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POTENTIOMETRIC INVESTIGATIONS OF EQUILIBRIA BETWEEN CAFFEIC ACID AND MANGANESE(II), COBALT(II), NICKEL(II) AND CADMIUM(II) IONS IN AQUEOUS SOLUTION

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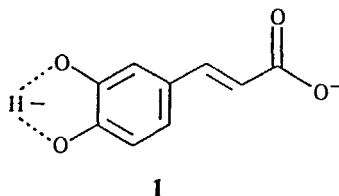
Aqueous solution equilibria have been investigated for the systems caffeate (*trans*-3-(3,4-dihydroxyphenyl)-propenoate)-manganese(II), -cobalt(II), -nickel(II) and -cadmium(II) by means of glass electrode potentiometry. The identities of the complex species formed and the corresponding formation constants have been determined with the aid of computer analysis. Conditions were: temperature, 25°C; ionic strength, 0.100 mol dm⁻³ with respect to chloride. Defining the ligand species, L²⁻, as the dianion, **1**, (one proton firmly bound to the catecholic moiety), the titration data can best be explained by postulating the following complexes: MnLH₁⁻, logβ_{11,1} = -4.88; MnLH₂²⁻, logβ_{11,2} = -15.55; NiLH₁⁻, logβ_{11,1} = -3.62; NiLH₂²⁻, logβ_{11,2} = -13.45; Ni₂LH₁⁺, logβ_{21,1} = -1.56; CoLH₁⁻, logβ_{11,1} = -4.12; Co₂LH₁⁺, logβ_{21,1} = 1.75; CdLH₁⁻, logβ_{11,1} = -4.91; CdL₂H₂⁴⁻, logβ_{12,2} = -12.29; CdL₃H₃⁻, logβ_{13,3} = -19.50. In each case the MLH₁⁻ complex constitutes the major species. By comparison with literature formation constants for related ligands, and considerations of the pH-ranges in which the MLH₁⁻ complexes form, it is concluded that the metal coordinates to the catecholate site of the caffeate ion.

Keywords: Caffeic acid, manganese(II), cobalt(II), nickel(II), cadmium(II), potentiometry

INTRODUCTION

The bioavailability to plants of metal ions, either as micronutrients or as toxins, is determined by the physico-chemical form of the metal ion, its speciation. The speciation of a particular metal ion is strongly influenced by coordinating ligands which may be present in the soil or in the hydroponic solution in which the plant grows. Under certain conditions of iron stress, phenolic ligands are exuded by the roots of so-called "iron-efficient" plants.¹⁻³ One of the root-exuded phenolic compounds of major importance is caffeic acid (*trans*-3-(3,4-dihydroxyphenyl)-propenoic acid).⁴ It has been postulated that the release of caffeic acid results in the reduction of iron(III) to iron(II), which is the necessary oxidation state of iron ions for absorption by plant roots.² Indeed the bio-available form of iron is the iron(II) aqua ion.⁵ Further, the caffeic acid molecule possesses two coordination sites, one at the catechol-type moiety and the other at the carboxylate group. Therefore a wide variety of metal-caffeate complexes can potentially be formed. In this paper the ligand species is defined as the dianion CaffH²⁻ (**1**).⁶

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Detailed investigations have already been made of the equilibria between caffeic acid and hydrogen, copper(II), zinc(II) and iron(II) ions⁶ and we are presently extending these solution equilibria studies to various other metal ions that occur either in nutrient and/or soil solutions. Once formation constants are obtained they can be added to the data being collected for computer-based speciation models of soil and plant nutrient solutions^{7,8} and thus contribute to an understanding of the role of complexation on the uptake of metals by plants.

EXPERIMENTAL

Chemicals

Caffeic acid (Aldrich) was purified by double recrystallization from water (found: C, 59.9; H, 4.4%; calc. for $C_9H_8O_4$: C, 60.0; H, 4.5%). All of the following solutions were prepared using carbonate-free, boiled out, glass-distilled water, and sodium chloride (BDH, Aristar grade) was added so as to produce solutions with a total chloride concentration of $0.100 \text{ mol dm}^{-3}$. The 0.1 mol dm^{-3} hydrochloric acid solution was prepared from Merck Titrisol ampoules and standardized against borax (Merck, G.R.) which had been recrystallized and stored as described by Vogel.⁹ The 0.1 mol dm^{-3} sodium hydroxide solutions were freshly prepared at frequent intervals by dilution of Merck Titrisol ampoules under nitrogen. These solutions were standardized against potassium hydrogen phthalate (Merck, G.R.). Manganese(II) chloride solution was made up from tetrahydrated manganese chloride salt (Merck, G.R.). Cobalt(II) chloride and nickel(II) chloride solutions were prepared from the hexahydrated cobalt(II) chloride salt and nickel(II) chloride salt, respectively (Merck, *pro analysi*). Cadmium(II) chloride solution was made up by dissolving cadmium oxide (Merck, extra pure) in concentrated hydrochloric acid (Merck, Suprapure). A standard zinc(II) chloride solution was prepared by dissolving accurately weighed amounts of granulated zinc metal (Merck, G.R.) in concentrated hydrochloric acid; the dissolution process was facilitated by the addition of a piece of platinum foil to the solution. The manganese(II), nickel(II) and cobalt(II) chloride solutions were standardized against $\text{Na}_2\text{H}_2\text{EDTA}^*$ (Merck, G.R.) according to the procedures described by Schwarzenbach.¹⁰ The cadmium(II) solution was standardized against $\text{Na}_2\text{H}_2\text{EDTA}$ following the procedure using indicator buffer tablets.¹¹ The acid content of the cadmium(II) solutions was determined by titration with sodium hydroxide. The $\text{Na}_2\text{H}_2\text{EDTA}$ solution was standardized against the aforementioned zinc(II) solution.¹¹

* EDTA = ethylenediaminetetraacetate

Potentiometric Measurements

The determination of the protonation constants for caffeic acid has already been described⁶ and the values obtained were used in this study. Formation constants for the ligand-metal complexes were determined by potentiometric titrations carried out in a Metrohm EA876-50 double-walled titration vessel. The vessel was thermostatted by circulating water at $25 \pm 0.1^\circ\text{C}$. Two Metrohm EA109 glass electrodes were used alternately with a Metrohm EA404 calomel reference electrode containing a saturated sodium chloride solution (BDH, Aristar grade) as electrolyte. The titrations were carried out under nitrogen, purified as previously described.¹² Owing to the greater ease of dissolving caffeic acid in alkaline as compared with acid solutions, the following experimental sequence was followed for the complexation titrations. An accurately weighed quantity of caffeic acid was placed in the titration vessel. An accurately measured volume of 0.1 M NaCl solution was added together with the sodium hydroxide/chloride solution from either a Radiometer ABU80 Autoburette or a Metrohm Dosimat E635-20 piston burette controlled by a Bondwell computer. The caffeic acid in the sodium hydroxide/chloride solution was first titrated with hydrochloric acid solution delivered from the Radiometer ABU80 Autoburette controlled by a Bondwell computer. The computer also recorded the volume delivered and the e.m.f. of the cell as measured by a Radiometer PHM64 pH meter. The protonation data obtained were used to calibrate the electrodes *in situ*, specifically for each individual titration. Immediately following the acid titration, accurately measured quantities of metal chloride solutions were added from a Metrohm E485 manual piston burette. The complexation titrations were then carried out by titrating these solutions back to the "basic" pH region with sodium hydroxide/chloride solution.

Computations

The electrode calibration parameters were determined specifically for each individual titration *in situ* by applying the protonation data of the relevant titration to the OBJE task of ESTA.¹³ The complexation data were processed initially by the ZBAR and QBAR tasks of ESTA in order to obtain experimental formation curves ($Z\text{bar}_{\text{obs}}$ versus $-\log[\text{free ligand}]$) and experimental deprotonation curves ($Q\text{bar}_{\text{obs}}$ versus $-\log[\text{free hydrogen ion}]$), respectively. Subsequently the OBJT task of ESTA was applied to obtain "best"-fitting chemical models and refined formation constants (β_{pqr}).^{*} To facilitate chemical model selection and hypothesis testing, the calculated formation constants were used to generate theoretical formation curves ($Z\text{bar}_{\text{calc}}$ versus $-\log[\text{free ligand}]$) and theoretical deprotonation curves ($Q\text{bar}_{\text{calc}}$ versus $-\log[\text{free hydrogen ion}]$) by the ZBAR and QBAR tasks of ESTA, respectively. It was necessary to carry out extensive computing before deciding on the "best" chemical model. The Hamilton test¹⁴ and Occam's razor¹⁵ were both used as aids for model selection and in addition we found it particularly useful to redefine the ligand as the triply charged anion, Caff^{3-} and to regenerate the calculated formation curves. Although the first protonation constant of the trianion is not known, a logarithmic

* β_{pqr} refer to the general complex $M_pL_qH_r$, where M = metal ion, L = ligand and H = proton. When $r = -1$, this refers to proton removal from the complex or to hydroxyl ion addition. Note that this convention corresponds to IUPAC recommendation I-10.3 in "Nomenclature of Inorganic Chemistry" (1990) but differs from the convention used in reference 6.

value of 13 seems reasonable by comparison with values obtained for catechol (1,2-dihydroxy benzene).^{16,17} In addition, the actual value used only affects the x axis position of the curve and not the profile of the curve. These formation function curves therefore proved to be useful in aiding model selection as they were more sensitive to the proposed model than calculated formation curves obtained using the dianionic caffeate as the ligand. The goodness of fit between the experimental and theoretical curves provided a measure of the validity and accuracy of the proposed chemical model.

Once the model had been selected, the formation constants were refined to give more precise values by using the OBJE task of ESTA with the weight at each titration point based on a standard deviation of the titre of 0.005 cm^3 and of the e.m.f. of 0.1 mV. Finally, the formation constants were applied to the SPEC task of ESTA to obtain the species distribution profiles of the complex species as a function of pH.

RESULTS AND DISCUSSION

The complexation of caffeic acid with manganese(II), cobalt(II), nickel(II) and cadmium(II) metal ions was investigated by carrying out a series of replicated titrations with total initial ligand concentrations ranging from $2.7\text{--}11.3 \text{ mmol dm}^{-3}$ and total initial metal concentrations covering the range $1.3\text{--}3.7 \text{ mmol dm}^{-3}$. Within these ranges, ligand : metal ratios were varied from 1:1–5:1, in order to facilitate the search for not only mononuclear binary complexes but also protonated, hydroxo- and oligonuclear species. It seems reasonable to consider oligonuclear complexes because of the existence of the two potential coordinating sites on the ligand. Titrations were carried out in duplicate, that is with identical starting concentrations of ligand and metal ions and, indeed, it was found that these titrations gave superimposable formation curves indicating good experimental reproducibility. However, the formation curves obtained for all four metal ions with caffeic acid using different ligand : metal ratios, fell on sets of non-overlapping curves as illustrated in Figure 1 for the case of the nickel(II)–caffeate system. The non-overlapping curves shown in Figure 1 indicate the presence not only of mononuclear binary complexes, but also of other types of metal complex such as protonated, hydroxo and/or oligonuclear species. Indeed, the “fanning back” pattern is typical of systems in which hydroxo–metal complexes are significant.

It was necessary to take these factors into consideration when applying ESTA to the potentiometric data. Numerous combinations of the stoichiometric coefficients p, q and r for the complex $M_pL_qH_r$ were investigated in order to obtain the best chemical model for each metal–caffeate system over the entire set of potentiometric data. The protonation constants of caffeic acid obtained in a previous study⁶ and the formation constants for the hydrolysis products produced by the reaction of the metal ions with water¹⁸ were included in the chemical modelling. After subjecting the titration data obtained for each metal–caffeate system to the computational procedures of ESTA as outlined above, the most consistent set of complexes was found for each system. These, together with their respective formation constants, standard deviations, Hamilton R-factor and the pH range for complex formation are given in Table I. No caffeate–metal ion (metal ion = Mn(II), Co(II), Ni(II) and Cd(II)) formation constants have previously been reported in the literature, so, where possible, formation constants for the catecholate–metal ion, the 3,4-dihydroxy hydrocinnamate (3-(3,4-dihydroxy phenyl)propanoate)–metal ion, the protocate-

chuate (3,4-dihydroxy benzoate)–metal ion and the homoprotocatechuate ((3,4-dihydroxy phenyl)ethanoate)–metal ion systems have been taken from the literature and are given in Table I for the purpose of comparison.

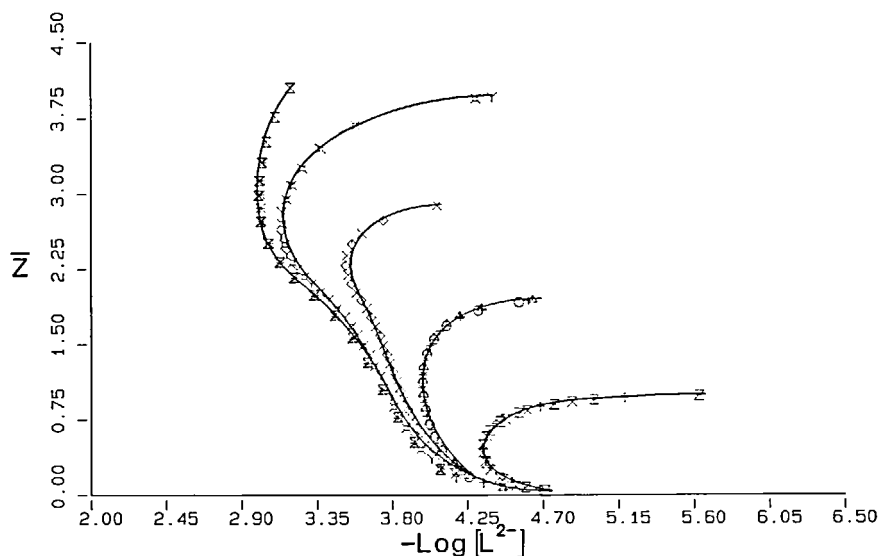


FIGURE 1 Formation curves obtained from the caffeate–nickel(II) formation constants in Table I, plotted together with experimental Zbar points. Initial concentrations (10^{-3} mol dm $^{-3}$) of caffeate and nickel(II) respectively are: 3.32 and 3.32 (†, X, Z), 5.33 and 2.67 (O, Δ, +), 6.00 and 2.00 (X, ◇), 7.00 and 1.75 (Y, †) and 6.68 and 1.34 (*, X̄) (165 points have been omitted for the sake of clarity).

The refined formation constants given in Table I were used to generate theoretical formation and deprotonation curves for each of the systems concerned. The excellent match with the corresponding experimental formation and deprotonation curves confirmed the validity of the chemical model proposed in Table I for each of the systems. This is clearly illustrated for example by the formation curves for the nickel(II)–caffeate system which are presented in Figure 1. A similar degree of matching was obtained for the other metal ion–caffeate systems in Table I. Figure 2 shows the species distribution for the cadmium(II)–caffeate system as a function of pH. This Figure is typical of the species distribution plots for the manganese(II)–, cobalt(II)– and nickel(II)–caffeate systems, and clearly shows that the major species is the 1:1 mononuclear complex. We propose that in this complex, the metal ion is bound at the more strongly coordinating catecholate site on the caffeate ligand and not at the weaker carboxylate site. In so doing, the single protons attached strongly to monoprotonated catecholate sites become released; the carboxylate groups remain deprotonated. The 1:1 formation constants obtained for manganese(II)–, cobalt(II)–, nickel(II)– and cadmium(II)–caffeate agree favourably with the values reported in the literature for the complexation of these metal ions by catechol, thus supporting the proposal of chelation of the metal ions by the fully deprotonated catecholate moiety of caffeate. Further, from the species distribution plots it can be seen that the 1:1 complexes occur in the pH range 6–10.5, and taking this into consideration it is unlikely that metal ion complexation occurs at the carboxylate group of caffeate.

TABLE I
Logarithms of the stability constants (β_{par}) for the complexes of caffeic acid at 25°C and I = 0.1 mol dm⁻³ Na[Cl].^a

Metal	p	q	r	log β_{par}	d	n _o	n _t	pH range	R _f	Literature data [ligand, T(°C), I(mol dm ⁻³), log β]	Ref
Mn ²⁺	1	1	-1	-4.88	0.004	248	10	7.0-10.5	0.0040	Heat ^{-b} , 25, 1.0 KNO ₃ , log $\beta_{1,1}$ = -5.58	16
	1	1	-2	-15.55	0.008					Heat ⁻ , 25, 0.1 KCl, log $\beta_{1,1}$ = -5.28	19
Ni ²⁺	1	1	-1	-3.62	0.004	379	12	6.6-9.5	0.0077	Heat ⁻ , 25, 1.0 KNO ₃ , log $\beta_{1,1}$ = -4.28	16
	1	1	-2	-13.45	0.016					Hhyd ²⁻ , ^b 30, 0.1 NaClO ₄ , log $\beta_{1,1}$ = -4.15	17
	2	1	-1	-1.56	0.012					Heat ⁻ , 30, 0.1 NaClO ₄ , log $\beta_{1,1}$ = -4.24 ^c	17
										Heat ⁻ , 25, 0.1 KCl, log $\beta_{1,1}$ = -4.06	19
Co ²⁺	1	1	-1	-4.12	0.004	214	9	6.7-9.0	0.0094	Heat ⁻ , 25, 1.0 KNO ₃ , log $\beta_{1,1}$ = -4.73	16
	2	1	-1	-1.75	0.015					Heat ⁻ , 25, 0.1 KCl, log $\beta_{1,1}$ = -4.40	19
Cd ²⁺	1	1	-1	-4.91	0.001	444	10	6.0-9.1	0.0090	Hhyd ²⁻ , 30, 0.1 NaClO ₄ , log $\beta_{1,1}$ = -4.46	17
	1	2	-2	-12.29	0.014					Heat ⁻ , 30, 0.1 NaClO ₄ , log $\beta_{1,1}$ = -4.90 ^c	17
	1	3	-3	-19.50	0.046					Hprot ²⁻ , ^b 30, 0.1 NaClO ₄ , log $\beta_{1,1}$ = -4.63	17
										Hprot ²⁻ , 30, 0.1 NaClO ₄ , log $\beta_{1,2}$ = -12.48	17
										Hhom ²⁻ , ^b 30, 0.1 NaClO ₄ , log $\beta_{1,1}$ = -4.65	17
										Hhom ²⁻ , 30, 0.1 NaClO ₄ , log $\beta_{1,2}$ = -12.37	17

^a d = standard deviation in log β ; n_o = number of observations; n_t = number of titrations; R_f = Hamilton R factor. ^b Formation constants for the alternatively defined ligands Heat⁻, Hhyd²⁻, Hprot²⁻ and Hhom²⁻ calculated from values reported for catecholate²⁻ (cat²⁻), 3,4-dihydroxy hydrocinnamate³⁻ (hyd³⁻), protocatechuate³⁻ (prot³⁻) and homoprotocatechuate³⁻ (hom³⁻), respectively, in the references quoted. ^c This value is approximate—see reference 17.

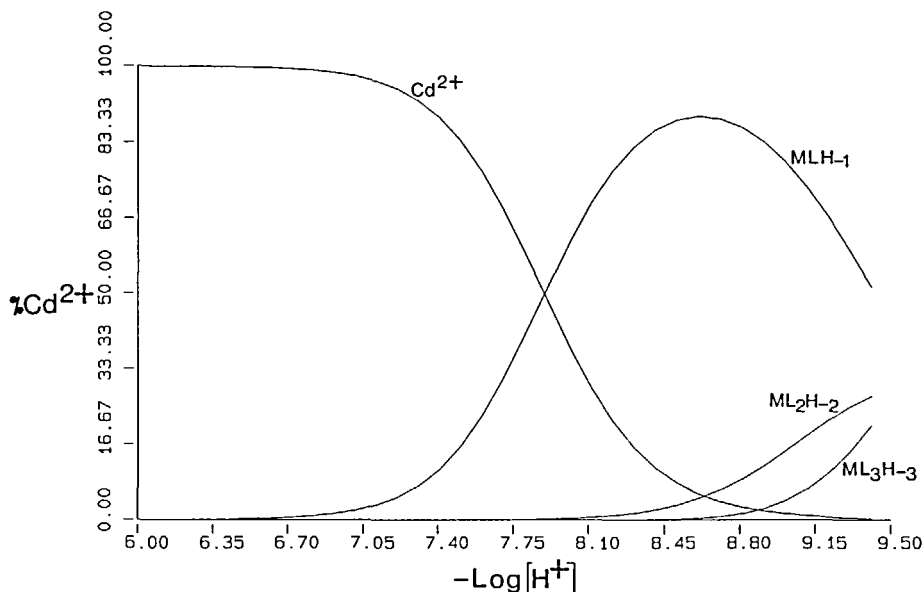


FIGURE 2 Distribution of species in the cadmium(II)-caffeate system. Total concentrations (10^{-3} mol dm $^{-3}$) are: cadmium(II) 1.779, and caffeic acid 8.893.

The manganese(II)-caffeate 11-2 complex is a minor species occurring towards the higher pH values. The most likely structure for this complex involves metal ion complexation at the fully deprotonated catecholate site and subsequent removal of a proton from a coordination water molecule at the metal ion centre. Although this hydroxy species has not been reported for the manganese(II)-catecholate system,¹⁶ it was also found in the present study of the nickel(II)-caffeate system. Again it appears as a relatively minor species, becoming more predominant in the higher pH region. Indeed, albeit a minor species, this 11-2 complex was found to be essential for the superimposability of the theoretical formation function curves obtained using the trianion definition of the ligand, with the corresponding observed formation function curves, particularly towards the higher pH regions for the manganese(II)- and nickel(II)-caffeate systems.

Both a 110 and 12-2 complex have been reported in the literature for the complexation of catechol and manganese.¹⁶ Accordingly, a series of five models incorporating the complexes 110 and 12-2 were tried in the computer analysis of our manganese(II)-caffeate data. The results are presented in Table II. Although it was possible to include a 110 and a 12-2 manganese(II)-caffeate complex (models 2, 3, 4 and 5), these complexes were excluded from the finally chosen model for the following reason: species distribution plots showed that the 110 and 12-2 complexes were minor species present to less than 5%. This probably accounts for the high standard deviation obtained for these species. Furthermore, the theoretical formation function curves obtained for caffeate defined as a trianionic ligand (see earlier discussion) level off at $Z_{\text{bar}} = 1$ for models 3 and 4. Figure 3 shows the good overlap of the theoretical formation function curve for model 1 obtained using the trianionic definition of the ligand, with the corresponding observed formation function curve.

TABLE II

Results of different computer models obtained from ESTA for the manganese(II)-caffeate system (standard deviations given in parentheses).

Model	1	2	3	4	5
$\log\beta_{110}$		1.93(.069)	1.77(.069)		
$\log\beta_{11-1}$	-4.90(.007)	-4.88(.005)	-4.89(.005)	-4.85(.008)	-4.87(.005)
$\log\beta_{11-2}$	-15.57(.009)	-15.57(.009)			-15.54(.031)
$\log\beta_{12-2}$			-13.06(.013)	-12.90(.016)	-14.48(.694)
R_f^a	0.00397	0.00386	0.00336	0.00786	0.00492

^a R_f = Hamilton R factor.

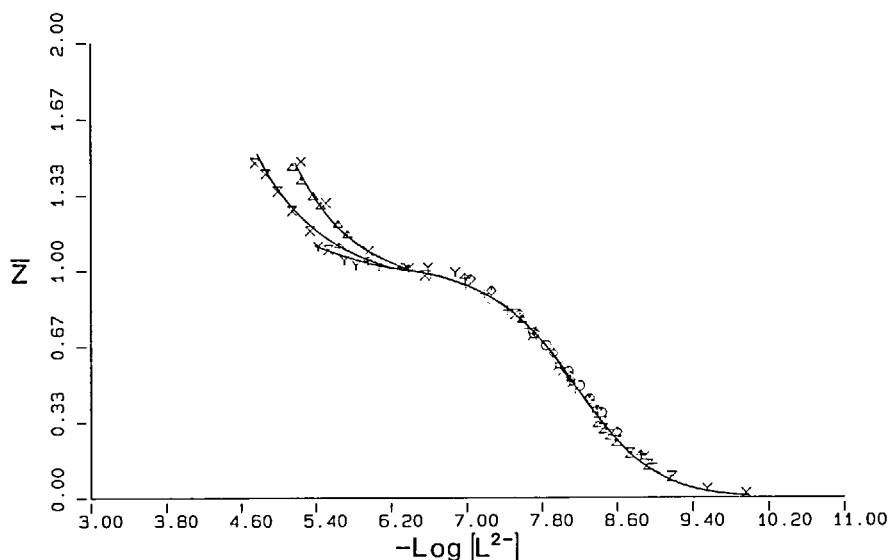


FIGURE 3 Formation function curves obtained for the manganese(II)-caffeate system with the ligand defined as the triply charged anion, together with the experimental Z_{bar} points (173 points have been omitted for the sake of clarity).

This excellent superimposability and the chemical plausibility of the species in model I leads us to propose that the 11-1 and 11-2 manganese(II)-caffeate species fit the observed chemical data "best" over the pH range studied.

Dinuclear mono(caffeate) complexes (21-1) appear as relatively minor species for nickel(II) between pH 6.3-9.5 and for cobalt(II) between 6.4-10.0. Similar complexation has been previously reported for the copper(II)-caffeate system,⁶ and the metal is obviously coordinated at each end of the ligand molecule in these 21-1 complexes.

Mononuclear bis(caffeate) complexes were searched for but not found for the manganese(II)-, cobalt(II)- and nickel(II)-caffeate systems. Although the corresponding mononuclear bis(catechol) complexes have been reported in the literature for manganese(II) and cobalt(II) metal ions,^{16,19,20} there are conflicting results for nickel(II)—a 12-2 nickel(II)-catechol complex has been reported by Athavale *et*

*al.*¹⁷ and by Jameson *et al.*,¹⁹ but not by Martell *et al.*¹⁶ who report precipitate formation. However both mononuclear bis(caffeate) and mononuclear tris(caffeate) complexes were found for cadmium(II)-caffeate. We believe that metal chelation occurs at the catecholate site resulting in four coordinated and six coordinated metal-ligand complexes. In the pH range under investigation, the tris complex occurs as only a very minor species towards the higher pH region. Mononuclear bis complexes have been reported for the complexation of cadmium with the protocatechuic and homoprotocatechuic acid¹⁷ and our formation constant for the cadmium(II)-caffeate 12-2 complex compares favourably with these reported literature values. Mononuclear bis and tris complexes have also been previously reported for the complexation of zinc with caffeic acid.⁶

Reference to Table I of this paper and Table 2 of reference 6 shows the formation constants of the 11-1 caffeate complexes of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) follow the Irving-Williams order.²¹ The caffeate-iron(II) 11-1 complex is anomalous in this respect, however.

It is interesting to compare the results in Table I for cadmium(II) with those reported in reference 6 for the zinc(II)-caffeate system. The 11-1 complex of zinc(II) is more stable than the corresponding mono complex of cadmium(II). This order of stability is the same as reported for catecholate complexes of zinc(II) and cadmium(II) and correlates with the affinity these metal ions have for hydroxide ions.²² The order of stability may be attributed to differences in hardness between the two metal ions, as documented by Hancock and Martell.²² Hancock's hardness factor, H_A , has a value of 4.26 for zinc(II) *c.f.* 3.31 for cadmium(II) (H_A = a measure of the relative ionicity *versus* covalence of the coordination bond). Thus zinc(II), being harder than cadmium(II), forms a more stable complex with caffeate, which may be expected to behave as a somewhat hard ligand. As indicated above, it appears that in the 11-1 complexes the metal coordinates to the catecholate moiety of caffeate. The latter is likely to resemble catecholate. Although catecholate has not been fully characterized in terms of hardness,²² as indicated above the stability of catecholate complexes correlates with the affinity of the metal ions involved for the hydroxide ion²² (which has a Hancock H_B value of 0.0 typical of a hard ligand). Thus, it may be assumed that catecholate tends to show hard character.

The values of Hancock's D_A factor are 4.0 for zinc(II) and 0.6 for cadmium(II).²² These suggest markedly less steric hindrance to the disruption of the hydration shell by an incoming ligand to the larger cadmium(II) ion than is the case for the smaller zinc(II) ion. This would tend to strengthen the cadmium(II) complexes *c.f.* those formed by zinc(II). It would thus appear that the hardness factor, H_A , dominates steric factors in determining the relative stabilities of cadmium(II) and zinc(II) complexes of caffeate.

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