans.

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Abstract

Birchwood 4-O-methylglucuronoxylan (MeGlcA-xylan) was modified by alkali treatment to produce hexenuronoxylan (HexA-xylan). The ability of MeGlcA-xylan and HexA-xylan to chelate metals such as Ca^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+} was investigated using dialysis technique and the energy change associated with metal-polysaccharide interaction was measured by Isothermal Titration Calorimetry (ITC). The results showed that most metals interact more strongly with MeGlcA-xylan than with HexA-xylan. The interaction intensity followed the order: Fe^{3+}>Co^{2+}>Zn^{2+}>Cu^{2+}>Mn^{2+}>Ca^{2+}. For Fe^{3+} and Cu^{2+} the interaction process was exothermic while for Co^{2+}, Zn^{2+}, Mn^{2+} and Ca^{2+} it was favored thermodynamically by entropy, indicating great hydrophobic interaction.

Keywords: Thermodynamic processes, calorimetry, complex.

Introduction

The interactions between metal ions and water-soluble hemicelluloses have gained interest due to their intrinsic properties as well as their potential applications and technological challenges. One good example is the so-called transition metal catalyzed hydrogen peroxide decomposition, which decreases the efficiency of hydrogen peroxide in pulp bleaching, and negatively affects pulp brightness stability and physical properties [1], [2]. In wood and pulp, the carboxylic acid groups responsible for the cation exchange behavior are mainly located on the xylan hemicelluloses. The uronic acids contain negative charged carboxylic groups, which are strong sites for metal ions attachment. Furthermore, uronic groups twist and fold to chemically interact with metal ions [2].

It is well known that HexA and other uronic acids are responsible for the strong affinity between kraft pulps and transition metals. However, it is not yet clear if the presence of the double bond adjacent to the carboxylic group makes the HexA chelating ability greatly amplified over that of its precursor, the MeGlcA.

In this study, Isothermal Titration Calorimetry (ITC) was used to investigate the thermodynamics of the interaction between metal ions and xylan in solution and dialysis was used to investigate retention processes between metal ion and xylan.

Experimental

Complexation's experiments of methylglucuronoxylans and hexenuroxylans with metal ions were performed using Birchwood xylan as source of 4-O-Methylglucuronoxylan and Hexenuroxylan was prepared from the former according Teleman et al. (1996) [3]. The pH of xylan solutions (7.0 g L^{-1}) was adjusted to 7.0. The solutions of metal ions used (0.01 mol L^{-1}) were added in form of $FeCl_3.6H_2O$, $CuSO_4.5H_2O$, $CoCl_2.6H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.H_2O$ and $CaCl_2.2H_2O$.

4-O-Methylglucuronoxylan and Hexenuronoxylan structures were confirmed by 1H NMR. NMR spectra were obtained using a Varian Mercury 300 instrument (300 MHz), using deuterated water as a solvent and tetramethylsilane (TMS) as internal standard (δ= 0).

- **Metal ion retention**

In the experiments of metal ions retention, xylan solutions (7.0 g L^{-1}, 25 mL) were placed inside the dialysis cell (compartment 1 or retentate), and metal ion solutions (0.01 mol L-1, 30 mL) were placed in the glass reservoir (compartment 2 or dialysate). The dialysis membranes used were of the type cellulose acetate (CA) with a nominal molecular weight cutoff 3,500Da. All dialysis experiments were carried out at room temperature.

Metals ions with high interaction rates with the polymer are retained by the macromolecule, which is not able to pass through the dialysis membrane, while others ions are eluted through the membrane until saturation is achieved. The water-soluble xylan ligand performance was evaluated by determining metal removal through atomic absorption spectrophotometry (AAS). The metal concentrations were measured by Atomic Absorption Spectroscopy (AAS) using a GBC Avanta spectrophometer equipped with hollow cathode lamps of Fe (at 248.3 nm), Cu (at 324.7 nm), Co (at 240.7 nm), Mn (at 279.5 nm), Zn (at 213.9 nm), Ca (at 422.7 nm).

After metal ion concentrations of permeate and feed were obtained, retention values (i) were calculated by using the following equation 1:

$$i = \frac{\left(c_1^{free} - c_1^{bound}\right) - c_2}{c^{initial}} \qquad (1)$$

c_1^{free} is the concentration of M free in the solution in compartment 1,c_1^{bound} is the concentration of M bound to the polymer in compartment 1, c_2 is the concentration of M in compartment 2 and $c^{initial}$ is the initial metal concentration.

- **Isothermal titration calorimetry (ITC)**

These experiments were performed using CSC-4200 (Calorimeter Science Corp.) microcalorimeter, which was controlled by ItcRun software. The ITC technique was used for measuring enthalpy changes resulting from the xylan-metal ion interactions.

All experiments were performed with the xylan solution in the cell and the metal ion solution in the syringe.The reaction cells (sample and reference) volume of the instrument is 1.8 mL, and the titrant was added in 5 µL (Hamilton microliter syringe) increments with time between injections equal to 60 min. The calorimeter was previously chemically (HCl/Tris titration) and electrically calibrated. For each operation, a sample of nearly 12.6mg of MeGlc-xylan or HexA-xylan was suspended in 1.8mL of water under stirring. Water (pH 7.0) was added to the reference cell. The temperature of the solution in the titration cell was 25 ±0.1°C. As metal ion solution is added, the cell volume is kept constant by an overflow of solutions, which is taken into account in the calculations of actual amount of xylan transferred.

For calculation of each ΔH curve, at least 20 injections were added in triplicate to the calorimeter cell. Raw data were obtained as a plot of heating rate (µcal/s) against time (min). These raw data were then integrated to obtain a plot of observed enthalpy change per mol of injected metal ion (ΔH_{obs},kJ/mol) against metal ion concentration (mM). All calculated ΔH relative standard deviations were lower than 1.0%.

Results and Discussion

Figure 1 shows the retention of all metal ions in presence of MeGlcA-xylan and HexA-xylan solutions at pH 7,0. The value i is an average from triplicate measurements. For both xylan solutions, it is observed great differences among the Fe^{3+} r values and those of the other metal ions. The higher Fe^{3+} interaction with xylans, in relation to others metals is the result of the higher binding constant for the complex Fe-xylan. It is believed that this occurs because of the larger charge-to-radius ratio of Fe^{3+} compared to other metals, which increases its attraction by the oxygen in the carboxylic groups present in xylans. The Fe^{3+} ion was the only one showing higher retention for the HexA-xylan solution in comparison to the MeGlcA-xylan solution.

For the other metals, higher retention values were always observed for the MeGlcA-xylan solution. This suggests that in HexA-xylan structure, the resonance between double bond of the oxygen from carboxylic group and the double bond adjacent to this group gives more negative character to the oxygen atom in the functional group [2].

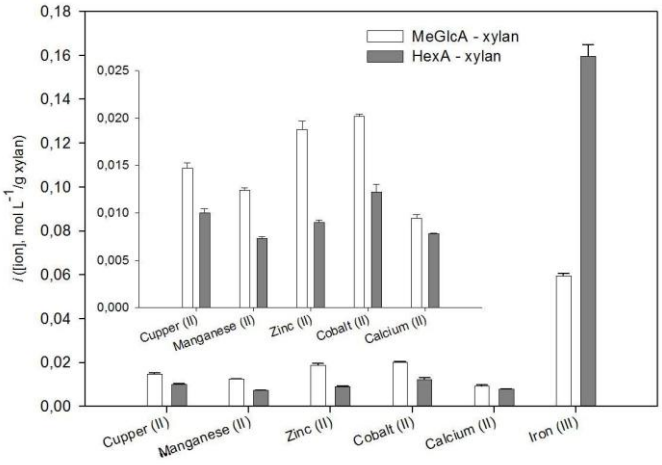

Figure 1. Metal ions retention on xylans by dialysis.

In order to discriminate between enthalpic and entropic contribution to M^{n+}-polysaccharide titrations between metal ions solutions and xylan solutions were performed using the ITC to establish the various contributions to the interaction energies measured during the titration. When an aqueous solution of a metal ion is titrated with a second aqueous solution containing a polysaccharide species to form the complex, heat energy is either absorbed or released, both because of dilution of the ligand, and because of the interaction complexation reaction itself [4]. Entropy changes also occur owing to structural rearrangements in the final mixture on bond formation and solvent restructuring. These two effects are captured by the well-known relation $\Delta G = \Delta H - T\Delta S$ (2).

ΔH measured directly by ITC correlate with the process of interaction Metal-xylan and can be subdivide into four terms as follow (3):

$$\Delta H = \Delta_{de\text{-}solv.}H_{xyl} + \Delta_{de\text{-}solv.}H_M^{n+} + \Delta_{conf.}H_{xyl} + \Delta_{int.}H_{xyl\text{-}M}^{n+} \quad (3),$$

Where the first two terms represents heat associated with the removal of water molecules surrounding the xylan and metal, i.e., the de-solvation process of xylan and metal, respectively; $\Delta_{conf.}H_{xyl}$ represents the heat associated with the conformation of xylan rearranged; and the last term means interaction formed between xylan and metal ion. This last term is exothermic while the two first terms are endothermic.

Isothermal titration calorimetry revealed the interaction of Fe^{3+} with HexA-xylan and MeGlcA-xylan to be enthalpically favorable (Fig. 2). At the beginning of the titration, when the rate r was lower than one ($r = \frac{M^{n+}}{[xylan]} \ll 1$),the $\Delta_{int.}H_{xyl\text{-}Fe}$ values were -175 kJ mol^{-1} and -120 kJ mol^{-1} for Fe-MeGlcA-xylan and Fe-HexA-xylan interaction, respectively. When r values rose due to increased Fe^{3+} concentration, an increase on $\Delta_{int.}H_{xyl\text{-}Fe}$ values was observed and they became less negative. These increase in enthalpy of the system suggested that, beyond the Fe-xylan interaction, there are conformational rearrangements on xylan chain and/or strong interactions between adjacent sites binding to the macromolecular chain. This range of energy is enough to become the enthalpy of interaction positive when r values are +6,0 kJ mol^{-1} for HexA-xylan titration.

The intersection of two curves (Fig. 2) could be explained by partial conversion from MeGlcA-xylan to HexA-xylan. First, the hexenuronic groups were fully complexed by Fe^{3+} until there are no more sites such hexenuronic acids in the chain of xylan. From the point of intersection of these curves, the sites of interaction between xylan and Fe^{3+} became the same as the MeGlcA.

Increasing r values result in higher positive charge density along xylan chains, which promote

electrostatic repulsions between xylose units and it is converted from a random coil structure into a more linear conformation. Also, conformational rearrangements occur at the expense of the change on solvation layer of polymeric chain.

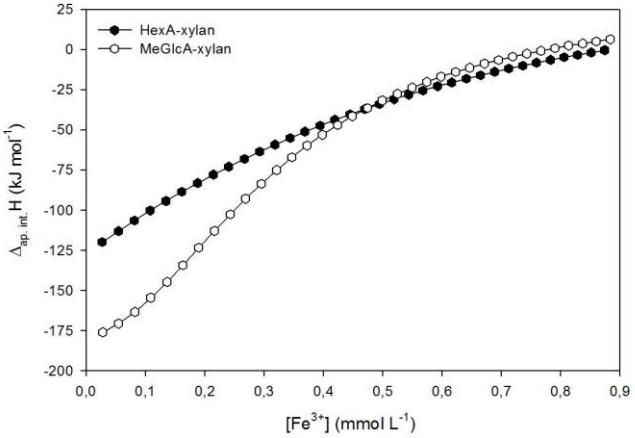

Figure 2. Apparent interaction enthalpy from titration of 0.01 mol L^{-1} Fe^{3+} into 7g L^{-1} xylan.

Interestingly, in spite of the larger Fe-HexA-xylan interaction than Fe-MeGlcA-xylan, the changes in enthalpy follow the reverse order. At Fe^{3+} concentration of 0.028 mol L^{-1}, the $\Delta_{ap.\ int.}H$ for MeGlcA-xylan was -120.0 kJ mol^{-1}. This value represents only 68.6% of the energy released on Fe-MeGlcA-xylan interaction (-176.0 kJ mol^{-1}). According Devenyns & Chauveheid (1997) [2], the difference in the complexation between Metal-HexA-xylan and Metal-MeGlcA-xylan is the presence of the double bond adjacent to the carboxylic group structure greatly amplifies HexA chelating ability.

Figure 3 shows ΔH for titration of Cu^{2+} and xylan versus metal ion concentration. So, calorimetric data of Cu-MeGlcA-xylan show ΔH more negative, when r << 1, and higher metal ion retention than Cu-HexA-xylan. It means that when MeGlcA-xylan interact with Cu^{2+}, larger energy release and/or a lower energy is absorbed in process involving solvation and changed conformation. Similarly to what was show for Fe^{3+}, the formation of the Cu^{2+} complex with the xylan is favored thermodynamically by enthalpy, but no significant difference in ΔH was observed between MeGlcA-xylan and HexA-xylan.

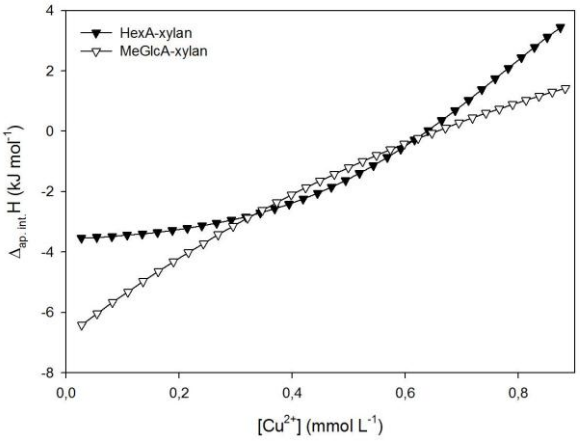

Figure 3. Heat evolved per mol from titration of 0.01 mol L^{-1} Cu^{2+} into 7g L^{-1} xylan.

Interaction of Zn^{2+} and Co^{2+} with MeGlcA-xylan and HexA-xylan is an entropy driven phenomenon at 25ºC (Fig. 4). Dialysis data (Fig. 1) show that interaction of Zn^{2+} and Co^{2+} had higher i value than Ca^{2+}, Cu^{2+} and Mn^{2+}. Calorimetric data indicate a greater hydrophobic interaction meaning that larger amounts of energy were expended for removing water molecules surrounding both xylan, Zn^{2+} and Co^{2+} (de-solvation). Co^{2+} can coordinate to carboxylate and hydroxy groups [5], but the sites linked are not well known. The less positive apparent interaction enthalpy associated with Co-HexA-xylan and Zn-HexA-xylan-interaction, when compared with Co-MeGlcA-xylan and Zn-MeGlcA-xylan, should be attributed to a more exothermic interaction between these metals with HexA-xylan. The small dependence of $\Delta_{ap.int.}H$ in relation of metal concentration suggests that Co-xylan or Zn-xylan is not enough intense to cause conformation change and/or site-site interaction.

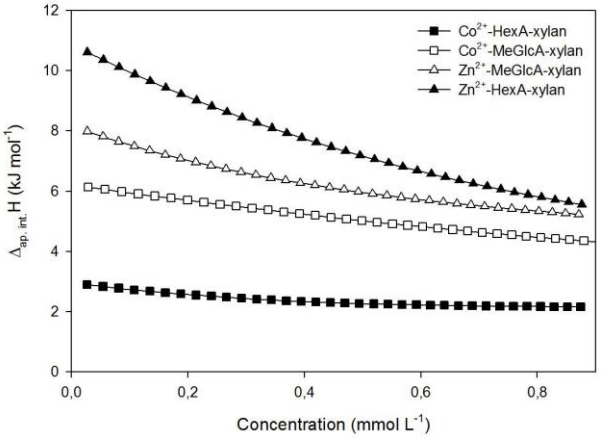

Figure 4. Apparent interaction enthalpy from titration of 0.01 mol L^{-1} Co^{2+} and Zn^{2+} into 7g L^{-1} xylan.

Ca^{2+} and Mn^{2+} have less interaction with xylan (Fig. 1). Ca^{2+} and Mn^{2+} have different driving forces when interacting with MeGlcA-xylan and HexA-xylan. The thermodynamic behavior of Ca^{2+} with xylan showed almost athermal, mainly to HexA-xylan, suggesting similar magnitude of energy in interaction Ca-xylan and de-solvation of xylan molecules and calcium ions (Fig. 5a).

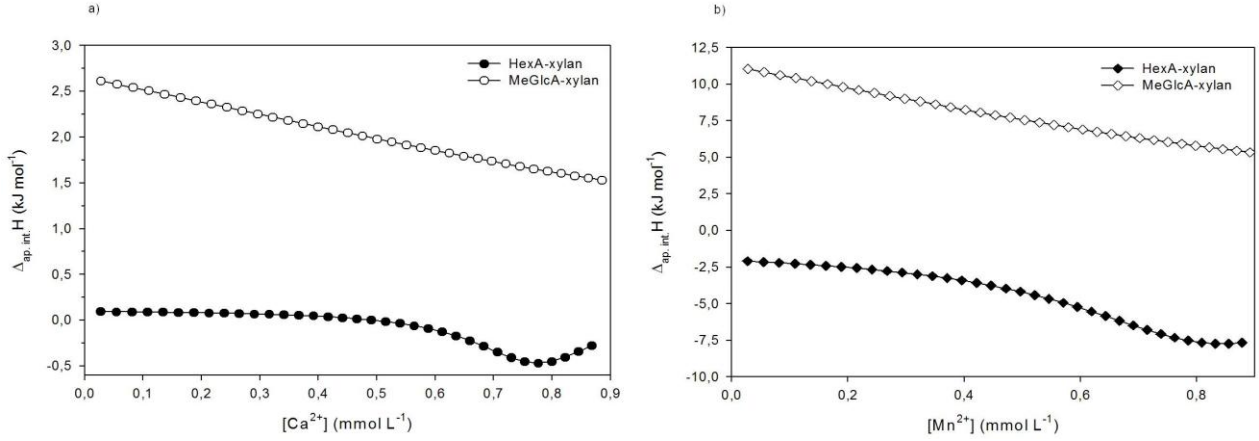

Figure 5. Apparent interaction enthalpy from titration of a) 0.01 mol L^{-1} Ca^{2+} into 7g L^{-1} xylan and b) 0.01 mol L^{-1} Mn^{2+} into 7g L^{-1} xylan .

Titration analyses of Mn^{2+} binding to MeGlc-xylan and HexA-xylan showed endothermic and exothermic binding event, respectively (Fig. 5b). It suggests higher affinity between Mn^{2+} and double bond in HexA-xylan against methoxyl group in MeGlcA-xylan, indicating that when Mn^{2+} and MeGlcA-xylan interacts de-solvation processes prevails.

Conclusions

The goal of this work was verify the ability of MeGlcA-xylan and HexA-xylan to chelate metal ions. We have used isothermal titration calorimetry (ITC) and dialysis techniques to study complexation enthalpies and metal ion retention by xylan. The results obtained by dialysis show higher capacity of MeGlcA-xylan to retain Ca^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+} and Zn^{2+} than HexA-xylan, the opposite being observed for Fe^{3+}. The highest retention values were obtained with Fe^{3+}, far from the other metals, and this was attributed to Fe^{3+} highest charge-to-radius ratio. Calorimetric data suggest that the interactions between Fe^{3+} and Cu^{2+} with xylan are enthalpically favorable, with the largest negative AH values observed for the interaction of Fe^{3+} with MeGlcA-xylan. The other metal-xylan interactions studied were entropically driven, except the interaction between Mn^{2+} and Ca^{2+} with HexA-xylan. Mn^{2+} seems be more attracted by double bond in HexA-xylan than methoxyl group in MeGlcA-xylan.

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