SHORT PAPER

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Interaction of metallic cations with lignins. Part 1: Stability of iron (III), manganese (II) and copper (II) complexes with phenolic lignin model compounds: coumaric, ferulic and sinapic acids and coniferyl alcohol[†]

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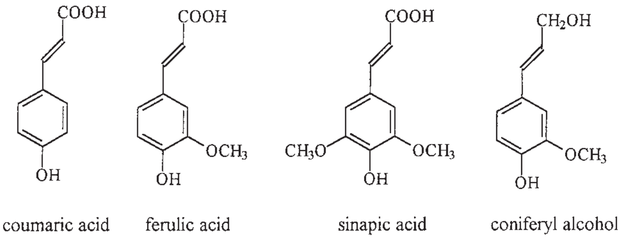
Dissociation constants of four monomeric molecular models of lignin and equilibrium constants of complex with iron (III) have been determined from potentiometric measurements

The mobility of dissolved organic compounds as lignin may significantly influence the mobility of transition metals in soil.[1] Organic complexes have long been recognized to have an impact on migration of metals in soil.[2] That is why knowledge of complexation and sorption process of metal cations such as manganese (II), iron (III) or copper (II) by lignins and their degradation products in soil is the most promising property to be evaluated in recent years.[3,4] Moreover the acidity of carboxylic and phenolic groups in lignin is extremely important in many areas of wood chemistry. In this paper we have studied in aqueous solution the protonation constants and the complexing ability of lignin model compounds towards manganese (II), iron (III) and copper (II): (Scheme 1).



Scheme 1

Complexity of the lignin structure has led us to work at first with these simple model molecules. These ligands form similar complexes to the natural lignin molecules. In a later work, we shall study the complexation of metal cations with oligomer molecules, obtained by condensation of monomers, and finally with lignin extracted from soils. A few stability constants of second and third transition row metals with *o*-coumaric acid have been briefly described in the literature.[5]

Protonation constants of ligands and equilibrium constants of the complexes (25 °C, I = 1 KNO_3) were determined by fitting the protometric titration curves with the program Protaf.[6] The study of ligand – metal complexation equilibria requires the determination of the acidity constants of the ligands, which were obtained from protometric titrations with KOH 0.1 mol L^{-1} until pH = 9 because of decomposition of the compounds (C_L from 2×10^{-4} to 1×10^{-3} mol l^{-1}). The constants are listed in Table 1 as well as the values obtained from literature.[7,8]

The pK_a values of the three acidic model compounds could be expected to be slightly different, because the methoxy group is a good electron donor. Moreover, intramolecular hydrogen bonds may be present between the phenolic hydrogen and the methoxy oxygen in ferulic and sinapic acids and this may influence the protonation constants of the phenolic group. But the pK_{a2} values of these three monomeric units are surprisingly very similar (see Table 1). However, the *para*-substituent notably affect the acidity of the phenolic group. In fact the acidic derivatives have lower pK_{a2} values (≈ 8.7) than alcoholic derivatives (9.05). This can be explained by the electron withdrawing effect of the carboxylic group. The variation in the carboxylic acidity of the three acids is also interesting to notice. Coumaric acid has a lower pK_{a1} value than ferulic or sinapic acids The electron donor character by inductive effect of the methoxy function probably can explain these values.

Precipitation which occurs at pH ≈ 5 and 6.5 for copper and manganese respectively, before any complex formation, prevents the determination of equilibrium constants. Analysis of the precipitates show the presence of metal hydroxides. For Fe^{3+} ion, complexes appear before precipitation of hydroxide occurs. Neutralization curves of metal – ligand systems were fitted by using the dissociation constants (pK_a) values and taking into account the hydroxo-complexes $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$ in order to determine the stability constants (see Table 2).

Distribution curves obtained from the stability constant values (Fig. 1) show the presence of a very large amount of complexes avoiding the predominant presence of hydroxo-species. The formation of these species is negligible above pH = 4. The titration curves obtained with the three acid ligands show an important first step which is consistent with the FeL^+, FeL_2^- or FeL_3^{3-} complexes. At higher pH values, for a best titration curves fitting, mixed complex appears such as $FeL_2(OH)^{2-}$ for ferulic acid (pH ≥ 7.5) or $FeL_2(OH)_2^{3-}$ for coumaric acid and coniferyl alcohol (pH ≥ 8). On the other hand a precipitate is formed with sinapic acid (pH ≥ 5.5). This is surprising because the overall stability constants listed in Table 2 reflect the high stability of FeL_2^- and FeL_3^{3-} species. In the pH range corresponding to soils (5 < pH < 9), these monomeric models of lignin are present as iron complexes or mixed hydroxo-complexes. In order to

Table 1 Protonation constants of model compounds[a] (25 °C, I = 1 M KNO_3)

model compounds	p$K_{a1(COOH)}$	p$K_{a2(OH)}$	pK_{a1}	pK_{a2}
coumaric acid	4.31 (0.01)	8.73 (0.04)	6.25[b]	9.50[b]
ferulic acid	4.46 (0.02)	8.71 (0.02)		9.39[c]
sinapic acid	4.40 (0.02)	8.76 (0.04		
coniferyl alcohol	–	9.05 (0.04)		9.53[c]

[a]Values in parentheses represent estimated standard deviations (95%) confidence). [b]Ref. 10 (I = 0.125 NaC10$_4$). [c]Ref. 11 (unknown conditions).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Log of equilibrium constant values for Fe^{3+} -monomeric model ligands[a]

Equilibrium	Coumaric acid (pH = 9)[b]	Ferulic acid (pH = 7.3)[b]	Sinapic acid (pH = 5.5)[b]	Coniferyl alcohol (pH = 11)[b]
$Fe^{3+} + L \rightleftarrows FeL$	10.91 (5)	13.72 (5)	12.30 (6)	13.4 (2)
$Fe^{3+} + 2L \rightleftarrows FeL_2$	19.82 (4)	18.59 (6)	–	23.42 (2)
$Fe^{3+} + 3L \rightleftarrows FeL_3$	25.79 (8)	–	–	32.2 (2)
$Fe^{3+} + 2L + OH^- \rightleftarrows FeL_2\,(OH)$	–	10.64 (7)	–	–
$Fe^{3+} + 2L + OH^- \rightleftarrows FeL_2\,(OH)_2$	4.6 (1)	–	–	7.1 (2)

[a]Values in parentheses represent estimated standard deviations for the last significant digit (95% confidence); charges are omitted for simplicity. [b]pH of precipitation.

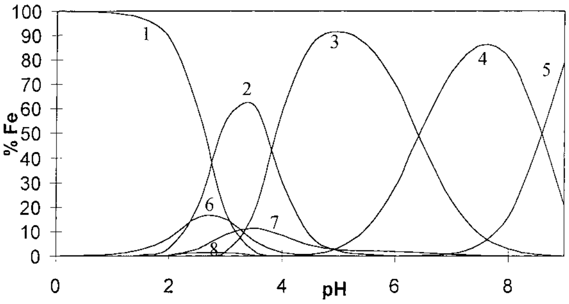

Fig. 1 Distribution curves of the Fe^{III}- coumaric acid complexes ($C_L = 5 \times 10^{-4}$ mol l^{-1}, $C_{Fe} = 1 \times 10^{-4}$ mol l^{-1},: (1) Fe^{3+}; (2) FeL^+; (3) FeL_2^-; (4) FeL_3^{3-}; (5) $FeL_2\,(OH)_2^{3-}$; (6) $Fe(OH)^{2+}$; (7) $Fe(OH)_2^+$; (8) $Fe_2(OH)_2^{4+}$.

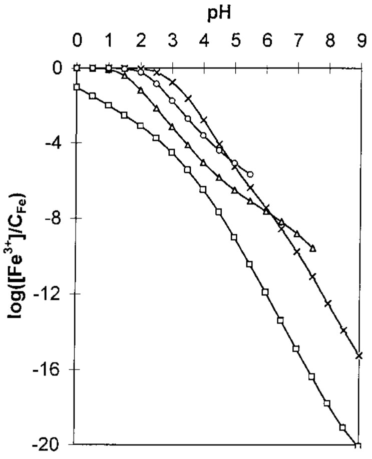

Fig. 2. Plots of log ($[Fe^{3+}]/C_{Fe}$) as a function of pH ($C_{Fe} = 10^{-4}$ mol l^{-1}; $C_L = 5 \times 10^{-4}$ mol l^{-1} for monomeric ligands) : (x) coumaric acid, (△) ferulic acid, (○) sinapic acid, (□) coniferyl alcohol.

compare the complexing ability of the different ligands towards iron (III), we plotted in Fig. 2 the logarithm of iron (III) molar fraction as a function of pH for each monomeric ligand. The plot shows clearly the greater chelating ability of coniferyl alcohol than the acid compounds from very strong acidic medium ($pH < 1$). While coumaric acid becomes the most complexing ligand among the three acidic monomeric species above pH = 7, ferulic acid and in minor importance sinapic acid are better iron chelators in acidic medium. In addition, exactly same results were obtained with compounds in which the carboxylic acid function was substituted by an ester group. This suggested a phenolic oxygen coordination mode which probably involved the methoxy group in the case of ferulic and sinapic acid or coniferyl alcohol. Furthermore, these compounds have greater stability constant values (ferulic acid : $\beta_{110} = 13.72$, sinapic acid : $\beta_{110} = 12.30$ and coniferyl alcohol : $\beta_{110} = 13.4$) than coumaric acid ($\beta_{110} = 10.91$), which is consistent with this coordination mode.

Experimental

Stock solutions of metal ions nitrates were prepared from reagents (*Fluka*) of the higher purity (> 99%) as well as coumaric, ferulic and sinapic acid (*Fluka*) solutions. Iron (III) nitrate solutions were titrated with EDTA (with salicyclic acid as an indicator; $pH \approx 2$), the excess of nitric acid have been titrated through the quantitative formation of the complex FeL_3 with maltol.[9] Concentrations of ligand solutions were determined from protometric titrations until $pH \approx 9$, because of an instability of pH above this value probably due to the decomposition of the ligand. Solutions were stable for several weeks (stability was controlled by UV spectra).

Coniferyl alcohol was prepared according to the procedure outlined by Ralph and Quideau.[10] Coniferaldehyde (1 g, 5.61 mmol) was dissolved in ethyl acetate (200 ml). Sodium borohydride (420 mg, 11.22 mmol, 2 equiv) was added and the solution was stirred for 1 h at room temperature. After pouring in water and extraction with ethyl acetate, coniferyl alcohol was obtained and recrystallized from dichloromethane / petroleum ether as very pale yellow powder (0.96 g, 97%). Melting point, ^1H and ^{13}C NMR spectra were identical to those reported previously.[10]

Protometric procedure: All measurements were performed at 25°C and at ionic strength equal to 1 mol^{-1}, in a potassium nitrate medium under a dynamic nitrogen atmosphere in order to avoid oxidation of the ligands. The protometric measurements were carried out in a thermoregularized cell. The glass electrode Metrohm type “U” has a very low alkaline error. The reference element Hg/Hg_2C1_2 was in contact with a solution containing KC1 of a concentration of 0.1 mol l^{-1} and KNO_3 0.9 mol l^{-1}. The procedure and apparatus used have been previously described.[11] The ratio R = C_L/C_M of total ligand to total metal concentration were used from 1 to 10. The metal-ligand systems were studied from metal concentrations C_M ranging from 1×10^{-4} to 8×10^{-4} mol l^{-1}.

Computations: Protometric data were processed by the computer program Protaf[6] in order to obtain the best-fit chemical model and refined stability constants β_{mlh} (β_{mlh} refers to the species $M_mL_lH_h$; a negative h value refers to the hydroxy ion). The program Protaf, which is based on the weighted least squares of the residues of the experimental variables (volume of titrant, pH) allows a simultaneous processing of ten titrations, each including 150 pairs of data (volume, pH).

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