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Thermodynamic stability of copper(II), manganese(II), zinc(II) and iron(III) complexes with chlorogenic acid

Jamal Améziane, Michel Aplincourt*, Laurent Dupont,
Frédéric Heirman, Jean-Claude Pierrard

GRECI, Laboratoire de chimie minérale, Université de Reims-Champagne-Ardenne,
BP 1039, 51687 Reims cedex 2, France

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Summary — Protometric studies were performed in aqueous solution at 20 °C and 1 mol dm^{-3} ionic strength (KNO_3) in order to determine the complexing ability of chlorogenic acid (H_3L) towards copper(II), manganese(II), zinc(II) and iron(III). A detailed qualitative examination of titration curves indicated formation of ML_n complexes (n = 1, 2 or 3). With Cu(II) and Fe(III) a protonated complex MLH is formed in acidic medium and with Zn(II) it seems likely that two mixed hydroxo complexes ZnL_2OH^{5-} and $ZnL_2(OH)_2^{6-}$ are present above pH = 10. Stability constants β_{mlh} defined as $[M_mL_lH_h]/[M]^m[L]^l[H]^h$ were computed and refined. The stability order of the complex species is Fe > Cu > Zn > Mn.

chlorogenic acid / copper(II) / manganese(II) / zinc(II) / iron(III) / complex / protometry / equilibrium constant

Résumé — Stabilité thermodynamique des complexes de l'acide chlorogénique avec le cuivre(II), le manganèse(II), le zinc(II) et le fer(III). *Une étude protométrique, en solution aqueuse, a été réalisée à 20 °C et à force ionique égale à 1 (KNO_3) dans le but de déterminer le pouvoir complexant de l'acide chlorogénique (H_3L) vis-à-vis du cuivre(II), du manganèse(II), du zinc(II) et du fer(III). Une analyse qualitative détaillée des courbes de titrage met en évidence la formation de complexes de type ML_n (n = 1, 2 ou 3). Avec le cuivre(II) et le fer(III), il se forme également un complexe protoné MLH en milieu acide et avec le zinc(II) on peut envisager, au dessus de pH = 10, la formation de deux complexes hydroxydés* $ZnL_2(OH)^{5-}$ *et* $Zn_2L_2(OH)_2^{6-}$. *Les constantes de stabilité* $\beta_{mlh} = [M_mL_lH_h]/[M]^m[L]^l[H]^h$ *ont été calculées et affinées à l'aide du programme Protaf. L'ordre de stabilité des espèces complexes est Fe > Cu > Zn > Mn.*

acide chlorogénique / cuivre(II) / manganèse(II) / zinc(II) / fer(III) / complexe / protométrie / constante de stabilité

Introduction

The availability to plants of metal ions is influenced by natural complexing agents which are present in soils [1]. Of special interest are phenolic compounds which may participate in the transport processes of metal ions from the surrounding soil to the plant roots [2, 3]. One of the most important of these phenolic compounds is chlorogenic acid, which is an important factor in plant metabolism. Seven elements essential for growth are required in relatively small amounts by plants. These micronutrients include Fe, Cu, Mn and Zn, which behave primarily as cations in soils, and three that assume anionic forms, B, Mo and Cl [4]. In this paper, we study in aqueous solution the complexing ability of chlorogenic acid towards the four micronutrient cations iron(III), copper(II), manganese(II) and zinc(II). Several studies [5–7] have already been carried out on chlorogenic acid-copper(II) interactions but they lead to contradictiory conclusions. For example, Lamy et al [6] concluded that chlorogenic acid forms monomeric complexes whereas Kiss et al [7] found oligomeric species.

Experimental section

Reagents

Chlorogenic acid was purchased from Fluka and used with no further purification. Its purity was controlled by C, H microanalysis and confirmed by protometric titration. Ligand solutions were kept away from light, in order to avoid a degradation, and were used, at the latest, five days after their preparation. The metal nitrates were Fluka products. To prevent hydrolysis, an excess of nitric acid was added to the stock solutions of manganese(II) and iron(III). Metal stock solutions were standardized by EDTA titrations using the appropriate indicators. All stock solutions were filtered on a Millipore filter (pore size 1.2 μm) before use and storage.

Experimental techniques

All measurements were performed at 20 °C and with the ionic strength adjusted to 1 with potassium nitrate.

Visible absorption spectra were recorded using a Perkin-Elmer Lambda 6 spectrophotometer linked to an Epson PC AX2 computer. A software developed by Perkin-Elmer

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(PECSS software) enabled the acquisition of the spectra. The reference cell contained a 1 mol dm^{-3} KNO_3 solution.

The protometric measurements were carried out in a thermoregularized cell at 20.0 ± 0.1 °C with a nitrogen stream over the solution to limit oxidation. The glass electrode Metrohm type 'U' has a very low alkaline error. The reference electrode had a double junction element. The reference element Hg/Hg_2Cl_2 was in contact with a solution of composition KCl 0.1 mol dm^{-3} and KNO_3 0.9 mol dm^{-3}. These were all equipped with an extension filled with an KNO_3 1 mol dm^{-3} solution. The procedures and apparatus used for protometric measurements have been described in detail previously [8].

Computations

The values of the protonation constants of the ligand and of the stepwise formation constants of the complexes were initially calculated by a method [9] derived from the methods of Bjerrum [10] and Rossotti and Rossotti [11]. The protometric data were then processed by the computer program Protaf [12] in order to obtain the best-fitting chemical models and refined stability constants β_{mlh} (β_{mlh} refers to the species $M_mL_lH_h$. When h is negative, this refers to the hydroxyl ion). The program Protaf, which is based on the weighted least-squares of the residues of the experimental variables (volume KOH, pH), allows a simultaneous processing of ten titrations each including 150 pairs of data (volume, pH).

Results

Protonation constants

The study of metal–ligand interactions requires prior determination of the ligand acidity constants.

Ligand solutions were prepared in the concentration range $3 \times 10^{-3} < C_L < 1.6 \times 10^{-2}$ mol dm^{-3} and neutralized by KOH solution (0.1 or 0.2 mol dm^{-3}) until pH = 12.5. In order to determine the stronger acidity, an amount of nitric acid HNO_3 was initially added to all ligand solutions.

The ligand studied was a triacid (H_3L). The values of the protonation constants K_h ($H_{h-1}L + H^+ \rightleftharpoons H_hL$; charges of the ligand species omitted for simplicity) were first obtained from calculation of $\bar{n}_H$, the average number of mol of protons fixed per mol of L^{3-}. The general expression of $\bar{n}_H$ is [13]:

$$\bar{n}_H = \sum_{h=1}^{h=H} h[H_hL] \Big/ \sum_{h=0}^{h=H} [H_hL]$$

$$= \sum_{h=1}^{h=H} h\beta_{01h}[H^+]^h \Big/ \sum_{h=0}^{h=H} \beta_{01h}[H^+]^h$$

where β_{01h}'s are the overall protonation constants

$$\beta_{01h} = \frac{[H_hL]}{[L][H^+]^h} = \prod_h K_h \text{ and } \beta_{010} \equiv 1$$

In the case of chlorogenic acid, the average number $\bar{n}_H$ was derived from experimental data as

$$\bar{n}_H = 3 - \frac{A}{C_L} \text{ with } A = [H_3O^+] - [OH^-] + [K^+] - [NO_3^-]$$

where the concentrations $[K^+]$ and $[NO_3^-]$ relate to the amounts of KOH titrant delivered and nitric acid initially added.

The protonation constants were then computed and refined with the program Protaf. The results obtained are listed in table I.

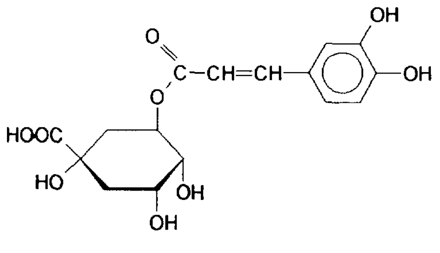
Table I. Protonation constants for chlorogenic acid.

log K_1 [a] *(OH in* meta *position)*	*log* K_2 *(OH in* para *position)*	*log* K_3 *(COOH)*	*reference*
12.06(1)[b]	8.30(1)	3.35(1)	this work
12.5	8.21	3.35	7
11.5	8.27	3.37	6

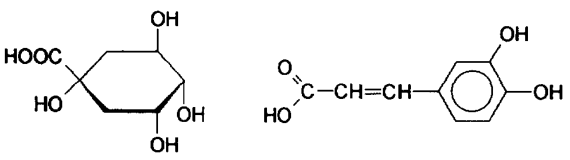
[a] K_h refers to $[H_hL]/[H_{h-1}L][H^-]$

[b] Values in parentheses represent 1σ standard deviation for the last significant digit.

The attributions of the three log K values, as shown in table I, were made by comparison with quinic [14] and caffeic [7, 15] acids (fig 1). The stronger acidity (log K_3) is attributed to the carboxylic group and the second acidity (log K_2) to the OH group in the *para* position relative to the substituant containing the quinic moiety. The weak acidity (log K_1) of the phenolic group in the *meta* position is due to internal hydrogen bonding between the phenolic oxygen in the *para* position and the *meta* phenolic hydrogen. Except for log K_1, our values are in good agreement with those of Lamy et al [6] and Kiss et al [7].



chlorogenic acid



quinic acid

caffeic acid

Fig 1. Structural formulae.

Chlorogenic acid–metal cation interactions

In order to prove the formation of complex species, solutions of variable ratio $R = C_L/C_M$ (total ligand to

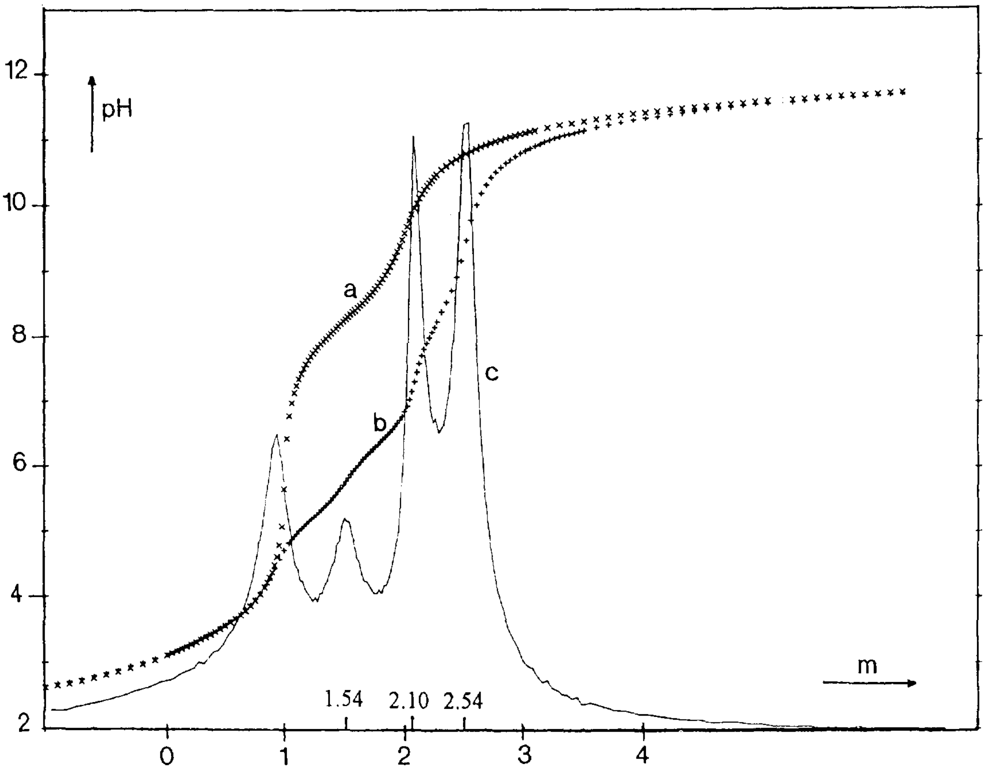


Fig 2. Titration curves for chlorogenic acid solutions ($C_L = 1.93 \times 10^{-3}$ mol dm^{-3}) in the presence of 2.02×10^{-3} mol dm^{-3} nitric acid: (a) chlorogenic acid alone; (b) chlorogenic acid + Cu^{2+}, $C_L/C_M = 3.7$; (c) derivative curve. The pH is given vs the number (m) of OH^- equiv per ligand mol, calculated after neutralization of acid HNO_3.

total metal concentration) were neutralized by KOH (0.1 or 0.2 mol dm^{-3}) until pH 12.5. If complexation occurs, neutralization curves of metal–ligand solutions show a decrease in pH and displacement of the equivalent points compared with those of the ligand alone at the same concentrations. Qualitative analysis of the shape of the titration curves leads to the determination of the stoichiometry of the main complexes formed. Copper(II), manganese(II), zinc(II) and iron(III) complexes were studied for total metal concentrations ranging from 5×10^{-4}–4×10^{-3} mol dm^{-3} and total ligand concentrations from 10^{-3}–1.2×10^{-2} mol dm^{-3}. This resulted in ligand:metal ratios R ranging from 2–8.

Figure 2 shows, for example, titration curves of the ligand alone (curve a) and in the presence of copper(II) (curve b), as well as the corresponding derivative curve (curve c). In order to facilitate the interpretation of the results, the pH is given vs the number (m) of OH^- equivalents per ligand mol, calculated after neutralization of the excess nitric acid. Curve b ($R = 3.7$) shows four equivalent points. The first point (pH = 4.5), situated slightly before 1 equiv OH^-, corresponds to neutralization of the carboxylic function of the ligand. Before this first equivalent point, curves (a) and (b) are superimposed which means that no complexation occurs below pH = 4.5. The second and third equivalent points (pH = 5.7, $m = 1.54$ and pH = 7.3, $m = 2.1$) are attributed respectively to the probable formation of the complexes CuL^- and CuL_2^{4-} according to:

$$0.27\ Cu^{2+} + H_3L + 1.54\ OH^- \rightarrow 0.27\ CuL^- + 0.73\ H_2L^- + 1.54\ H_2O$$

and

$$0.27\ Cu^{2+} + H_3L + 2.08\ OH^- \rightarrow 0.27\ CuL_2^{4-} + 0.46\ H_2L^- + 2.08\ H_2O$$

At pH = 5.7 or 7.3, we can consider that the major form of the free ligand is H_2L^-. Finally, the position of the fourth equivalent point (pH = 9.5, $m = 2.54$) corresponds to neutralization of the second acidity of the excess ligand molecules.

Similar qualitative studies were carried out on the neutralization curves obtained with the other two divalent cations Mn(II) and Zn(II). These neutralization curves are superimposable on that of the ligand alone until pH = 6 in the case of Zn(II) or pH = 7 in the case of Mn(II), which corresponds in both cases to nearly one equivalent of OH^- added. The titration curves always show two clear equivalents points: the first point (pH ≈ 5.8) corresponds to the neutralization of the stronger ligand acidity; the second point (pH ≈ 10) is attributed both to the formation of the 1/2 complexes (MnL_2^{4-} or ZnL_2^{4-}) and to the neutralization of the second acidity of the excess ligand molecules.

Unlike the divalent cation -ligand systems, in the case of iron(III) the complexation takes place as early as

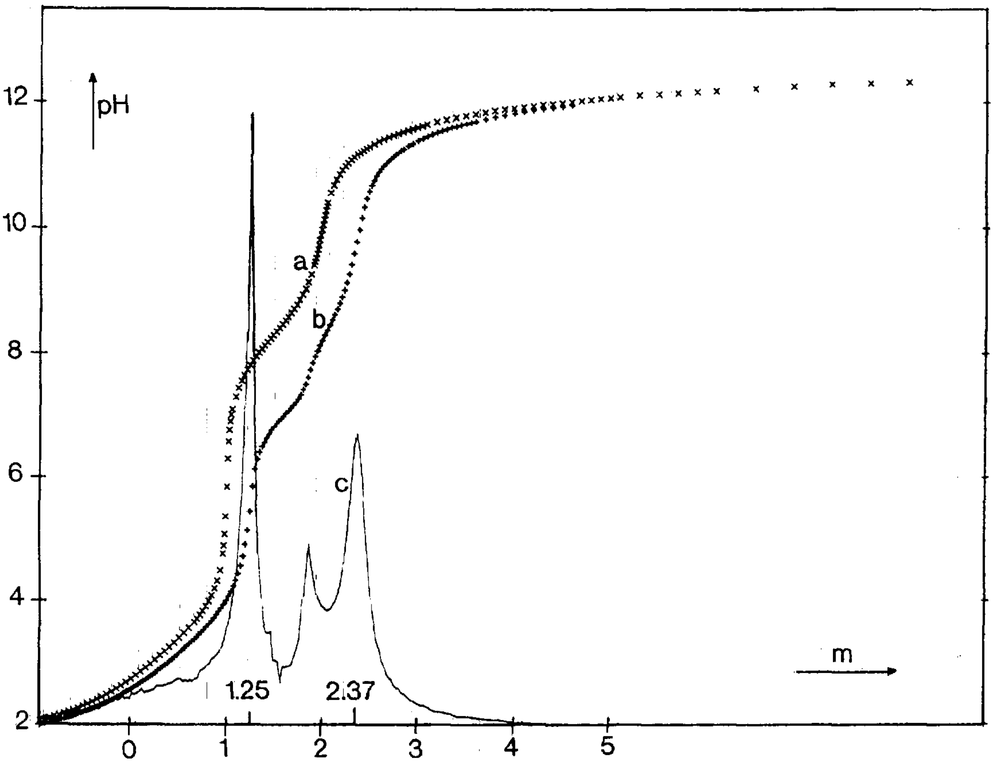


Fig 3. Titration curves for chlorogenic acid solutions ($C_L = 7.8 \times 10^{-3}$ mol dm^{-3}) in the presence of 7.72×10^{-3} mol dm^{-3} nitric acid: (a) chlorogenic acid alone; (b) chlorogenic acid + Fe^{3+}, $C_L/C_M = 8$; (c) derivative curve. The pH is given vs the number (m) of OH^- equiv per ligand mol, calculated after neutralization of acid HNO_3.

the beginning of the titrations, because the neutralization curves of the iron(III)–ligand solutions always lie below that of the ligand alone (see, for example, fig 3, curves a and b). Under the experimental conditions used for the potentiometric measurements, precipitation occurs near pH ≈ 5, at the first equivalent point of the neutralization curves. This may be due to the precipitation of the neutral complex FeL. The neutralization curve b ($R = 8$) shows three equivalent points, at $m = 1.25$, 1.9 and 2.37. The first point (pH = 5.5, $m = 1.25$) is attributed both to the formation of the complex FeL and to the neutralization of the strongest acidity of the excess ligand molecules:

$$0.125\ Fe^{3+} + H_3L + 1.25\ OH^- \rightarrow 0.125\ FeL + 0.875\ H_2L^- + 1.25\ H_2O$$

The last point (pH = 10, $m = 2.37$) may well be related to the formation of the higher complex FeL_3^{6-} and to the neutralization of the two strongest acidities of the excess ligand molecules according to:

$$0.125\ Fe^{3+} + H_3L + 2.37\ OH^- \rightarrow 0.125\ FeL_3^{6-} + 0.625\ HL^{2-} + 2.37\ H_2O$$

Between these two sharp equivalent points, the presence of a less well-defined point at $m = 1.9$ seems to indicate that the higher complex FeL_3^{6-} is totally formed at pH ≈ 7.7.

In conclusion, protometric titrations indicate that chlorogenic acid forms two successive complexes, ML^- and ML_2^{4-}, with the three divalent cations (M(II) = Cu(II), Mn(II) or Zn(II)) and three successive complexes, FeL, FeL_2^{3-} and FeL_3^{6-}, with iron(III).

Chlorogenic acid–metal cation stability constants

With iron(III), under the experimental conditions used for potentiometric measurements, precipitation occurs near pH ≈ 5. At this pH value only the neutral complex FeL is formed (vide supra), and thus only the first complexation equilibrium between Fe^{3+} and FeL can be quantitatively studied by potentiometry and the corresponding formation constant determined.

In order to determine the formation constants of the complexes FeL_2^{3-} and FeL_3^{6-}, the iron(III)–ligand system was studied using absorption spectrophotometry. Spectra of chlorogenic acid–iron(III) solutions were recorded from pH 3–10. The ratio $R = C_L/C_M$ was close to 3.2 and the low metal concentration $C_M = 5 \times 10^{-5}$ mol dm^{-3} was chosen to avoid the formation of any precipitate in the solutions. Absorption spectra exhibit two isosbestic points. The first point was observed at 575 nm for solutions of pH > 6.5 and corresponds to the FeL_2^{3-}/FeL_3^{6-} equilibrium. The other point, located near 800 nm for solutions of pH 5–6.5, corresponds to the FeL/FeL_2^{3-} equilibrium. The equilibrium between Fe^{3+} and the 1:1 complex FeL, occurs before pH = 5 but no isosbestic point was observed because the Fe^{3+}

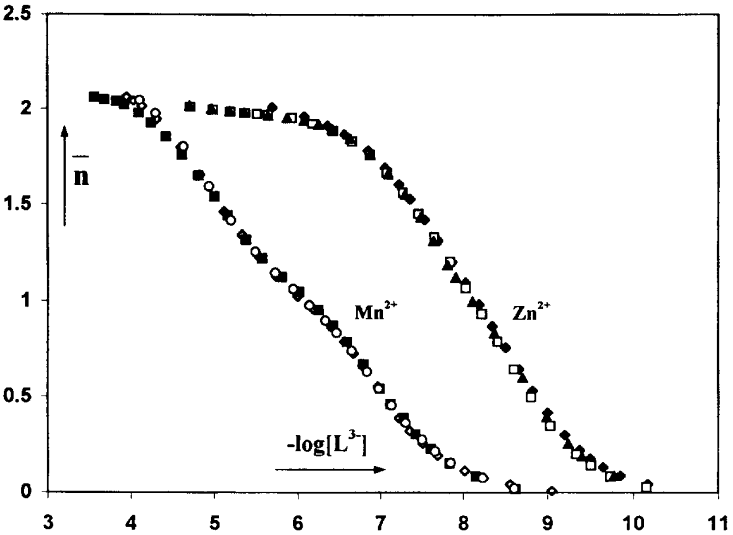


Fig 4. Experimental formation curves (Bjerrum plot).
Zn^{2+}: (♦) $C_M = 3.28 \times 10^{-3}$ mol dm^{-3}, $R = C_L/C_M = 3.56$; (□) $C_M = 2.46 \times 10^{-3}$ mol dm^{-3}, $R = 4.74$; (▲) $C_M = 1.64 \times 10^{-3}$ mol dm^{-3}, $R = 2.38$.
Mn^{2+}: (◇) $C_M = 1.59 \times 10^{-3}$ mol dm^{-3}, $R = C_L/C_M = 3.67$; (■) $C_M = 1.19 \times 10^{-3}$ mol dm^{-3}, $R = 4.89$; (○) $C_M = 7.96 \times 10^{-4}$ mol dm^{-3}, $R = 7.33$.

species does not absorb in the wavelength range studied. The spectra were recorded immediately after the preparation of the solutions because the absorbance slowly changed with time, and thus it was not possible to calculate accurate values for the stepwise formation constants of the complexes FeL_2^{3-} and FeL_3^{6-}.

The potentiometric data were evaluated assuming coordination of the phenolic hydroxy groups only. This catecholate mode of coordination is supported by the fact that the neutralization curves of chlorogenic acid, alone and in the presence of a divalent cation, are superimposable in the acidic region corresponding to the deprotonation of the carboxylic group. In addition, with iron(III) the formation of the complex FeL_3^{6-} is in agreement with a bidentate behavior of the ligand, from the two oxygens of the catechol group.

Stepwise formation constants were first calculated by a method [9] derived from the methods of Bjerrum [10] and Rossotti [11], using $\bar{n}$, the average number of ligands bound per mol of metal ion, and $[L^{3-}]$, the concentration of the free deprotonated form of the ligand. The variables $\bar{n}$ and $[L^{3-}]$ were derived from the experimental data as:

$$\bar{n} = \left(C_L - [L^{3-}] \sum_{h=0}^{h=3} \beta_{01h} [H^+]^h \right) / C_M$$

and

$$[L^{3-}] = (3C_L - A) / \sum_{h=1}^{h=3} h\beta_{01h} [H^+]^h$$

where A is the term previously defined (see the expression for $\bar{n}_H$). With the three divalent cations M^{2+}, the formation number $\bar{n}$ reached values close to 2 which confirms the successive formation of the ML^- and ML_2^{4-} species (for example, see fig 4).

For the different M^{2+}–ligand systems studied, the formation curves are superimposable for different values of the ratio R, indicating the absence of polynuclear complexes (such as those possible with such a multifunctionnal ligand). However, with Cu(II) a poor overlap was observed for low $\bar{n}$ values, which seems to indicate the presence of protonated complexes in acidic medium ($pH < 5.5$). With reference to previous works [6, 15], we suggest the formation of the CuHL species in which the carboxylic group remains protonated. In the case of iron(III), superposition of the formation curves takes place only in the region of $\bar{n} = 0.5$–1 for pH solutions ranging from 3–5.5. The $\bar{n}$ values were calculated up to pH = 5.5, because above this pH value, corresponding to the first equivalent point observed in the titration curves, precipitation occurs in solution. Like in the case of Cu(II), the poor overlap observed for $pH < 3$ may suggest the formation of the protonated complex $FeHL^+$. Finally the stability constants β_{mlh} were fitted to the experimental data using the Protaf computer program. The set of overall stability constants is reported in table II.

Table II. Overall stability constants for the chlorogenic acid–metal systems[a].

Metal	*log* β_{110}[b]	*log* β_{120}	*log* β_{111}
Cu^{2+}	12.74(1)	23.35(1)	16.92(7)
Mn^{2+}	7.02(1)	12.13(1)	–
Zn^{2+}	8.79(1)	16.20(1)	–
Fe^{3+}	17.64(6)	–	22.20(5)

[a] values in parentheses represent 1 σ standard deviation for the last significant digit.

[b] $\beta_{mlh} = \dfrac{[M_mL_lH_h]}{[M]^m[L]^l[H]^h}$ (the charges are omitted for simplicity).

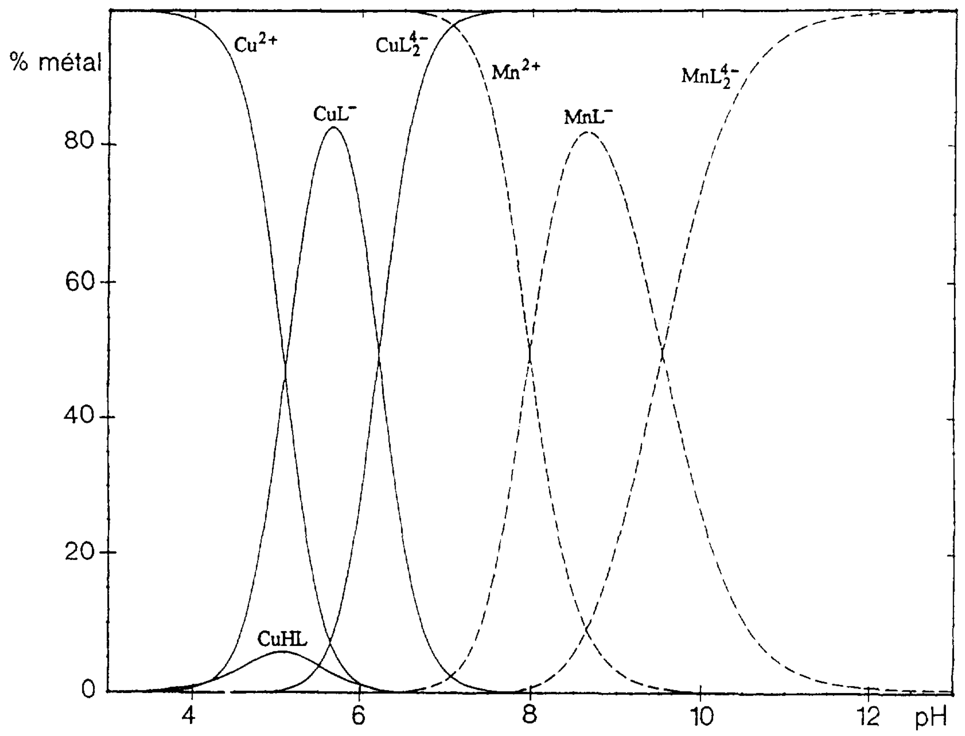


Fig 5. Distribution curves for copper(II)–chlorogenic acid and manganese(II)–chlorogenic acid systems as a function of pH. $C_M = 1.0 \times 10^{-3}$ mol dm^{-3}; $C_L = 4.0 \times 10^{-3}$ mol dm^{-3}. The relative concentration of each species is given as a percentage of the total metal concentration C_M.

Discussion and conclusion

The neutralization curves of the metal–ligand systems were computed using the values of the β_{mlh} stability constants (table II) and taking into account the hydroxo species ($MnOH^+$, $Mn_2(OH)^{3+}$ or $ZnOH^+$; $CuOH^+$, $Cu_2(OH)_2^{2+}$ or $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$) [16–20]. Except for the Zn^{2+}–ligand system, the calculated curves are in very good agreement with the experimental titration points over the whole pH range studied.

In the case of Zn(II), the neutralization curves were first computed with the assumption of two complexes ZnL^- and ZnL_2^{4-} only. Under these conditions, the fit between the experimental and the calculated titration curves above the second equivalent point (pH > 10) was not satisfactory. This may be due to the eventual formation of mixed hydroxo complexes in the basic medium. Such a result was not obtained with the other metal cations studied, so it is not ascribed to experimental errors in pH measurements or to partial degradation of the ligand. Numerous combinations of mixed hydroxo complexes of general formula $ZnL_l(OH)_h$ were therefore tried in the calculation and the best fit was obtained with the two species ZnL_2OH^{5-} and $ZnL_2(OH)_2^{6-}$. The corresponding constants β_{mlh} were computed by the Protaf program and their values are respectively: $\log \beta_{12-1} = 4.30(3)$ and $\log \beta_{12-2} = -8.05(5)$ (values in parentheses represent 1σ standard deviation for the last significant digit).

Species-distribution curves (for example, fig 5) show that the catechol-coordinated complexes formed are sufficiently stable to prevent the formation in solution of the ionic hydroxo species $M_m(OH)_h$ and to avoid the precipitation of the insoluble hydroxides. For each metal cation studied, the distribution curves of the complexes (fig 5) are in agreement with the shape of the experimental neutralization curves; for example for Cu(II), the complex CuL^- is the major species at pH = 5.7 and the formation of the complex CuL_2^{4-} is almost complete near pH = 7.3 (fig 5) which is in agreement with the positions of the equivalent points (fig 2, curve b).

In the cases of Fe(III) and Cu(II), complexation takes place in acidic medium and if we envisage a catecholate mode of coordination (vide supra), the carboxylic group of the ligand is still partly protonated. This leads us to suggest the formation of the complexes $FeHL^+$ and CuHL. The formation of CuHL was previously reported by Lamy et al [6]. On the other hand, Kiss et al [7] suggested coordination via the carboxylate site, leading to the CuH_2L^+ species. We did not find this protonated species but its existence is not incompatible with our results; however, if it forms, it is far less stable than the catechol-coordinated chelates because chlorogenic acid behaves in this case as a monodentate ligand. Between pH 4 and 8, Kiss et al [7] reported also the formation of the dinuclear species Cu_2L^+ and $Cu_2L_3^{5-}$. This disagrees completely with our results because the formation curves that we obtained are well superimposed in the pH range 4–8, indicating that only mononuclear complexes are formed.

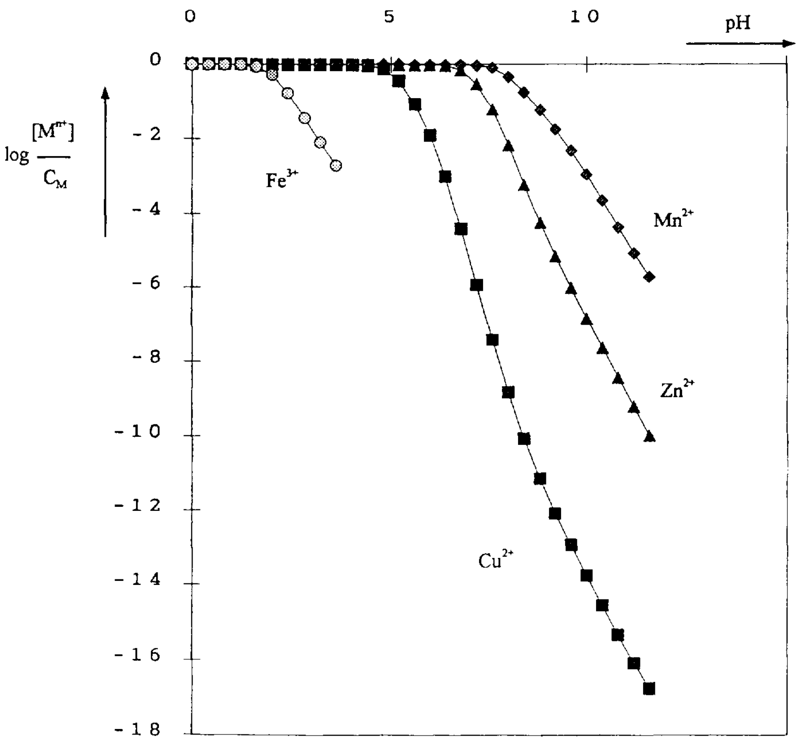


Fig 6. Plots of log ([Mn$^+$]/C_M) for metal-ligand systems as a function of pH (C_M = 8.0 × 10^{-4} mol dm^{-3}; C_L = 4.0 × 10^{-3} mol dm^{-3}).

In order to compare the complexing ability of chlorogenic acid with copper(II), manganese(II), zinc(II) and iron(III), we plotted the molar fraction (on a logarithmic scale) of the free metal cations as a function of pH for given ligand/metal ratios (fig 6). Such a plot shows clearly the enormous difference in stability between the complexes formed with the four metal cations. Chelation occurs in strongly acidic medium (pH ≈ 2) with iron(III) but only above pH ≈ 7 with manganese(II), and, for instance, at pH = 10, the free copper(II) concentration is almost 12 log units smaller than the free manganese(II) concentration.

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