J. Chem. Eng. Data **2002,** *47,* 289−296

Stability Constants for Aluminum(III) Complexes with the 1,2-Dihydroxyaryl Ligands Caffeic Acid, Chlorogenic Acid, DHB, and DASA in Aqueous Solution

Martin L. Adams, Brendon O'Sullivan, Alison J. Downard, and Kipton J. Powell*

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Equilibrium constants are reported for the aluminum(III) complexes with four ligands that contain the 1,2-dihydroxyaryl group: *trans*-3-(3′,4′-dihydroxyphenyl)propenoic acid (caffeic acid), 3-(3′,4′-dihydroxycinnamoyl)-1,3,4,5-tetrahydroxycyclohexanecarboxylic acid (chlorogenic acid), 3,4-dihydroxybenzylamine (DHB), and 1,2-dihydroxyanthraquinone-3-sulfonic acid (DASA). The protonation and complexation reactions were studied by potentiometric and spectrophotometric titrations in aqueous solution at 25 °C ($I = 0.10$ M KCl). The complexation reactions were studied for ligand/metal ratios in the range from 1.3 to 5.9. For caffeic and chlorogenic acids (H_3L), the experimental data were consistent with the formation of six mononuclear Al−ligand species, each involving catecholate coordination: $AlHL^+$, AlL, $Al(OH)L^-$, AlL_2^{3-}, $Al(OH)L_2^{4-}$, and AlL_3^{6-}. For DHB (H_2L), the data were consistent with the formation of six monomeric and one dimeric Al species: $AlHL^{2+}$, $Al(HL)_2^+$, $Al(HL)_3^0$, $Al(HL)_2L^-$, $Al(HL)L_2^{2-}$, AlL_3^{3-}, and $(OH)_2Al_2(HL)_2^{2+}$, in which HL has a protonated amino group. On the basis of the DASA (H_2L^-) titration data, three monomeric and one dimeric Al−ligand species were proposed: AlL^0, AlL_2^{3-}, $Al(OH)L_2^{4-}$, and $Al_2(OH)_2L_4^{8-}$. The relative stability of the 1:1 complexes, AlL, was DASA > chlorogenic acid > caffeic acid > DHB. This indicates the progressive electron-withdrawing effects of the ring substituents $-SO_3^-$ < $-CH{=}CH{\cdot}CO{\cdot}O{\cdot}(C_6H_{10}O_3){\cdot}COOH$ < $-CH{=}CH{\cdot}COOH$ < $-NH_3^+$.

Introduction

To ascertain the effect of ring substituents on the stability of aluminum(III) complexes with 1,2-dihydroxyaryl ligands, the solution equilibria have been studied for four contrasting ligands. Caffeic acid, *trans*-3-(3′,4′-dihydroxyphenyl)propenoic acid, and its precursor chlorogenic acid, 3-(3′,4′-dihydroxycinnamoyl)-1,3,4,5-tetrahydroxycyclohexane carboxylic acid (Figure 1), are both important in plant metabolism and nutrition.[1−4] They have been identified as exudates from living leaves and roots of the invasive agricultural weeds *Hieracium pilosella* and *H. praealtum*.[5] Their ability to exude polyphenolic compounds can explain their competitive advantage over other pasture species through (i) phenolic complexation of the toxic free Al^{3+} fraction in acidic soil solution or (ii) the influence of phenols on soil nitrogen availability.[6,7] No reliable thermodynamic data are available for the aluminum complexes of these ligands, although their stability constants with various divalent metal ions have been reported.[3,8−11]

In contrast, DASA (1,2-dihydroxyanthraquinone-3-sulfonic acid) is an important ligand for the indirect electroanalysis of Al. It has been used for Al^{3+} analysis by adsorptive cathodic stripping voltammetry[12,13] and for the flow injection amperometric determination of total and reactive Al^{3+} species.[14,15] Coordination to DASA can occur at one of two sites, with binding by "hard" cations such as Al^{3+} occurring at the 1,2-dihydroxyaryl position and by other cations at the 1,9-keto-α-hydroxy position.[16−18] The equilibrium reactions of Al^{3+} with DHB analogues, namely, the neurotransmitter catecholamines (nor)epinephrine, L-DOPA, serotonin, and dopamine, were investigated by Kiss and co-workers.[19] By analogy with these results, coordination of Al^{3+} to DHB is expected to occur at the hard oxygen donor 1,2-diydroxyaryl moiety, in preference to the primary amine.

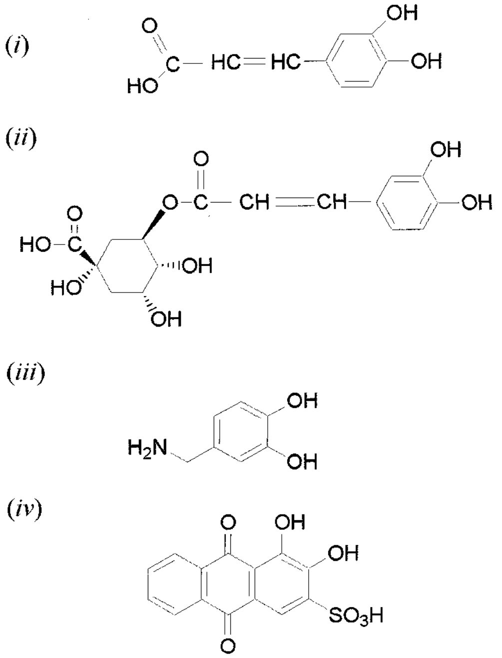

Figure 1. Structures of ligands used in this work: (i) caffeic acid, (ii) chlorogenic acid, (iii) 3,4-dihydroxybenzylamine (DHB), and (iv) 1,2-dihydroxyanthraquinone-3-sulfonic acid (DASA).

This paper reports a study of the solution equilibria between Al^{3+} and the four 1,2-dihydroxyaryl ligands, based on potentiometric and spectrophotometric titrations in aqueous solution ($I = 0.10$ M KCl, 25.0 °C). Concentration-

---

* Corresponding author. E-mail: k.powell@chem.canterbury.ac.nz.

10.1021/je010279e CCC: $22.00

Table 1. Ligand Microanalysis Results

		%C		%H		%N		%S	
ligand	formula	obs	calc	obs	calc	obs	calc	obs	calc
caffeic acid	$C_9H_8O_4$	60.14	60.00	4.55	4.48				
chlorogenic acid	$C_{16}H_{18}O_9$	53.41	54.24	5.30	5.12				
DHB	$C_7H_{10}O_2NBr$	37.98	38.2	4.71	4.6	6.24	6.4		
DASA	$C_{14}H_7O_7NaS$	42.62	49.1	2.31	2.1			8.22	9.4

dependent cumulative formation constants are reported for the reactions

$$pH^+ + qAl^{3+} + rH_nL^0 \rightleftharpoons H_pAl_q(H_nL)_r^{(p+3q)+} \qquad \beta_{pqr}$$

Experimental Section

Materials. Samples of caffeic acid [*trans*-3-(3′,4′-dihydroxyphenyl)propenoic acid], chlorogenic acid [3-(3′,4′-dihydroxycinnamoyl)-1,3,4,5-tetrahydroxycyclohexanecarboxylic acid; min 95%], and DASA (1,2-dihydroxyanthraquinone-3-sulfonic acid) were obtained from Sigma. DHB·HBr (3,4-dihydroxybenzylamine hydrobromide, 98%) was obtained from Aldrich. Ligands were dried under vacuum to constant mass before use and stored in the dark at room temperature. Purity was checked by carbon-13 NMR spectroscopy, titrimetric analyses, and elemental microanalyses, the results of which (except for DASA, Table 1) were in good agreement with the theoretical results. Subsequent analysis of the supplied DASA by ICP−OES and $AgNO_3$ potentiometric titration indicated the presence of sodium and potassium chlorides and one water of crystallization. These impurities were considered inert.

Standard alkali solutions were prepared by mass from KOH pellets (BDH AnalaR) using CO_2-free water and were stored in sealed polypropylene containers under oxygen-free nitrogen. Solutions were standardized before use by acid−base titration against weighed amounts of tris-(hydroxymethyl)aminomethane hydrochloride (trizma hydrochloride) (SigmaUltra, >99%, Sigma). Acidified Al^{3+} stock solutions were prepared from aluminum chloride $AlCl_3 \cdot 6H_2O$ (Puratronic, 99.9995%, Alfa) and standardized gravimetrically as the oxinate.[20] The excess acid in the Al solutions was determined by titration against standard alkali using the method of Gran[21] for end-point determination. The supporting electrolyte of potassium chloride (BDH AnalaR) was prepared by adding appropriate amounts of oven-dried pure salt directly to all working and titration solutions to give an ionic strength of 0.10 M. Acid-washed glassware and analytical-grade water (18 MΩ cm^{-1}) were used throughout.

Potentiometric Titrations. Potentiometric measurements were performed at 25.0 ± 0.1 °C in a water-jacketed thermostated glass titration cell that accommodated a glass bulb electrode (Russell SWR757), a reference electrode (laboratory-built double-sleeved calomel electrode), a gas line for O_2-free nitrogen, and an autoburet tip. Nitrogen gas, preequilibrated with 0.10 M KCl at 25 °C and scrubbed of CO_2 (NaOH) and O_2 (V^{2+}, H^+, Zn/Hg)[22], was passed under titrand solution surfaces for ca. 120 min before titrations and then continuously maintained over the titrand surface for the duration of the titration.

The addition of standard alkali titrant (ca. 0.25 M) to ligand solutions was done using an ABU80 autoburet (Radiometer, Copenhagen). The solution pH was determined using a PHM64 pH meter (Radiometer). Both the autoburet and the pH meter were computer-controlled, which allowed for the controlled addition of titrant and the controlled acquisition of data after predefined solution equilibration conditions were met. Electrodes were calibrated as H^+ concentration probes before and after each analytical titration by addition of standard alkali to strong acid in 0.10 M KCl. In this paper, pH refers to $-\log_{10}[H^+]$.

Spectrophotometric Titrations. Spectrophotometric titrations were used to study the deprotonation reaction of the least acidic phenolic groups ($pK_a > 10.6$) for DASA and caffeic and chlorogenic acids. These titrations were effected by incremental additions of ca. 3 M KOH titrant solution to ca. 50 μM solutions of ligands in 0.10 M KCl. An Alitea XV peristaltic pump (Alitea, Sweden) was used to circulate solution from the thermostated titration cell through Teflon tubing to a 70-μL flow cell (Starna). Spectrophotometric measurements were made with a HP8452a diode-array UV−vis spectrophotometer (Hewlett-Packard, Palo Alto, CA) using the Hewlett-Packard software supplied with the instrument. To minimize oxidation of the deprotonated ligands, rapid titrations were performed over a pH range of ca. 10.6−13.4.

The method of Ågren[23] was used to determine the K_a value ($pK_a = \log \beta_{-201}/\beta_{-301}$) for the least acidic group in DASA from titrations in the pH range 9.5−11.6. For caffeic and chlorogenic acids, for which data were required at pH 12−13, the alternative approach of Kennedy and Powell[24] was used because Ågren's method can not be applied to systems in which the ionic strength of the titrand solution (and hence the value of pK_a) is not constant. For these acids, pK_a values were calculated for 16 data points using the measured absorbance, the previously measured molar absorptivities (ϵ_{HL} and ϵ_L), and the concentration of H^+ (which was calculated from the concentration of OH^- after each titrant addition and from pK_w at the applicable ionic strength[25]). The pK_a values gave a linear plot against $I^{1/2}/(1.0 + I^{1/2})$; the least-squares line was extrapolated to give a pK_a value valid at $I = 0.10$ M.

Because of the low solubility of the 1:1 Al−DASA complex and the high free-proton concentration at the pH at which this species forms (pH 2.6−3.5), determination of the β value by potentiometry was considered unreliable. Instead, we adapted Ågren's method to make it applicable to reactions between a metal (Al) and a protonated ligand H_nL to give the complex $AlH_{n-m}L$. For this 1:1 complex, the following equation can be derived from the mass balance, reaction equilibrium, and Beer−Lambert equations

$$\frac{T_L}{A} = \frac{1}{K\epsilon_{Al(H_{n-m}L)}}\left([H]^m \frac{A - \epsilon_{H_nL}T_L}{A[Al]}\right) + \frac{1}{\epsilon_{Al(H_{n-m}L)}} \qquad (1)$$

where T_L is the total ligand concentration, A is the absorbance, K is the value of the equilibrium constant, ϵ_i is the molar absorptivity of species i, and m is the number of protons displaced from H_nL on coordination.

Trial values of m were tested to find the value that gives a linear plot from eq 1. The molar absorptivity for the complex was taken from the inverse intercept, which, together with the slope, gives the value of the equilibrium constant. The equation, however, assumes the presence of only two forms for the ligand, free H_nL and complexed $AlH_{n-m}L$. Thus, there must be no significant side equilibria

Table 2. Aluminum(III) Hydrolysis Constants (β_{pq}) Used in This Work[a]

species	*p*, *q*	log β_{pq}[b]
$Al(OH)^{2+}$	−1, 1	−5.33
$Al(OH)_2{}^{+}$	−2, 1	−10.91
$Al_3(OH)_4{}^{5+}$	−4, 3	−13.13
$Al_{13}(OH)_{32}{}^{7+}$	−32, 13	−107.41
$Al(OH)_4{}^{-}$	−4, 1	−23.30
K_w	−1, 0	−13.79

[a] $I = 0.10$ M, 25 °C. [b] β_{pq} values are defined according to the reaction $p\mathrm{H}^+ + q\mathrm{Al}^{3+} \rightleftharpoons \mathrm{Al}_q(\mathrm{OH})_p{}^{(p+3q)+}$.

Table 3. Refined Cumulative Equilibrium Constants, β_{pqr}, and Derived Stepwise Constants, p*K*, for the Caffeic Acid and Chlorogenic Acid Systems, 25 °C, 0.10 M KCl

	caffeic acid (H_3L)		chlorogenic acid (H_3L)		
pqr	log β_{pqr}[a]	σ[b]	log β_{pqr}[a]	σ[b]	proposed product
−101	−4.382	0.001	−3.359	0.004	H_2L^-
−201	−13.055	0.001	−11.610	0.002	HL^{2-}
−301	−25.7[c]	0.2	−23.9[c]	0.3	L^{3-}
−211	−4.88	0.01	−3.91	0.02	$AlHL^+$
−311	−9.45	0.01	−8.17	0.03	AlL^0
−411	−15.53	0.04	−13.79	0.03	$Al(OH)L^-$
−612	−22.24	0.02	−19.28	0.05	$AlL_2{}^{3-}$
−712	−30.73	0.06	−27.65	0.15	$Al(OH)L_2{}^{4-}$
−913	−39.23	0.04	−34.01	0.08	$AlL_3{}^{6-}$

derived constants

	this work[d]	lit	this work[d]	lit	
p$K_{(COOH)}$	4.382	4.37[e] 4.41[f] 4.45[g]	3.359	3.35[e] 3.35[h] 3.37[g]	H_2L^-
p$K_{(OH1)}$	8.672	8.55[e] 8.72[f] 8.66[g]	8.251	8.21[e] 8.30[h] 8.27[g]	HL^{2-}
p$K_{(OH2)}$	12.6	12.5[e] 11.8[g]	12.3	12.5[e] 11.5[g] 12.06[h]	L^{3-}

[a] β_{pqr} values are defined according to the equation $p\mathrm{H}^+ + q\mathrm{Al}^{3+} + r\mathrm{H}_3\mathrm{L} \rightleftharpoons \mathrm{H}_p\mathrm{Al}_q(\mathrm{H}_3\mathrm{L})_r{}^{(p+3q)+}$. [b] σ is the standard deviation for each constant. [c] Spectrophotometric determination. [d] This work, 0.10 M KCl, 25 °C. [e] Kiss et al.,[9] 0.20 M KCl, 25 °C. [f] Linder and Voyé,[8] 0.10 M NaCl, 25 °C. [g] Lamy et al.,[3] 0.10 M $NaClO_4$, 25 °C. [h] Améziane et al.,[11] 1.0 M KNO_3, 20 °C.

involving differently protonated forms of the ligand, nor any significant hydrolysis of the metal ion. The term for the ordinate variable contains the concentration of free metal, $[Al^{3+}]$. This quantity can be accurately calculated only with prior knowledge of the equilibrium constant for the complex. However, if a large excess of metal over ligand is used, then the change in free metal ion concentration throughout the course of the reaction is negligible, and $[Al^{3+}]$ can be approximated by the total concentration of metal. For systems that meet these conditions, eq 1 can be used to calculate complex formation constants.

Two titrations were performed in the pH range 2.5−3.5 using [DASA] = 48 μM and $[Al^{3+}]$ = 1.33 and 2.26 mM to give 10 and 16 spectra, respectively. Plots were formed using data taken from 7 wavelengths for each spectrum over the ranges 320−326, 400−404, and 480−500 nm (where the wavelengths were chosen for maximum differences in absorbance for the free and complexed ligand). Calculations were performed in both directions, i.e., using ϵ_i values for free and complexed DASA, to yield two measurements of β_{-211} for each wavelength analyzed from each titration.

Numerical Analyses. The program SUPERQUAD[26] was used to determine refined values of the cumulative formation constants (β_{pqr}) from potentiometric data. Aluminum hydrolysis constants used in the calculations (Table 2) were derived from potentiometric data for 0.10 M KNO_3 at 25 °C.[27] The constant for the formation of $Al(OH)_4{}^-$ was calculated by the method of Millero and Schreiber[28] from the thermodynamic constants of Palmer and Wesolowski,[29] assuming $\gamma[Al(OH)_4{}^-] = \gamma(OH^-)$.

The program SOLGASWATER[30] was used to calculate distribution diagrams and Z_c curves from the refined stability constants (where Z_c represents the average number of protons bound *per* ligand). A comparison of the experimental and calculated values of Z_c allowed for an assessment of the fit of the proposed model. Experimental values of Z_c were calculated using the expression

$$Z_c = \frac{H - [H^+] + K_w[H^+]^{-1}}{L_T} \tag{2}$$

where H is the total acidity (M), $[H^+]$ is the free acidity (M), K_w is the water hydrolysis constant (M^2), and L_T is the total ligand concentration (M).

Results

Method Validation. A potentiometric study was performed on the $H^+/Cu^{2+}/L^-$−histidine system ($I = 0.10$ M KCl, 25 °C) to confirm the validity of the titration techniques and computational methods used in this work. The protonation and metal stability constants for this system (β_{pqr}: $p\mathrm{H}^+ + q\mathrm{Cu}^{2+} + r\mathrm{L}^- \rightleftharpoons \mathrm{H}_p\mathrm{Cu}_q\mathrm{L}_r$) have been critically reviewed by IUPAC.[31] Good agreement was obtained between the formation constants determined in this work and the IUPAC-recommended values (in parentheses ± σ): log β_{111} = 14.11 ± 0.01 (14.11 ± 0.02), log β_{011} = 10.14 ± 0.004 (10.16 ± 0.03), log β_{212} = 27.2 fixed (27.2 ± 0.1), log β_{112} = 23.86 ± 0.01 (23.81 ± 0.07), log β_{012} = 18.21 ± 0.02 (18.11 ± 0.09), log β_{-111} = 1.92 ± 0.04 (2.0 ± 0.2), log β_{-222} = 7.99 ± 0.02 (7.9 ± 0.1).

H^+−Al^{3+}−Caffeic Acid (H_3L) System. The values of β_{-101} and β_{-201} were determined from 9 potentiometric titrations (409 data points) using caffeic acid concentrations of 0.72−3.1 mM. The pK_a for the least acidic functional group was determined from replicate spectrophotometric titrations and used to calculate β_{-301} [pK_a = log($\beta_{-201}/\beta_{-301}$)]. Isosbestic points held at ca. 285 and 390 nm when titrations were performed under rigorously deoxygenated conditions. Absorbance data for the calculation of K_a were obtained at 344 nm. The relative concentrations of HL^{2-} and L^{3-} for each solution were calculated using ϵ_{HL} = 18861 (mol L^{-1} cm)$^{-1}$ and ϵ_L = 5285 (mol L^{-1} cm)$^{-1}$.

Complex formation with Al^{3+} was investigated by performing 9 potentiometric titrations (348 data points) with concentrations varied over the ranges 0.18−0.39 mM for Al^{3+} and 0.38−1.2 mM for caffeic acid. The stoichiometric metal-to-ligand ratio was varied over the range from 1:1.6 to 1:4.5. Titration data were analyzed numerically using SUPERQUAD[26] to give the refined stability constants reported in Table 3. To verify the validity of the calculated β_{pqr} values, a selection of experimental and calculated titration curves was plotted as the Z_c function for a range of metal-to-ligand ratios (Figure 2). The solid curves are calculated from the refined β_{pqr} values. Experimental Z_c values below 0.0, obtained for titrations performed at low metal/ligand ratios, confirm the formation of mixed hydroxo−metal−ligand species, e.g., $Al(OH)L^-$ and $Al(OH)L_2{}^{4-}$ (Table 3).

H^+−Al^{3+}−Chlorogenic Acid (H_3L) System. The values of β_{-101} and β_{-201} were determined from 8 potentio-

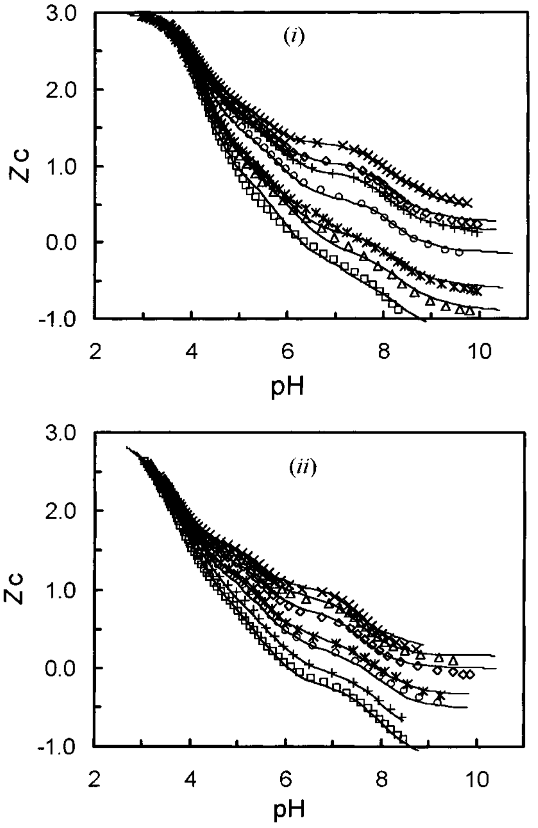

Figure 2. Z_c curves for the system H^+−Al^{3+}−H_3L when H_3L is (i) caffeic acid and (ii) chlorogenic acid. The symbols show experimentally derived values of Z_c. The solid lines were calculated using the refined constants given in Table 3. Metal/ligand ratios: ×, 1:4.0; ◇, 1:3.6; +, 1:3.1; ○, 1:2.4; ∗, 1:2.2; △, 1:1.8; □, 1:1.6.

metric titrations (396 data points) with the concentration of chlorogenic acid varied from 0.72 to 3.1 mM. The pK_a for the least acidic functional group was determined from replicate spectrophotometric titrations, as for caffeic acid. Three isosbestic points held at ca. 268, 298, and 400 nm. Absorbance data were obtained at 356 nm, where ϵ_{HL} and ϵ_L were 20 944 (mol L^{-1} $cm)^{-1}$ and 8911 (mol L^{-1} $cm)^{-1}$, respectively.

Complex formation with Al^{3+} was investigated by performing 9 potentiometric titrations (406 data points) with Al^{3+} concentrations in the range 0.20−0.42 mM and chlorogenic acid concentrations in the range 0.41−0.83 mM. Stoichiometric ratios of metal to ligand were varied from 1:1.5 to 1:5.5. The refined stability constants are reported in Table 3. The Z_c plots (Figure 2) indicate significant formation of hydroxo−metal−ligand species at low ligand/metal ratios.

H^+−Al^{3+}−DHB (H_3L^+) System. The values for β_{-n01} (Table 4) were determined from 6 potentiometric titrations (300 data points) with the concentration of DHB varied from 0.87 to 4.0 mM. Complex formation with Al^{3+} was investigated by performing 10 titrations (674 data points) with the DHB concentration varied from 1.46 to 3.65 mM and the Al^{3+} concentration varied from 0.56 to 1.17 mM. The Al^{3+}-to-DHB ratio was varied between 1:1.33 and 1:5.9. β_{pqr} values were derived from these data using SUPERQUAD[26] and are reported in Table 4. Selected experimental and calculated Z_c titration curves for the DHB system are shown in Figure 3.

Table 4. Refined Cumulative Equilibrium Constants for the DHB System, 25 °C, 0.10 M KCl

pqr	log $\beta_{pqr}{}^a$	σ^b	proposed product
−101	−8.577	0.002	H_2L^0
−201	−18.901	0.002	HL^-
−301	−32.0	estimated	L^{2-}
−211	−5.58	0.006	$AlHL^{2+}$
−412	−13.74	0.013	$Al(HL)_2{}^+$
−613	−25.51	0.023	$Al(HL)_3{}^0$
−713	−35.55	0.055	$AlL(HL)_2{}^-$
−813	−46.39	0.098	AlL_2HL^{2-}
−913	−56.79	0.072	$AlL_3{}^{3-}$
−622	−19.58	0.041	$Al_2(OH)_2(HL)_2{}^{2+}$

[a] β_{pqr} values are defined according to the equation $p\mathrm{H}^+ + q\mathrm{Al}^{3+} + r\mathrm{H}_3\mathrm{L}^+ \rightleftharpoons \mathrm{H}_p\mathrm{Al}_q(\mathrm{H}_3\mathrm{L})_r{}^{(p+3q+r)+}$. [b] σ is the standard deviation for each constant.

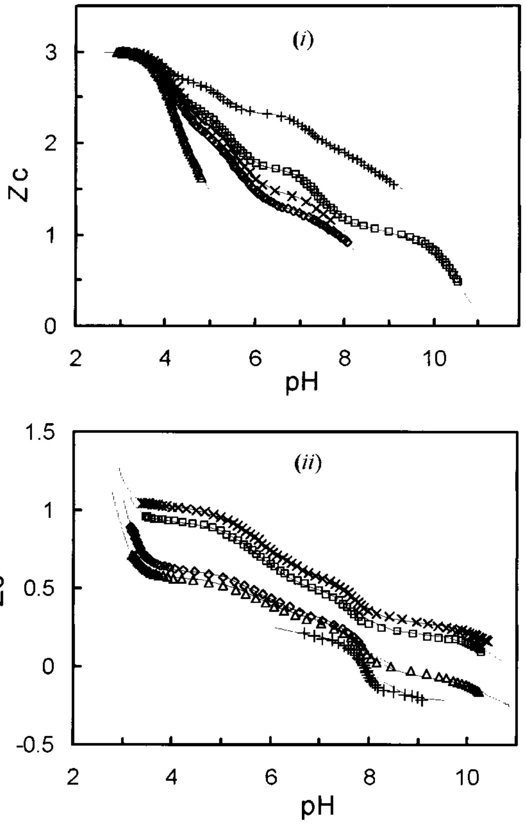

Figure 3. Z_c curves for the system H^+−Al^{3+}−H_nL when H_nL is (i) DHB and (ii) DASA. The symbols show experimentally derived values of Z_c. The solid lines were calculated using the refined constants given in Tables 4 and 5. For i, metal/ligand ratios: +, 1:5.9; □, 1:3.1; ×, 1:2.6; ◇, 1:2.3; △, 1:1.3. For ii, metal/ligand ratios: ×, 1:4.1; □, 1:3.7; ◇, 1:2.9; △, 1:2.8; +, 1:2.5.

H^+−Al^{3+}−DASA (H_2L^-) System. The proton dissociation constants for H_2L^- were determined from 10 potentiometric titrations (685 data points) with the concentration of DASA varied from 1.2 to 3.3 mM. The pK_a for the less acidic −OH group was also determined spectrophotometrically using the method of Ågren.[23] The average value for pK_a obtained from Ågren plots using data from 19 spectra (pH 9.5−11.6) at 10 wavelengths was 10.95 (σ = 0.03), in excellent agreement with the potentiometric value (10.942, with σ = 0.007).

The β value for the 1:1 Al−DASA complex was determined spectrophotometrically using the modified Ågren method, a large excess of Al over DASA, and pH < 3.5. This approach was employed because the complex is sparingly soluble (ca. 1 × 10^{-4} M in 0.10 M KCl) and, in the pH range where it forms (2.6−3.5), the H^+ concentration is up to 20 times greater than the solubility. In this pH range, H_2DASA^- is the dominant protonation state

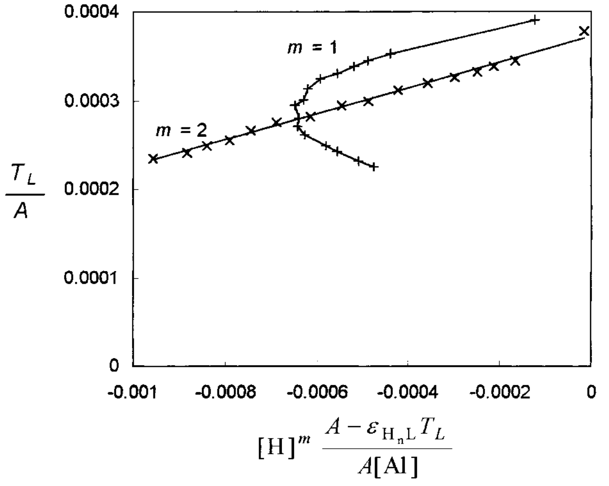

Figure 4. Modified Ågren plot for the calculation of β_{-211}. m gives the number of protons displaced by Al from H_2DASA^-; the horizontal axis is labeled for $m = 2$ data only. Absorbance values were collected at 404 nm. [DASA] = 48 μM, $[Al^{3+}]$ = 2.26 mM.

Table 5. Refined Cumulative Equilibrium Constants for the DASA System, 25 °C, 0.10 M KCl

pqr	log β_{pqr}[a]	σ[b]	proposed product
−101	−5.798	0.004	HL^{2-}
−201	−16.740	0.003	L^{2-}
−102	−3.571	0.02	$H_3L_2^{3-}$
−211[c]	−2.550	0.04	AlL^0
−412	−5.236	0.009	AlL_2^{3-}
−1024	−22.77	0.03	$Al_2(OH)_2L_4^{8-}$
	derived constants[d] for L^{3-}		
	this work[e]	lit	
101	10.942	10.96[f] 10.91[g]	HL^{2-}
201	16.740	16.7[g]	H_2L^-
302	29.909		$H_3L_2^{3-}$
011	14.19[c]	14.11[f]	AlL^0
012	28.244	26.93[c,f]	AlL_2^{3-}
−112		34.1[f]	$Al(OH)L_2^{4-}$
−224	44.19		$Al_2(OH)_2L_4^{8-}$

[a] β_{pqr} values are defined according to the equation $pH^+ + qAl^{3+} + rH_2L^- \rightleftharpoons H_pAl_q(H_2L)_r^{(p+3q-r)+}$. [b] σ is the standard deviation for each constant. [c] Spectrophotometric determination. [d] Derived constants refer to the reaction $pH^+ + qAl^{3+} + rL^{3-} \rightleftharpoons H_pAl_qL_r^{(p+3q-3r)+}$. [e] This work, 0.10 M KCl, 25 °C. [f] Couturier,[34] 0.10 M $NaClO_4$, 25 °C. [g] Wu and Forsling,[33] 0.10 M KCl, 25 °C.

[$pK_{a(H_2DASA^-)}$ = 5.80], and it can be assumed that this is the only state that is significantly formed. The hydrolysis of Al^{3+} can be neglected at pH < 4.0. Two plots obtained from the spectrophotometric data are displayed in Figure 4. They confirm that $m = 2.0$, where m is the number of protons displaced from H_2DASA^- in the reaction $Al^{3+} + H_2DASA^- = Al(DASA) + 2H^+$. The other Al−DASA stability constants were determined from 9 potentiometric titrations (453 data points) with DASA concentrations in the range 0.71−2.0 mM and Al^{3+} concentrations in the range 0.5−0.25 mM. The ligand-to-metal ratio was varied from 1:2.4 to 1:4.0. Data were analyzed using the program SUPERQUAD;[26] β_{pqr} values are reported in Table 5.

The stoichiometry of the complex formed at pH 9.2 defined the end member of the equilibrium model. The stoichiometry was determined from a continuous variation plot utilizing 15 solutions in which the sum of concentrations ($[Al^{3+}]$ + [HDASA]) was held constant at 10 μM (0.05 M NH_4Cl/NH_4OH buffer; 0.10 M KCl; Figure 5). Absorbances were measured at 322 nm after 20 min of equilibration. A complex with Al/DASA = 1:2 is indicated by the inflection at [HDASA]/[Al] = 2.0. This complex was assigned the dimeric composition $[Al_2(OH)_2(DASA)_4]^{8-}$ (see Discussion). The Z_c curves calculated from the refined constants are shown in Figure 3.

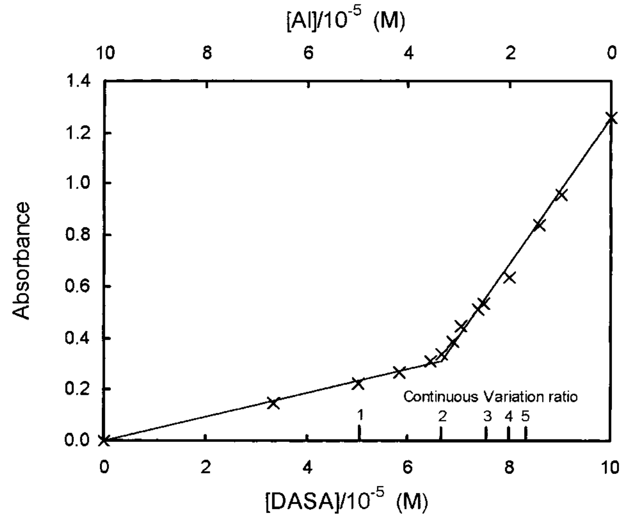

Figure 5. Continuous-variation plot for the system Al^{3+}−DASA at pH 9.2.

Discussion

Proton Complexes. The β_{-101} and β_{-201} values for caffeic and chlorogenic acids obtained from potentiometric titrations are in excellent agreement with literature values (footnotes e-h, Table 3). The β_{-101} values are assigned to the carboxyl group, $pK_{a(COOH)}$. The carboxyl group of chlorogenic acid is more acidic (pK_a = 3.359) than that of caffeic acid (4.382), an effect attributed to the adjacent alcoholic hydroxyl group on the quinic acid residue of chlorogenic acid.[9]

The $pK_{(OH1)}$ values for caffeic and chlorogenic acids [log($\beta_{-101}/\beta_{-201}$), Table 3] indicate that their phenolic groups are slightly more acidic than those in catechol and related ligands.[9,32] This might indicate an electron-withdrawing effect of the carboxylate group acting across the double bond of the side chain.[8] This effect is not seen for the structurally related ligands 3,4-dihydroxyphenylethanoic acid and 3,4-dihydroxyphenylpropanoic acid, both of which have saturated side chains and higher $pK_{(OH1)}$ values, namely, 9.33 and 9.43, respectively.[9] The agreement between literature $pK_{(OH2)}$ values [$pK_{(OH2)} = \log(\beta_{-201}/\beta_{-301})$] and those reported here (Table 3) is poorer. The *o*-diphenolate species formed at high pH readily undergo oxidation and subsequent polymerization reactions, which make the determination of accurate $pK_{(OH2)}$ values difficult. In this work, attempts to obtain a reliable value of $pK_{(OH2)}$ for DHB were unsuccessful as a result of rapid oxidation. The log β_{-301} value estimated from the spectra is −32.0.

The $pK_{(OH2)}$ values reported by Lamy et al.[3] for caffeic and chlorogenic acids are unlikely to be accurate, as they were derived from potentiometric titrations and fall considerably outside the range for reliable pH measurements by glass bulb electrodes. The value for caffeic acid reported in this work is similar to that reported by Kiss et al.;[9] however, the value for chlorogenic acid falls between their value and that of Améziane et al.[11]

The derived protonation constants β_{101} and β_{201} determined for $DASA^{3-}$ (10.942 and 16.740, respectively) agree with those reported by other workers under similar conditions (Table 5). Wu and Forsling[33] reported values of 10.91

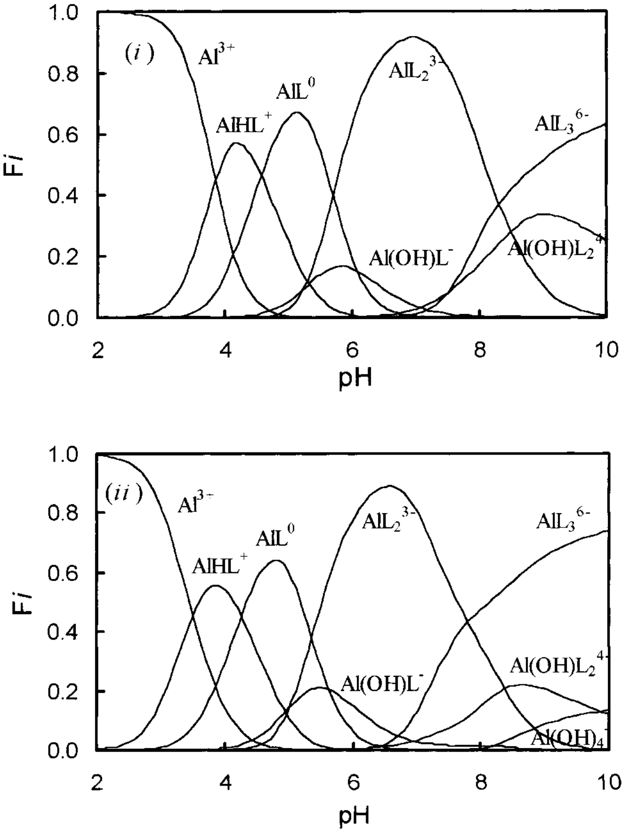

Figure 6. Speciation diagrams for the Al^{3+} and (i) caffeic and (ii) chlorogenic acid systems using the stability constants given in Table 3. F_i is the fraction of total metal present as the designated species. [Al] = 1 mM, [ligand] = 2.5 mM.

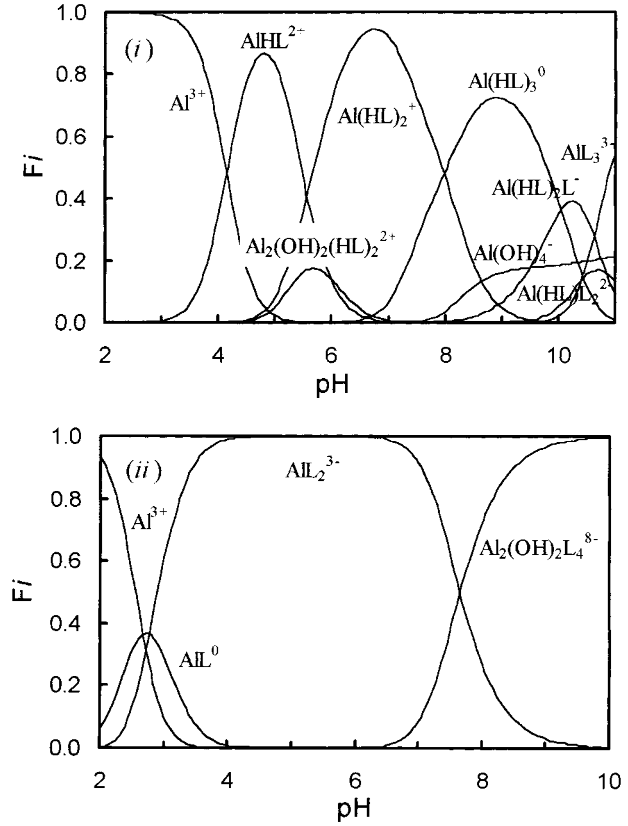

Figure 7. Speciation diagrams for the Al^{3+} and (i) DHB and (ii) DASA systems using the stability constants given in Tables 4 and 5, respectively. F_i is the fraction of total metal present as the designated species. [Al] = 1 mM, [ligand] = 2.5 mM.

and 16.7 for the two respective constants ($I = 0.10$ M NaCl, 25 °C), whereas Couturier[34] reported $\beta_{101} = 10.96$ ($I = 0.10$ M $NaClO_4$, 25 °C). We postulate the formation of the dimeric species $[H_3(DASA)_2]^{3-}$ on the basis of the improved numerical fit to the potentiometric data. This species reaches its maximum concentration at pH 5.8, where the concentrations of $[HDASA]^{2-}$ and $[H_2DASA]^{-}$ are equal. Ingman[35] proposed a similar dimerization for alizarin fluorine blue, which also has the 1,2-dihydroxyanthraquinone structure of DASA.

Caffeic and Chlorogenic Acid−Al^{3+} Complexes. No stability constants have been reported for the H^+−Al^{3+}−H_3L system with H_3L = chlorogenic acid; for H_3L = caffeic acid, a reported value for the 1:1 complex[36] (log $K_1 = 15.06$, $I = 0$ M) was derived from spectrophotometric measurements in the pH range 3.8−4.5. For both ligands, a model assuming the six species $AlHL^+$, AlL^0, $Al(OH)L^-$, AlL_2^{3-}, $Al(OH)L_2^{4-}$, and AlL_3^{6-} provided the best numerical fit to the experimental data using the program SUPERQUAD.[26] Species distribution diagrams are shown in Figure 6. The monoprotonated complex ($AlHL^+$) forms at low pH. As the pH increases, complex formation proceeds in a stepwise fashion via AlL^0 and AlL_2^{3-} and the hydroxo species $Al(OH)L^-$ and $Al(OH)L_2^{4-}$ (formed from the hydrolysis of AlL^0 and AlL_2^{3-}) to give AlL_3^{6-} as the series end member.

Two structures for $AlHL^+$ are possible. Al^{3+} can coordinate via the catecholate moiety (with the side-chain carboxyl group still protonated) or via the carboxylate group and one phenolate group (with the other phenolic group remaining protonated). The former structure is favored on the basis of steric strain and is also supported by the β_{-211} values. For caffeic acid, the equilibrium constant for the derived reaction $AlHL^+ \rightleftharpoons AlL^0 + H^+$ is log $K' = -4.57$ (Table 3), a value similar to that obtained for the deprotonation of the carboxyl group in the free ligand (log $\beta_{-101} = -4.382$). In contrast, for chlorogenic acid, the log K' value (−4.26) is smaller than log β_{-101} for the free ligand (−3.359). For the structurally related ligand 3,4-dihydroxybenzoic acid, the log K' value calculated from published data[24,32,37] is −4.7. It should be noted, however, that K' refers to a ligand in which the phenolic groups are deprotonated and coordinated to a stronger acid (Al^{3+}). Importantly, the pH range for the deprotonation of $AlHL^+$ (ca. pH 3−5; Figures 6 and 7) is below the ranges for deprotonation of the phenolic groups [$pK_{(OH1)} = 8.672$ and 8.251 for caffeic and chlorogenic acids, respectively].

Simultaneous coordination of metal ions to both the carboxyl and catechol sites, as well as formation of oligomeric structures, has been observed for the binding of caffeic and chlorogenic acids to various divalent metal ions.[8−10] The possible presence of Al−ligand oligomeric species was evaluated in this work. However, the inclusion of various species into the speciation model either worsened or did not improve the goodness of fit. This reflects the marked preference of the hard acid Al^{3+} for the harder phenolate donor groups in forming binary complexes.

DHB−Al^{3+} Complexes. A species distribution diagram for the Al^{3+}−DHB system is shown in Figure 7. DHB (H_3L^+) binds to Al via its catecholate moiety to form 1:1, 1:2, and 1:3 complexes. Each coordinated ligand has a noncoordinated ammonium group; in the free ligand, this group has $pK_a = 10.32$. Stepwise deprotonation of these groups in the tris complex, $Al(HL)_3^0$ ($p\ q\ r = -6\ 1\ 3$), yields the species with $p\ q\ r$ coefficients of (−7 1 3), (−8 1 3), and (−9 1 3). The average difference between log β_{-n13} and log

$\beta_{-(n+1)13}$ is 10.43, which approximates the pK_a value for the free ligand, 10.32. Thus, the acidity of the ammonium group is relatively unaffected by coordination of DHB to Al^{3+}. During numerical modeling of the potentiometric data, substantial improvements to the fitting were obtained by including a dimer species into the model, $[Al_2(OH)_2(HL)_2]^{2+}$. This is consistent with the model developed by Kiss et al.[9] for other Al−catecholamine systems. The species $[Al(OH)HL]^+$ and $[Al(OH)(HL)_2]^0$, which have been postulated for analogous ligands,[24] did not improve the goodness of fit for the solution compositions used in this work.

DASA−Al^{3+} Complexes. Figure 7 shows a species distribution diagram for the Al^{3+}−DASA system. The derived formation constant for the 1:1 complex, log $\beta_{011} = 14.19$, is consistent with the value reported by Couturier[34,38] (14.11), both having been determined spectrophotometrically. The reaction stoichiometry was confirmed as $Al^{3+} + H_2DASA^- = Al(DASA)^0 + 2H^+$ (Figure 4). This suggests that Al^{3+} coordinates to DASA at the 1,2-*ortho*-diphenolate, rather than at the 1,9-quinoid phenolate, site. The low solubility of this complex is consistent with its zero net charge.

The log K_n values for the stepwise reactions $Al^{3+} + DASA^{3-} \rightleftharpoons Al(DASA)$ (14.19) and $Al(DASA) + DASA^{3-} = Al(DASA)_2{}^{3-}$ (14.05) are approximately equal, indicating that the 1:2 complex forms almost concurrently with the 1:1 complex. The potentiometric value derived for log β_{012} (28.244) (Table 5) contrasts with the spectrophotometric determination of Couturier[34] (26.93).

Above pH 7.0, a buffer region in which 1 equiv of alkali was consumed per Al^{3+} ion was observed in potentiometric titrations. In the buffer region, DASA is singly protonated. The buffer region was not consistent with the reaction $Al(DASA)_2{}^{3-} + HDASA^{2-} = Al(DASA)_3{}^{6-} + H^+$ because it was also observed for solutions with compositions $2 < [DASA]/[Al^{3+}] < 3$. A continuous-variation study at pH 9.2, approximating the end-point pH, indicated a 1:2 stoichiometry for the product (Figure 5). Couturier[34] suggested formation of $[Al(OH)(DASA)_2]^{4-}$, but inclusion of this species in the present model did not reduce the least-squares residuals. The abrupt flatness of the buffer region indicates a reaction with exchange of multiple protons. Inclusion of the species $[(Al(OH)(DASA)_2)_x]^{4x-}$ in the numerical refinement gave the minimum residual for $x = 2$, i.e., for inclusion of a dimer with the formula $[Al_2(OH)_2(DASA)_4]^{8-}$. A crystallographic study of aluminum calcium alizarinate, $[(Al(OH)(alizarin)_2Ca)_2]$, by Wunderlich and Bergerhoff[39] established a structure in which two Al^{3+} ions are bridged by two hydroxide ions, the coordination sphere of each Al^{3+} ion being completed by the 1,2-diphenolate sites of two alizarin ligands. The calcium ions fill the 1,9-quinoid phenolate coordination sites. This structure offers strong support for a value of $x = 2$ for DASA. Cyclic voltammetric studies[40] on Al^{3+}−DASA solutions at pH 8.9 indicated that a complex is formed that has an oxidation potential different from that for $Al(DASA)_2{}^{3-}$. This finding was interpreted by us as indicating the formation of a tris complex, but the current work has established the formation of the dimer $[Al_2(OH)_2(DASA)_4]^{8-}$.

Conclusions

The solution chemistry of the H^+−Al^{3+}−H_nL systems for caffeic acid, chlorogenic acid, DHB, and DASA has been examined using potentiometric and spectrophotometric techniques. Equilibrium constants are reported. The values for the ligand deprotonation reactions are in good agreement with the results of other workers. For caffeic and chlorogenic acids, the formation of six mononuclear Al−ligand species was proposed to adequately rationalize the experimental data. No evidence was found for oligomeric species, despite reports by previous workers of the formation of such complexes for these ligands with various divalent metal ions.[8−10]

The interaction of DHB with Al conforms to the pattern observed for other catecholamines, viz., 1,2-dihydroxyaryl coordination. The species derived for the H^+−Al^{3+}−DASA system support previous observations by Couturier,[34,38] although the use of potentiometric techniques in this work has revealed the presence of the new dimer species $[Al_2(OH)_2(DASA)_4]^{8-}$.

The relative stability of the 1:1 Al^{3+} complexes can be derived from the values of log β_{-211} for the respective ligands. β_{-211} defines the reaction $-2H^+ + Al^{3+} + H_nL^0 \rightleftharpoons H_{-2}Al(H_nL)^+$ in which the coordinating ligand loses its 1,2-dihydroxyaryl protons but not the protons associated with the $-COOH$ or $-NH_3{}^+$ substituents. The observed order, DASA (log $\beta_{-211} = -2.55$) > chlorogenic acid (−3.91) > caffeic acid (−4.88) > DHB (−5.58), indicates the progressive electron-withdrawing effects of the ring substituents $-SO_3{}^- < -CH{=}CH{\cdot}CO{\cdot}O{\cdot}(C_6H_{10}O_3){\cdot}COOH < -CH{=}CH{\cdot}COOH < -NH_3{}^+$. This is consistent with the crossover points observed in Figures 6 and 7.

Literature Cited

(1) Olsen, R. A.; Brown, J. C.; Bennett, J. H.; Blume, D. Reduction of Fe^{3+} as it relates to Fe chlorosis. *J. Plant Nutr.* **1982**, *5*, 433−445.

(2) Römheld, V.; Marschner, H. Mechanism of iron uptake by peanut plants. I. Fe^{III} reduction, chelate splitting and release of phenolics. *Plant Phys.* **1983**, *71*, 949−954.

(3) Lamy, I.; Seywert, M.; Cromer, M.; Scharff, J.-P. Simple and mixed ligand complexes of copper(II) with polyfunctional phenolic compounds as models of natural substances. *Anal. Chim. Acta* **1985**, *176*, 201−212.

(4) Linder, P. W.; Voyé, A.; Cocks, S. The effect of caffeic acid on the speciation of metal ions in plant nutrient solutions. In *Metal Speciation in the Environment*; NATO ASI Series; Broekaert, J. A. C., Güçer, Ş., Adams, F., Eds.; Springer-Verlag: Berlin, 1990; Vol. G23, pp 91−104.

(5) Makepeace, W.; Dobson, A. T.; Scott, D. Interference phenomena due to mouse-ear and king devil hawkweed. *N. Z. J. Bot.* **1985**, *23*, 79−90.

(6) Northup, R. R.; Yu, Z.; Dahlgren, R. A.; Vogt, K. A. Polyphenol control of nitrogen release from pine litter. *Nature* **1995**, *377*, 227−229.

(7) Northup, R. R.; Dahlgren, R. A.; McColl, J. G. Polyphenols as regulators of plant−litter−soil interactions in northern California's pygmy forest: A positive feedback? *Biogeochemistry* **1998**, *42*, 189−220.

(8) Linder, P. W.; Voyé, A. Potentiometric investigations of the equilibria between caffeic acid and copper(II), zinc(II), iron(II) and hydrogen ions in solution. *Polyhedron* **1987**, *6*, 53−60.

(9) Kiss, T.; Nagy, G.; Pécsi, M. Complexes of 3,4-dihydroxyphenyl derivatives. 10. Copper(II) complexes of chlorogenic acid and related compounds. *Polyhedron* **1989**, *8*, 2345−2349.

(10) Cocks, S.; Linder, P. W.; Voyé, A. Potentiometric investigations of equilibria between caffeic acid and manganese(II), cobalt(II), nickel(II) and cadmium(II) ions in aqueous solution. *J. Coord. Chem.* **1992**, *25*, 211−220.

(11) Améziane, J.; Aplincourt, M.; Dupont, L.; Heirman, F.; Pierrard, J.-C. Thermodynamic stability of copper(II), manganese(II), zinc(II) and iron(III) complexes with chlorogenic acid. *Bull. Soc. Chem. Fr.* **1996**, *133*, 243−249.

(12) Van den Berg, C. M. G.; Murphy, K.; Riley, J. P. The determination of aluminum in seawater and freshwater by cathodic stripping voltammetry. *Anal. Chim. Acta* **1986**, *188*, 177−185.

(13) Hernandez-Brito, J. J.; Gelado-Caballero, M. D.; Pérez-Peña, J.; Herrara-Melián, J. A. Fast determination of aluminium reactive to 1,2-dihydroxyanthraquinone-3-sulfonic acid in seawater. *Analyst* **1994**, *119*, 1593.

(14) Downard, A. J.; Powell, H. K. J.; Xu, S. Flow-injection analysis for aluminum with indirect amperometric detection. *Anal. Chim. Acta* **1992**, *256*, 117−123.

(15) Downard, A. J.; Powell, K. J.; Money, S. D. Speciation determination of aluminium (Al^{3+}) by flow injection amperometry via the

1,2-dihydroxyanthraquinone-3-sulfonic acid complex. *Anal. Chim. Acta* **1999**, *349*, 111−120.

(16) Zittel, H. E.; Florence, T. M. Voltammetric and spectrophotometric study of the zirconium−alizarin Red S complex. *Anal. Chem.* **1967**, *39*, 320.

(17) Bakola-Christianopoulou, M. N. Synthesis and study of some bivalent metal chelates of 1,2-dihydroxy-9,10-anthracenedione and 5-hydroxy-1,4-naphthalenedione. *Polyhedron* **1984**, *3*, 729.

(18) Larsen, J.; Zink, J. I. Ligand-centred luminescence and deactivation by ligand field states in alizarin complexes. *Inorg. Chim. Acta* **1990**, *169*, 71.

(19) Kiss, T.; Sovago, I.; Martin, R. B. Complexes of 3,4-dihydroxyphenyl derivatives. 9. Al^{3+} binding to catecholamines and tiron. *J. Am. Chem. Soc.* **1989**, *111*, 3611−3614.

(20) Vogel, A. I. *A Textbook of Quantitative Inorganic Analyses including Elementary Instrumental Analysis*, 3rd ed.; Longmans: London, 1961.

(21) Gran, G. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* **1952**, *77*, 661−670.

(22) Russell, J. M. R. A thermodynamic study of transition metal oxime complexes. Ph.D. Thesis, University of Canterbury, Christchurch, New Zealand, 1977.

(23) Ågren, A. The complex formation between iron(III) ion and some phenols, IV. The acidity constant of the phenolic group. *Acta Chem. Scand.* **1955**, *9*, 49−56.

(24) Kennedy, J. A.; Powell, H. K. J. Aluminium(III) and iron(III) 1,2-diphenolato complexes: A potentiometric study. *Aust. J. Chem.* **1985**, *38*, 659−667.

(25) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed; ACS Monograph Series No. 137. Reinhold Publishing Corp.: New York, 1958.

(26) Gans, P.; Sabatini, A.; Vacca, A. SUPERQUAD: An improved general program for computation of formation constants from potentiometric data. *J. Chem. Soc., Dalton Trans.* **1985**, *6*, 1195−1200.

(27) Brown, P. L.; Sylva, R. N.; Batley, G. E.; Ellis, J. The hydrolysis of metal ions. Part 8. Aluminium (III). *J. Chem. Soc., Dalton Trans.* **1985**, 1967−1970.

(28) Millero, F. J.; Schreiber, D. R. Use of the ion pairing model to estimate activity coefficients of the ionic components of natural waters. *Am. J. Sci.* **1982**, *282*, 1508−1540.

(29) Palmer, D. A.; Wesolowski, D. J. Aluminium speciation and equilibria in aqueous solutions: II. The solubility of gibbsite in acidic sodium chloride solutions from 30 to 70 °C. *Geochim. Cosmochim. Acta* **1992**, *56*, 1093−1111.

(30) Eriksson, G. An algorithm for the computation of aqueous multicomponent, multiphase equilibria. *Anal. Chim. Acta* **1979**, *112*, 375−383.

(31) Pettit, L. Critical survey of formation constants of complexes of histidine, phenylalanine, tyrosine, L-dopa and tryptophan. *Pure Appl. Chem.* **1984**, *56*, 247−292.

(32) Pettit, L. D.; Powell, H. K. J. *SC Database: Stability Constant Database*; IUPAC, Academic Software: Oxford, U.K., 1997.

(33) Wu, L. M.; Forsling, W. Potentiometric and spectrophotometric study of calcium and alizarin red-S complexation. *Acta Chem. Scand.* **1992**, *46*, 418−422.

(34) Couturier, Y. Composition and stability of aluminum(III) complexes with alizarin-3-sulfonic acid. *Bull. Soc. Chim. Fr.* **1987**, 963−968.

(35) Ingman F. Acidity stability constants of alizarin fluorine blue. *Talanta* **1973**, *20*, 135.

(36) Sikora, F. J.; McBride, M. B. Aluminium complexation by protocatechuic and caffeic acids as determined by ultraviolet spectrophotometry. *Soil Sci. Soc. Am.* **1990**, *54*, 78−86.

(37) Kennedy, J. A.; Munro, M. H. G.; Powell, H. K. J.; Porter, L. J.; Yeap Foo, L. The protonation reactions of catechin, epicatechin and related compounds. *Aust. J. Chem.* **1984**, *37*, 885−892.

(38) Couturier, Y. Thermodynamic study of aluminum(III) alizarin-3-sulfonic acid system. *Bull. Soc. Chim. Fr.* **1989**, 756−760.

(39) Wunderlich, C. H.; Bergerhoff, G. Constitution and colour of alizarin and purpurin dyes. *Chem. Ber.* **1994**, *127*, 1185−1190.

(40) Downard, A. J.; O'Sullivan, B.; Powell, K. J. A voltammetric study of the aluminium complexes of catechol and 1,2-dihydroxyanthraquinone-3-sulfonic acid. *Polyhedron* **1996**, *15*, 3469−3479.

Received for review October 16, 2001. Accepted December 17, 2001.

JE010279E