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Metal ion complexation with lignin derivatives

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Abstract

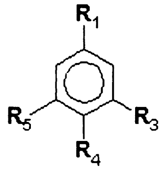
Isothermal titration calorimetry (ITC) coupled with structural characterization methods was used to characterize a heterogeneous mixture of polyphenolic compounds obtained from the chemical modification of lignin from a residual waste product. The mixture could be represented effectively as a single pseudo-compound ($C_{20}H_{19}O_{14}N_2$) with well-defined molecular weight (525 g/mol). It has three acidic sites with pK_a values at 2.7, 4.8 and 10.8. The complexation with all assayed cations yielded a order Cu $>$ Pb $>$ Mg and metal ion complexation stoichiometry of two metal ions per lignin molecule. Formation enthalpies and entropies were also determined.

Keywords: Lignin; Complexation; Metal ions; Titration calorimetry

1. Introduction

Lignin is an amorphous, polyphenolic, highly cross-linked polymer consisting of polyphenyl propane units joined by carbon–carbon, and carbon–ether bonds, and is the major non-cellulosic component of wood [1], comprising 17–30% of its weight [2]. The significant environmental burden posed by this waste byproduct in a number of industries, particularly in pulping and paper manufacturing, could be alleviated to a large extent if the lignin could be converted chemically to produce value-added fine chemicals. Its reuse in this manner would not only provide an environmental advantage in reducing the amount of waste product, but at the same time it could provide an additional revenue source for the industries involved.

The lignin obtained from plant biomass as either a byproduct or as a waste can be modified chemically to have a large number of active carboxyl, amine and hydroxyl (phenolic or not) sites that would be readily available for complexation with metal ions in industrial applications. Such degradation of lignin can be achieved by alkaline nitrobenzene oxidation, permanganate oxidation, acidolysis, hydrogenolysis or thioacetolysis to release low molecular weight units containing aromatic rings with several constituents [3] having the structure



Lignin degradation compounds.

where **R** corresponds to: H, COOH, CHO, OCH_3, OH or CH=CH–CH_2OH. These lignin-derived fine chemicals can be produced in both soluble and insoluble forms and could be considered as replacements for commercial chelating agents or ion exchange resins for the removal of heavy metal ions from aqueous discharge streams; indeed, examples of their ability to complex with heavy metal ions abound in the literature [4–13].

A strong potential market for these chelating agents is in the industrial plants of the pulp and paper industries in which the waste lignin is produced in the first place. Examples of these applications include not only classical water softening operations, but also the new pulp bleaching processes in which hydrogen peroxide is substituted for chlorinated reagents. These processes have the drawback that bleaching activity is decreased by reactions of metal ions with the peroxide. Currently, commercial chelating agents must be used to complex the ions and render them unavailable for reactions with the peroxide, but they are expensive and their accumulation in the environment can lead to additional environmental contamination. Clearly, the introduction of an

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inexpensive, naturally biodegradable agent produced from lignin, which is of very low toxicity at the concentrations at which it would be used, could provide an attractive alternative to the use of these conventional chelating agents. They are generally not well characterized, however, and this lack of characterization may be an impediment to their use in these and other industrial applications.

The purpose of this paper is to report on the preparation and characterization of a lignin product, and to determine the thermodynamic parameters for the complexation of three metal ions with these lignin derivatives using ultra-sensitive isothermal titration calorimetry (ITC). While similar results have been reported in the literature on fulvic and humic acids [14,15], which have chemistries and structures similar to those of lignin, no such results are available for the lignin-derived chemicals considered here. We also point to the value of titration calorimetry as an important tool for exploring complexation thermodynamics for compounds for which convenient analytical techniques, such as ion-specific electrodes, are not readily available.

2. Isothermal titration calorimetry (ITC)

Isothermal titration calorimetry is a powerful experimental technique for the simultaneous determination of all binding parameters (equilibrium constant, enthalpy, entropy, free energy and stoichiometry), often in a single experiment, as it measures directly the heat interactions associated with the metal complexation processes [16–18]. When an aqueous solution of a metal ion is titrated with a second aqueous solution containing a ligand species to form the chelated complex, heat energy is either absorbed or released, both because of dilution of the ligand, and because of the complexation reaction itself. 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

$$-RT \ln K = \Delta G = \Delta H - T\Delta S \tag{1}$$

where R is the gas constant, T the absolute temperature and K the equilibrium constant for the complexation reaction.

The ultra-sensitive isothermal titration calorimeter contains two cells, in one of which is placed the reference solvent (usually water) and in the other the solution to which the ligand is added dropwise. These two cells are monitored with thermocouples that can detect any variation in the temperature precisely (down to 10^{-4} °C) and compensate for it by exchanging energy between the cells to re-establish isothermal conditions. The heat flux is monitored and is typically reported as power versus time as shown by the thermogram in Fig. 1. The peak associated with any given injection can be integrated to give the heat evolved or absorbed by the solution to maintain isothermal conditions following the thermal event.

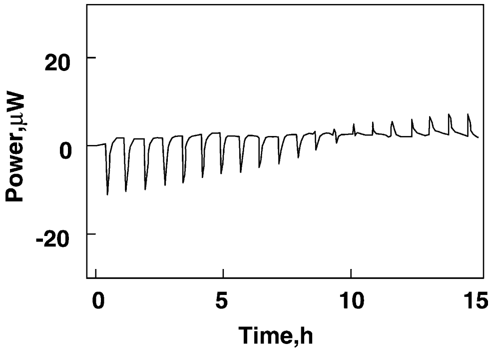

Fig. 1. Thermogram for the titration of a 3 mM solution of copper with 10 ml aliquots of a 15 mM lignin solution at pH = 5.0. The copper solution volume was 3 ml.

At constant pressure, the heat is related to the interaction enthalpy ΔH by

$$\Delta Q = \Delta H(\Delta n_{\mathrm{M}})\, V_{\mathrm{cell}} \tag{2}$$

where Δn_{M} denotes the change in the total moles of metal ions bound to the lignin molecules following any given injection (and release protons from lignin molecules), and V_{cell} the volume of solution being titrated. The total heat released after a given number, m, of injections can be determined by summing all the ΔQ values to give

$$Q_{\mathrm{b}} = \sum_{j=1}^{m} \Delta Q_j = \Delta H[M]_{\mathrm{b}}\, V_{\mathrm{cell}} \tag{3}$$

where $[M]_{\mathrm{b}}$ is the total concentration of bound metal ions after the m injections.

Since the lignin molecules may bind more that one metal ion, we must consider the series of reactions (the released protons and the electrical charges are not shown)

$$\begin{aligned} &M + L \leftrightarrow ML, && k_1 = [ML]/[M][L] \\ &M + ML \leftrightarrow M_2L, && k_2 = [M_2L]/[M]^2[L] \\ &\ldots \\ &M + M_{n-1}L \leftrightarrow M_nL, && k_n = [M_nL]/[M]^n[L] \end{aligned} \tag{4}$$

where n is the total number of binding sites on a lignin molecule and the equilibrium constant is conditional at each pH value. Taking in account that we will have a fixed set of concentrations to use in order to find out the equilibrium constant, we can force the equilibrium constants to be the same for each reaction, then we can write [19]

$$K = \frac{[ML]}{[M][L]} = \frac{[M_2L]}{[M][ML]} = \ldots = \frac{[M_nL]}{[M][M_{n-1}L]} \tag{5}$$

or, taking in account the real stoichiometry

$$k_i = \frac{[M_iL]}{[M]^i[L]} = K^i \tag{6}$$

where K^i corresponds to a global constant (β_i).

Then, after some algebraic manipulation, the average fraction of metal ion binding sites occupied can be shown to be

$$\phi = \frac{\sum_{i=1}^{n} i[M_iL]}{\sum_{i=0}^{n} [M_iL]} = \frac{\sum_{i=1}^{n} ik_i[M]^i[L]}{\sum_{i=0}^{n} k_i[M]^i[L]} = \frac{\sum_{i=1}^{n} iK^i[M]^i}{\sum_{i=0}^{n} K^i[M]^i} = \frac{nK[M]}{1+K[M]} \qquad (7)$$

The total metal ion concentration is

$$[M]_\mathrm{T} = [M] + [M]_\mathrm{b} = [M] + [L]_\mathrm{T}\phi = [M] + [L]_\mathrm{T}\frac{nK[M]}{1+K[M]} \qquad (8)$$

This equation is a quadratic in $[M]$, which can be solved to yield the free concentration of metal ions in solution as a function of the total metal and lignin-ion concentrations. The concentration of bound metal ions can then be determined to be

$$[M]_\mathrm{b} = [M]_\mathrm{T} - [M] = [M]_\mathrm{T} + \frac{(1+nK[L]_\mathrm{T} - K[M]_\mathrm{T}) - \sqrt{(1+nK[L]_\mathrm{T} - K[M]_\mathrm{T})^2 + 4K[M]_\mathrm{T}}}{2K} \qquad (9)$$

Thus, the total heat released or absorbed when the lignin solution has been titrated with a metal ion solution (or vice versa) when the total lignin and metal ion concentrations are $[L]_\mathrm{T}$ and $[M]_\mathrm{T}$, respectively, is

$$Q_\mathrm{b} = \Delta H \left([M]_\mathrm{T} + \frac{(1+nK[L]_\mathrm{T} - K[M]_\mathrm{T}) - \sqrt{(1+nK[L]_\mathrm{T} - K[M]_\mathrm{T})^2 + 4K[M]_\mathrm{T}}}{2K} \right) V_\mathrm{cell} \qquad (10)$$

The relevant parameters characterizing the chelation reaction, n, K, and ΔH, can then be determined as those values giving the best fit of this expression to the cumulative heat release curves.

This method has been used for several applications, including a wide range of biochemical systems [17,18], metal ion binding [21], receptor ligand interaction [22], membrane system interaction [23], molecular binding to polymers [24], determination of acid sites on activated carbons [25], and enthalpy changes in emulsion systems [26].

3. Material and methods

3.1. Reagents

The reagents $CuNO_3{\cdot}3H_2O$, Na_2SO_4, $NaNO_3$, KNO_3, $Mg(NO_3)_2{\cdot}6H_2O$ and $Pb(NO_3)_2$ obtained from Aldrich were p.a. in all cases and used without further purification. The solvent used for extraction, methyl ethyl ketone (MEK), was HPLC-grade from Fluka.

3.2. Lignin preparation

The lignin derivative solution supplied by Cellutech LLC was a dark brown aqueous sample obtained from the degradation of a waste coniferous lignin from hydrolysis plants. It was purified by several stages. The pH was adjusted to a value of 1.5 by addition of sulfuric acid, at the same time the possible calcium present (that would interfere in the later experiments) was precipitated in the form of calcium sulfate. The resulting aqueous solution was saturated in sodium sulfate and then agitated in the presence of MEK for the extraction of the desired species. The solvent was then eliminated under vacuum at liquid nitrogen temperature, the low temperature being necessary to avoid possible condensation reactions between low molecular weight species that would yield undesirable higher structures. The final product was a fine grain brown powder. Samples of lignin derivatives for all the following experiments were obtained by solution of this purified powder in aqueous media.

3.3. Lignin characterization

The mean molecular weight of the purified lignin was obtained by gel permeation chromatography (GPC) using a set of three styrene-divinylbenzene copolymer gel columns of 50, 500 and 10^4 from Polymer Laboratories (Separation Science Division) at 40 °C. Degassed HPLC-grade tetrahydrofuran (THF) was employed as the mobile phase with a flow rate of 1.0 ml/min controlled by a Beckman 126 HPLC pump. The calibration was performed with narrow molecular weight monodisperse polystyrene standards ranging from 162 to 4,000,000 g/mol with detection by a Beckman 166 variable wavelength UV detector operating at 254 nm. Elemental analyses using a Perkin-Elmer 640-C analyzer yielded the relative amounts of C, H, S and N in the samples, while the percentage of oxygen was calculated by difference.

The samples were prepared by simple dissolution in Milli-Q water. The solution pH was determined to be very acidic at about 2 for solutions of 0.1–0.2 g in 10 ml. The solubility of the product increased with increasing pH, as is true for all humic substances.

The concentration of acidic sites and their pK_a were determined by acid–base titration. Aqueous solutions of the lignin derivatives were titrated with 0.02 M HCl after adjusting the pH at a value of 11 with sodium hydroxide and the pH determined with a pH-meter (Corning) using a combined electrode. The ionic strength was kept constant by the addition of sodium nitrate up to a constant concentration of 0.1 M. The equilibrium constants were obtained from the experimental data using the Gran mathematical treatment [20] and the concentrations of the acidic groups were determined from the equivalence points in the titrations.

The complexation of copper was first studied using copper-selective potentiometry to provide reference data for a comparison with those obtained by titration calorimetry. A Corning pH/ion meter 150 with copper-selective electrodes (Corning) was used to follow the titration of 40 ml of 9×10^{-4} M Cu(II) solution at a pH of 6 with diluted 0.2 g/100 ml (0.004 M) lignin solution. The corresponding complexation constants were calculated using the methods described in Bresnahan et al. [15].

3.4. *Isothermal titration calorimetry (ITC)*

An ultra-sensitive ThermoMetric TM 2277 thermal activity monitor (TAM) was used for the titration calorimetry experiments. For copper and magnesium, 3 ml of 3 mM metal nitrate solutions at several pH values were titrated with 10 μl aliquots of 15 mM lignin solution at a the same pH. For lead, 3 ml of 1.1 mM lignin at pH 6.0 were titrated with 10 μl aliquots of 10 mM lead solution. In all cases the exchange of heat required to maintain isothermal conditions in the cells by compensating for heat effects associated with the dilution and complexation interactions was monitored on-line and recorded in computer files for later analysis. The deconvolution of the signal yielded the conditional formation constant (K), stoichiometry (n) and enthalpy (ΔH) associated with the complexation reaction. This data fitting was performed using partial least squares regression. Two pH values were tested in the case of copper. The consistency of the system was checked by performing blank titrations in which lignin solution was added to water, diluted sodium chloride, and several copper solutions with concentrations above and below their saturation with lignin.

4. Results and discussion

The quality of the product obtained in the lignin derivative preparations depended on the conditions used in the solvent (MEK) elimination step. The desired final product was a dry solid powder, obtained by sublimation of the solvent with intermittent liquid nitrogen cooling, as described in the Section 3. Evaporation of the solvent at 0 °C yielded a solid product containing some moisture, while at room temperature the resulting product was a dark brown thick paste; neither of these products was satisfactory and both were discarded.

The mean molecular weight of the lignin derivatives was determined to be 525 ± 10 g/mol by GPC (0.002 mol/g), while elemental analysis indicated their average composition to be 4.82% N, 47.41% C, 3.64% H and 0.12% S. This composition corresponds to a molecular formula of $C_{20}H_{19}O_{14}N_2$, suggesting that the average lignin molecule is a highly oxidized dimmeric unit with the likely presence of some amino groups. Sulfur concentration was negligible.

The acidic site concentrations determined by acid–base titration yielded three equivalent points of 0.004, 0.004 and 0.008 mol/g, respectively, with corresponding pK_a values of 2.7 ± 0.1, 4.8 ± 0.1 and 10.8 ± 0.1. These results are compared in Table 1 with those found in the literature for lignin model compounds. While our lignin derivatives can be a complex mixture of compounds having no single, unique structure, their active sites are expected to be similar to those of nitrosalicylic acid, which is in fact what we observed. Our lignin derivatives showed a third, intermediate pK_a of 4.8, however, that is not apparent in the case of nitrosalicylic acid, but is close to the intermediate pK_a value observed for aminosalicylic acid, and can be attributed to the presence of the amino groups as inferred from the elemental analysis results described earlier.

The titration of 40 ml of a 9×10^{-4} M Cu(II) solution at $\text{pH} = 6$ with a 0.2 g/100 ml (0.004 M) lignin solution was monitored using a copper-selective electrode (Corning) to give results for the copper chelation for comparison with those obtained from isothermal titration calorimetry. The calculations [15], expressed in terms of the complete binding of two metal ions to a lignin molecule (i.e. two binding sites occupied per aromatic ring for a dimmeric lignin derivative, MW of 525 g/mol), yielded a value for the complexation constant ($K_2 = [M_2L]/[M]^2[L] = K^2 = \beta_2$) of $\log \beta_2 = 9.36$, which result is in agreement with those of Bresnahan et al. [15] and Raskhin and coworkers [12] for model compounds. It is point out that this constant is actually the result of all possible processes taking place (i.e. the exchange of protons or sodium with metal ions at a constant pH) and the combination of the total required sites and molecules. In the literature, values corresponding to complexation constants with lignin considering the concentration of the acidic sites instead of actual lignin concentration are usually reported [27]. In the present work, purified dimmeric lignin derivative that is water soluble was used as the complexation (chelation) agent. Similar results are found when using kraft lignin in the work of Crist et al. for the stoichiometry of copper/lignin, two acidic sites per copper atom.

Table 1
Characteristics corresponding to lignin model compounds

Compound	pK_{a1}	pK_{a2}	pK_{a3}	$\log K$ (CuL)	H (kJ/mol)
5-Methyl-3-nitrosalicylic acid	2.78	10.8	–	8.82	−23
5-Isopropyl-3-aminosalicylic acid	1.89	4.81	13.8	11.16	−10.8

Source: Raskin and coworkers [12].

A series of titrations was performed using the isothermal titration calorimeter to establish the various contributions to the interaction energies measured during the titration of the metal ion solutions with the lignin solution. In addition to the direct enthalpies of formation of the lignin-ion complexes, these experiments also provided information on the effects due to dilution and hydration of the lignin titrant and of the solution ionic strength. Fig. 1 shows a representative trace for the calorimeter response when excess copper (Cu(II)) was titrated with lignin. The series of negative peaks reflects the endothermic complexation of copper with lignin [18], while the decrease in the peak amplitudes with further addition of the lignin solution was indicative of the approach to saturation conditions. Near saturation, the peaks became positive, reflecting simply the exothermic heat of dilution of the lignin solution, which was taken into account in the subsequent analysis of the thermograms. Similar results were obtained in the titration of Mg(II) solutions with lignin. Experiments done under no saturation conditions yielded a series of repeated negative peaks corresponding to complexation. Experiments adding lignin derivative on distilled water yielded repeated positive peaks corresponding to the dilution heat.

The interactions between lead and the lignin derivatives were sufficiently weak that titrations with lignin solutions yielded only small signals that were difficult to analyze. To enhance the sensitivity, the metal ion concentrations were increased and the experiment was performed in the reverse manner, i.e. 10 μl aliquots of 10 mM lead solution were added to 3 ml of 1.1 mM lignin solution at pH 6.0.

A small effect of ionic strength was observed in these titrations: the heats of dilution corresponding to injection of lignin solution into water and 0.05 M NaCl were 0.763 and 0.851 mJ per injection, respectively. The signal for the sodium chloride solution increased slowly with subsequent injections due to a small, but finite, interaction between lignin and sodium. Consequently, the presence of a low salt concentration will not affect to this titrations and, on the other hand, the signal corresponding to sodium is very low.

The interaction energy per mole of the metal ion was obtained by integrating the power over any given peak with respect to time, and is shown for copper as a function of the lignin-to-copper molar ratio in Fig. 2. In determining molar concentrations, lignin was taken as the determined mean molecule with molecular weight of 525 ± 10 g/mol obtained from gel permeation chromatography. Similar results are shown in Fig. 3 for the titration of a lignin solution with lead.

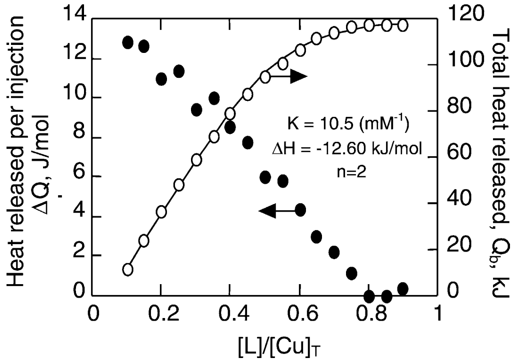

Fig. 2. Heat released per injection and cumulative heat released for the injection of a 3 mM solution of copper with 10 ml aliquots of a 15 mM lignin solution at pH = 5.0. The copper solution volume was 3 ml. The solid line is the curve fit of the model equation to the experimental data. Regression parameters are given in the figure.

Thermodynamic parameters obtained from the titration curves for Cu(II), Mg(II) and Pb(II) under different conditions are summarized in Table 2. The results for copper at a pH of 6 ($\log \beta_2 = 9.92$) compare reasonably well with those obtained with the reference method using copper-selective potentiometry ($\log \beta_2 = 9.36$) and with $\log K$ values corresponding to model compounds shown in Table 1. It is important to notice that these model compounds are monomeric units, and so, stoichiometry 1:1 for these monomers is equivalent to 2:1 in dimmeric units used in our case (the ratio metal ion:aromatic ring is in both cases 1:1). This demonstrates the utility of isothermal titration calorimetry, which in addition to providing the complexation constants also allows direct measurements of other thermodynamic parameters that cannot be determined directly using potentiometry. Moreover, this approach can be used more generally as it is not restricted to a limited range of species, in contrast to potentiometry, which can be used only for species for which selective electrodes are available.

A comparison of the results at pH values of 5.0 and 6.0 shows the importance of proton competition with metal ions for the binding sites. Titration at pH lower than 3 was not possible due to the partial precipitation of lignin and at values higher than 10 because of lignin instability. A stoichiometry of two metal ions per lignin molecule ($n = 2$) was determined for copper and magnesium, but n was only 1.5 for lead, instead of the expected $n = 2$, for which only fairly weak signals were obtained. Thus, the real

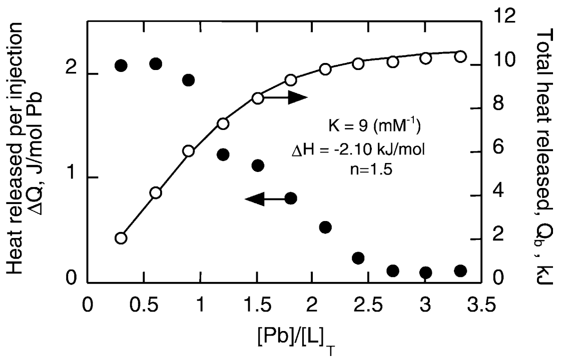

Fig. 3. Heat released per injection and cumulative heat released for the injection of a 1.1 mM lignin solution with 10 ml aliquots of a 10 mM lead solution at pH = 6.0. The lignin solution volume was 3 ml. The solid line is the curve fit of the model equation to the experimental data. Regression parameters are given in the figure.

Table 2
Results for the complexation of metal ions with the lignin derivative as obtained by titration calorimetry

Metal ion	pH	n	$\log K$ (M^{-1})	$\log \beta_2$ (M^{-2})	G (kJ/mol)	H (kJ/mol)	S (kJ/mol K)
Cu^{2+}	5	2.0 ± 0.1	4.07 ± 0.10	8.14 ± 0.20	−23.22 ± 0.01	−12.60 ± 0.01	0.0356 ± 0.0001
Cu^{2+}	6	2.0 ± 0.1	4.96 ± 0.15	9.92 ± 0.30	−28.30 ± 0.01	−13.56 ± 0.01	0.0495 ± 0.0001
Cu^{2+}	6	2.0 ± 0.1	4.93 ± 0.15[a]	9.86 ± 0.30	−28.13 ± 0.01	−11.36 ± 0.01[a]	0.0563 ± 0.0001
Mg^{2+}	6	2.0 ± 0.1	3.11 ± 0.19	6.11 ± 0.38	−17.74 ± 0.12	−2.66 ± 0.12	0.0506 ± 0.0012
Pb^{2+}	6	1.5 ± 0.1	3.93 ± 0.21	7.86 ± 0.31	−22.42 ± 0.11	−2.10 ± 0.11	0.0694 ± 0.0011

The values of the equilibrium constants are conditional at the corresponding pH. Values of $\log K$ correspond to a hypothetic 1:1 stoichiometry and $\log \beta_2$ are those corresponding to stoichiometry 2:1. The values of n are the experimental.

[a] Injection volume 5 µl, all other 10 µl. Larger number of collected data points.

complexation constants for copper and magnesium have to be those corresponding to $\log \beta_2$, obtained by the product of n times $\log K$ present in Table 2. The interaction of magnesium with lignin is weaker than that of copper, as reflected in the relative magnitudes of the complexation constants and enthalpies summarized in Table 2. It is difficult to compare the complexation constant for lead directly with those for copper and magnesium because of the different complexation stoichiometry for lead. In this paper, $\log K$ data is given in order to observe the separated effects of the site and the stoichiometry, which in turn might be driven by the ionic size, and β_2 for lead is supplied in Table 2 assuming 1:2 stoichiometry, although it differs from the experimental value, showing some kind of low effectiveness for this metal ion.

Then, the order of the complexation strengths for the three species considered here ($Cu^{2+} > Pb^{2+} > Mg^{2+}$) is similar to the complexation behavior exhibited by metal ions with humic acids ($Cu^{2+} > Ba^{2+} > Pb^{2+} > Cd^{2+} > Ca^{2+}$) [28]. The selectivity is probably due to differences in the electronegativities of the different metals combined with the ionic radius. As the electronegativity rank ordering ($Mg < Cu < Pb$) is different from that observed for the selectivities of the lignin for these metal ions, this might not be the only effect. On the other side, in both systems, the chelation takes place by the simultaneous interaction of the metal ion with two sites of the aromatic lignin ring (vicinal –OH and –COOH), which suggests that the metal ion size should play an important role in the selectivity of the lignin for different ions. Two of the ions (Cu^{2+} and Mg^{2+}) have similar radii and the chelation in both cases happens to take place in a 2:1 (ion:lignin) stoichiometry. And so, the electronegativity will decide the affinity between site and ion. The case is different for Pb^{2+}, its size may partially prevent the formation of the chelate or just make it more difficult to be formed. That would explain both aspects observed in the experimentation. On one side, the stoichiometry seems to be unexpectedly smaller. On the other side, although the electronegativity value would make more stable the complex with lead, this is not the final case. Some references can be found in the literature where similar affinities are shown for Cu(II) and Pb(II) by carboxylic and phenolic groups [29,30] when single site complexation takes place. Others [27] explain that this order takes place when amine groups are present. In our case, chelation occurs by double site simultaneous action and that could be a factor affecting our system, where now the size can play a role.

The combination of these two effects may explain, beyond the affinity concept, the chelation order of strength and experimental stoichiometry. The formation of the metal ion complexes with the lignin derivatives is favored thermodynamically both enthalpically and entropically, as is evident from the negative enthalpies and positive entropies of formation listed in Table 2. This entropic driving force for the complexation is most likely a reflection of the entropic gain derived from the release of waters of hydration when the ion is complexed with the lignin derivatives.

5. Conclusion

Chemically modified lignin from a residual waste product is a heterogeneous mixture of polyphenolic compounds, and this lack of homogeneity is often an impediment to its use as a chemical complexing agent for water treatment. We have used isothermal titration calorimetry coupled with other structural characterization methods to show that such mixtures can be represented effectively as a single pseudo-compound with well-defined molecular weight, acidic sites, and metal ion complexation stoichiometry and formation enthalpies. The results obtained show a clear trend in the metal ion complexation constant and stoichiometry that could be ascribed to a combined effect of electronegativity and ionic size. It can happen that not all the sites available for the binding of copper and magnesium are available for complexation with lead. The strength of the complexation reactions is such that the complexes formed are sufficiently strong to bind the metal ions. Lignin chelating agents of the type studied here are amenable to detailed characterization, both structural and thermodynamic, which should ease their commercial introduction in areas such as wastewater treatment, environmental remediation, controlled release of fertilizers and soil amendment.

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