On the Possibility of determining the Thermodynamic Parameters for the Formation of Weak Complexes using a Simple Model for the Dependence on Ionic Strength of Activity Coefficients: Na^+, K^+, and Ca^{2+} Complexes of Low Molecular Weight Ligands in Aqueous Solution

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Alkali-metal and calcium(II) complexes of monocarboxylate A^- (acetate and salicylate), dicarboxylate A^{2-} (malonate, maleate, succinate, malate, tartrate, phthalate, and oxydiacetate), or amino acid HA (glycine or L-histidine) ligands have been studied potentiometrically, using a glass–saturated calomel electrode, at different temperatures and ionic strengths. The monocarboxylate ligands form [MA] and the dicarboxylates [MA] and [M(HA)] species (charges omitted) with both alkali metals and calcium. Glycine and L-histidine form $[MA]^+$ and $[M(HA)]^{2+}$ {and $[M(H_2A)]^{3+}$ for L-histidine} complexes with Ca^{2+}, whilst alkali metals form only $[M(HA)]^+$ with glycine. Some interesting regularities in the formation constants are pointed out. From the dependence on temperature of formation constants, values of ΔH° and ΔS° have been determined. The function $\log \beta = f(I)$ has been carefully studied in the range $0.02 \leqslant I \leqslant 1$ mol dm^{-3}. The reliability of a new model for the dependence on ionic strength of formation constants (when dealing with weak complexes it is in practice impossible to use the constant ionic medium method) is widely discussed. Two methods of calculation are described and the more general method has been checked by simulated curves.

Recently, an interesting lecture by Bjerrum [1] was based on the question: 'How far is it possible to determine small stability constants in aqueous solution?' This question arises from the uncertainties in determining activity coefficients when working with high and varying concentrations. In the last five years some of us have been concerned with the study of weak alkali [2–9] and alkaline-earth [10–15] metal complexes of low molecular weight inorganic and organic ligands. These investigations showed that, when taking into account all possible interactions among components (including the background), the dependence on ionic strength of formation constants is the same, in the range $0 < I \leqslant 1$ mol dm^{-3}, for all reactions, if allowance is made for the charges involved and for the stoicheiometry. Some systematic studies on the protonation of inorganic and organic acids,[16] mixed-ligand complexes,[17] literature data on hydrolysis and transition metal–amino acid complexes,[18] mixed-metal complexes,[19] and protonation of cationic acids[20] confirmed these findings.

Let us examine the relevance of the above question and hence the need to find a quantitative answer. The studies [2–15] on weak alkali and alkaline-earth metal complexes were related to several problems such as the speciation of natural fluids, the presence of alkali-metal complexes in the constant medium equilibrium investigations, the difference between medium and ionic strength dependence of formation constants, the stabilizing properties of alkali-metal complexes in some biological fluids, and the chemicophysical properties of simple electrolyte solutions (in most cases the differences in activity coefficients of salt solutions at the same ionic strength can be explained by the formation of weak complexes [21]). Therefore, we can assert that the above question is not useless, and that the quantitative knowledge of the formation of weak complexes represents an important problem (from both practical and theoretical points of view) to be solved.

Experimental and calculation procedures relating to the determination of stability constants $\beta > 10^3$ dm^3 mol^{-1} are well established and standard procedures have been widely reported. On the contrary, very few papers have dealt with low stability constant determinations (for example only one review has been published on alkali-metal complexes in solution [22]). Several reasons account for this: (*i*) the difficulty in distinguishing between activity and complex formation factors; (*ii*) the impossibility of using the constant ionic medium method; and (*iii*) the low perturbation of measured physical properties, when weak complexes are formed, that requires high accuracy techniques.

Bearing in mind the above considerations, we report here a systematic study on the stability (at different temperatures and ionic strengths) of Na^+, K^+, and Ca^{2+} (and, in some cases, Li^+) complexes of low molecular weight ligands [acetate(1−), salicylate(1−), malonate(2−), maleate(2−), succinate(2−), malate(2−), tartrate(2−), phthalate(2−), oxydiacetate(2−), glycinate(1−), and L-histidinate(1−); throughout the present paper these anions are indicated as A in the formulae]. Particular attention has been paid to the following problems: (*i*) the validity of a general equation for the dependence on ionic strength of formation constants and hence the validity of the hypothesis of a non-individual dependence on ionic strength of activity coefficients of different ions, as proposed in previous work;[16–20] (*ii*) the importance of rigorous methods of calculation; and (*iii*) the influence of experimental errors on the consistency of calculated stability constant values.

Experimental

Materials.—The ligands (Fluka puriss or Merck p.a. products) were used without further purification; their purity, checked by alkalimetric titrations, was always >99.5%. Stock

solutions of alkali-metal ions were prepared from their corresponding chloride or nitrate salts (C. Erba, purity >99.5%) previously dried in an oven at 110 °C or in vacuum; calcium nitrate stock solutions were prepared from Fluka purum reagents and standardized by ethylenediaminetetra-acetate titrations.[23] Tetraethylammonium iodide (NEt_4I) (Fluka puriss) was recrystallized from methanol. NaOH and KOH stock solutions were prepared from concentrated ampoules (C. Erba or B.D.H.) and standardized against potassium hydrogenphthalate (Fluka puriss). HCl and HNO_3 stock solutions were prepared from B.D.H. concentrated ampoules and standardized against NaOH or KOH.

Apparatus.—The free hydrogen-ion concentration, h, was measured by three different potentiometric systems: (*a*) a model 801A ORION potentiometer; (*b*) a model E600 METROHM potentiometer; (*c*) a semiautomatic homemade potentiometer built with an Analog Devices millivoltmeter, Printel printer, and Mosteck logic circuits in order to add a pre-established volume of titrant and to print the corresponding e.m.f. value. The use of different equipment ensured avoiding systematic errors. The potentiometers were coupled with glass-saturated calomel electrodes supplied by ORION and METROHM. In all cases the instrumental resolution was ±0.1 mV. The titrant solution (NaOH or KOH) was delivered by a model 882 AMEL dispenser (minimum reading 0.001 cm^3) or by a microsyringe (minimum reading 5 000 divisions cm^{-3}). The electrode couples were systematically calibrated, in $-\log h$ (pH) units, by titrating HCl or HNO_3 (5 mmol dm^{-3}) with standard NaOH or KOH, under the same conditions as the solution under study. The measurement cells (50 cm^3) were thermostatted at T ±0.2 °C. During the titrations magnetic stirring was employed. All the titrations were carried out by bubbling purified N_2 through the solution.

Procedure.—An aqueous solution (25—50 cm^3) containing the acid under study (5—10 mmol dm^{-3}) was titrated with standard NaOH or KOH (0.1—1 mol dm^{-3}) up to the pH corresponding approximately to neutralization (30—50 experimental points). The alkali metal and calcium ion concentrations were varied in the ionic strength range $0.02 \leqslant I \leqslant 1$ mol dm^{-3} (some mixtures of M and NEt_4I were also analyzed). An excess of strong acid (5—10 mmol dm^{-3}) was added to all solutions in order to complete the protonation of the anionic species and to calculate directly the internal standard electrode potential E°_{int} (E°_{ext} is the corresponding value calculated by separate calibration). If $|E^\circ_{int} - E^\circ_{ext}| > 1$ mV the titration was rejected. The reproducibility of potentiometric systems was ±0.005 pH units. Other experimental details were as previously reported.[2-20]

Whilst the majority of data reported in this work are original, some experimental data have been drawn from previous works; in these cases the thermodynamic parameters were recalculated and some experiments repeated in order to check previous findings.*

Throughout this paper the uncertainties in the parameters are three times the standard deviation.

Calculations relating to the determination of protonation constants were performed using the non-linear least-squares computer programs ACBA[24] and/or ESAB.[25] Calculations relating to the determination of formation constants and their dependence on temperature and ionic strength were performed by the two methods described in the next section. All thermodynamic parameters are expressed in the molar scale.

Calculations

Weak Complexes of Monoprotic Acids.—If we consider a monoprotic acid HA that forms a complex species [MA] with a metal M, the mass balance equations can be described by equations (1)—(3).† These equations reduce, when neglecting

$$C_M = m + \beta_{10}ma \quad (1)$$

$$C_A = a + \beta_{10}ma + \beta_{01}ha \quad (2)$$

$$C_H = h + \beta_{01}ha - \beta_{0-1}h^{-1} \quad (3)$$

the formation of [MA], to equations (4) and (5), where

$$C_A = a' + \beta'_{01}ha' \quad (4)$$

$$C_H = h + \beta'_{01}ha' - \beta_{0-1}h^{-1} \quad (5)$$

primes indicate conditional quantities, *i.e.* quantities calculated without allowing for complex formation. By equating (2) and (4) and substituting for a and a' from (3) and (5), equations (6)—(8) are obtained where $\Delta\log\beta_{01} = \log\beta_{01} - \log\beta'_{01}$.

$$\beta_{01} = \beta'_{01}(1 + \beta_{10}m) \quad (6)$$

or

$$\log\beta_{01} = \log\beta'_{01} + \log(1 + \beta_{10}m) \quad (7)$$

or

$$\beta_{10} = (10^{\Delta\log\beta_{01}} - 1)\,m^{-1} \quad (8)$$

Equations (6)—(8) can also be used in the case of polyprotic acids which have very separate protonation steps [equation (9)], and when $[MAH_j]$ is the most important species in the

$$K_{0(j-1)} \gg K_{0j} \gg K_{0(j+1)} \cdots \quad (9)$$

range pH = $\log K_{0j} \pm 1$. For example, in the case of a triprotic acid, the formation constant of the species [M(HA)] can be calculated by using (6)—(8) when the conditions of (10) apply.

$$\frac{\beta_{11}}{\beta_{01}} \gg \beta_{10} \times \frac{K_{01}}{K_{02}} \text{ and } \frac{\beta_{11}}{\beta_{01}} \gg \frac{\beta_{12}}{\beta_{02}} \quad (10)$$

Similar conditions can be found for each protonation step of polyprotic acids, and in this case equation (6) becomes (11).

$$K_{0j} = K'_{0j}\left[1 + \frac{\beta_{1(j-1)}}{\beta_{0(j-1)}}m\right] \quad (11)$$

Methods of calculating β_{10} (or β_{1j}) are discussed in Appendix A. In previous work[12,13] we sometimes used this method

* Acetate and succinate: experimental data and calculations from refs. 4, 12, 14, and 15; Na^+ and Ca^{2+} complex formation constants were checked by means of four titration curves per system: previously reported values were fully confirmed. Malate, tartrate, oxydiacetate, L-histidinate, and salicylate: new experimental data and calculations (salicylic acid was considered as monoprotic, pH ≤ 4). Malonate, maleate, and phthalate: experimental data from refs. 4, 12, and 13; calculations repeated.

† C_M, C_A, C_H are the analytical concentrations of the metal, the ligand, and the proton respectively; m, a, h indicate the corresponding free concentrations. The formation constants β_{pq} refer to the reaction (charges omitted for clarity) $pM + A + qH \rightleftharpoons [M_pAH_q]$; thus $\beta_{pq} = [M_pAH_q]m^{-p}a^{-1}h^{-q}$; $\beta_{0-1} = K_w$; β_{0q} = protonation constants. The stepwise protonation constants K_{0q} refer to the reaction $H + [H_{q-1}A] \rightleftharpoons [H_qA]$. In previous work[17,19] we used three or four (when dealing with ternary systems) indices to define the formation constants, β_{pqr} or β_{pqrs}; in this work, since the stoicheiometric coefficient of the ligand is always one (because of the weakness of the complexes and experimental conditions, *i.e.* $C_M > C_A$), we have used only two indices.

Table 1. Ligand protonation constants[a] at $I' = 0.25$ mol dm^{-3}

	pq[b]	T(°C)	log β_{pq}	C_{pq}[c]	$-D_{pq}$[c]		pq[b]	T(°C)	log β_{pq}	C_{pq}[c]	$-D_{pq}$[c]
Acetate	01	10	4.586	0.62	0.26	Malate	01	10	4.74(3)	0.96	0.47
		25	4.571	0.58	0.20			25	4.74(2)	1.15	0.62
		35	4.578	0.56	0.16			37	4.73(2)	0.86	0.39
		45	4.599	0.53	0.12		02	10	8.05(3)	1.51	0.60
								25	8.02(2)	1.53	0.60
Salicylate	01	10	2.78(2)	0.48	0.22			37	7.99(3)	1.39	0.60
		25	2.74(1)	0.49	0.22						
		37	2.73(2)	0.50	0.22	Tartrate	01	10	4.04(3)	0.89	0.38
		45	2.73(3)	0.51	0.22			25	4.01(2)	0.82	0.39
								37	3.98(2)	0.89	0.40
Malonate	01	10	5.35(2)	1.30	0.70		02	10	6.95(4)	1.53	0.60
		25	5.36(2)	1.18	0.50			25	6.87(2)	1.37	0.60
		37	5.42(2)	1.06	0.30			37	6.84(2)	1.46	0.60
		45	5.45(3)	1.00	0.20						
	02	10	8.04(4)	1.95	0.92	Phthalate	01	10	5.06(3)	1.29	0.40
		25	8.06(3)	1.72	0.60			25	5.09(2)	1.26	0.40
		37	8.10(3)	1.75	0.50			37	5.14(3)	1.32	0.40
		45	8.15(4)	1.70	0.49		02	10	7.82(3)	2.05	0.70
								25	7.91(2)	1.88	0.48
Maleate	01	10	6.00(2)	1.36	0.48			37	7.95(3)	1.90	0.67
		25	6.02(2)	1.25	0.40						
		37	6.03(2)	1.16	0.34	Oxydiacetate	01	12.5	3.88(2)	0.83	0.30
	02	10	7.80(4)	2.29	0.91			25	3.97(1)	0.95	0.41
		25	7.79(4)	2.13	0.79			37	4.02(2)	0.75	0.20
		37	7.79(3)	2.00	0.70			48	4.11(2)	0.85	0.29
							02	12.5	6.75(2)	1.62	0.75
Succinate	01	15	5.27	1.01	0.37			25	6.79(1)	1.66	0.75
		25	5.26	0.94	0.32			37	6.85(3)	1.70	0.75
		37	5.26	0.85	0.26			48	6.96(3)	1.69	0.75
		45	5.27	0.80	0.22						
	02	15	9.34	1.63	0.56	L-Histidinate	01	10	9.42(3)	0.48	0.20
		25	9.31	1.52	0.48			25	9.06(2)	0.39	0.20
		37	9.30	1.34	0.39			37	8.76(2)	0.53	0.20
		45	9.30	1.30	0.33		02	10	15.72(3)	0.69	0.20
								25	15.07(2)	0.57	0.20
Glycinate	01	10	9.90(3)	0.41	0.10			37	14.59(2)	0.53	0.20
		25	9.55(2)	0.49	0.27		03	10	17.52(4)	0.51	0.20
		37	9.25(2)	0.38	0.20			25	16.82(3)	0.53	0.20
	02	10	12.33(5)	0.60	0.18			37	16.42(3)	0.43	0.20
		25	11.95(3)	0.74	0.25						
		37	11.62(3)	0.59	0.20						

[a] Values in parentheses represent >95% confidence limits. [b] The indexes pq refer to the reaction $p\mathrm{M} + \mathrm{A} + q\mathrm{H} \rightleftharpoons [\mathrm{M}_p\mathrm{AH}_q]$. [c] Adjustable parameters for each complex species [see equation (18)].

(Appendix A) incorrectly and in this work we report the correct formation constants calculated with the method, described in Appendix B, independent of the conditions (9) and (10).

Weak Complexes of Polyprotic Acids.—When dealing with polyprotic acids for which the conditions (9) and (10) are not valid, a different approach must be followed. The mass balance equations are given by (12)—(14),* and, when neglecting the formation of weak complexes, by (15) and (16). By equating (14) and (16) and substituting for a and a' from (13) and (15) equation (17) is obtained.

$$C_{\mathrm{M}} = m + a\Sigma p\beta_{pq}m^p h^q \quad (12)$$

$$C_{\mathrm{A}} = a(1 + \Sigma\beta_{pq}m^p h^q) \quad (13)$$

$$C_{\mathrm{H}} = h + a\Sigma q\beta_{pq}m^p h^q \quad (14)$$

$$C_{\mathrm{A}} = a'(1 + \Sigma\beta'_{0q}h^q) \quad (15)$$

$$C_{\mathrm{H}} = h + a'\Sigma q\beta'_{0q}h^q \quad (16)$$

$$\frac{\Sigma q\beta'_{0q}h^q}{1 + \Sigma\beta'_{0q}h^q} = \frac{\Sigma q\beta_{pq}m^p h^q}{1 + \Sigma\beta_{pq}m^p h^q} \quad (17)$$

By using equation (17) it is possible to calculate all the stability constants (β_{pq}) of the species formed in the system, including polynuclear species. Calculation methods using equation (17) are discussed in Appendix B.

Dependence on Ionic Strength of Activity Coefficients and of Formation Constants.—As already mentioned,[16–20] a general equation, log $\beta = f(I)$, can be used for all the formation constants if allowance is made for the stoicheiometry and for the charges involved in the reaction. The semi-empirical Debye–Hückel type equation† (18) can be used for taking into account the dependence of log β_{pq} on I for each complex species. Furthermore it has been shown that C_{pq} and D_{pq} can be expressed,[16–20] for all the complex species by equations† (19) and (20).

* See footnote (†) on previous page.

† See footnote on p. 2357.

Table 2. Formation constants[a] for alkali-metal complexes at $I' = 0.25$ mol dm^{-3}

	M	pq[b]	T(°C)	log β_{pq}	C_{pq}[c]	$-D_{pq}$[c]
Acetate	Li^+	10	25	0.13	0.69	0.34
	Na^+	10	10	−0.37	0.56	0.19
			25	−0.27	0.59	0.21
			35	−0.21	0.60	0.22
			45	−0.15	0.62	0.24
	K^+	10	10	−0.35	0.63	0.24
			25	−0.43	0.60	0.21
			35	−0.35	0.58	0.19
			45	−0.17	0.56	0.17
Salicylate	Na^+	10	25	−0.5(1)	0.6	0.4
	K^+	10	10	−0.6(1)	0.6	0.4
			25	−0.5(1)	0.6	0.4
			37	−0.5(1)	0.6	0.4
			45	−0.4(1)	0.5	0.3
Malonate	Li^+	10	37	0.95(4)	1.05	0.37
		11	37	5.63(5)	1.6	0.55
	Na^+	10	10	0.56(5)	1.25	0.65
			25	0.57(4)	1.20	0.52
			37	0.60(4)	1.06	0.38
			45	0.61(5)	1.01	0.21
		11	10	5.1(1)	1.9	0.9
			25	5.15(6)	1.7	0.6
			37	5.21(6)	1.6	0.56
			45	5.25(9)	1.6	0.4
	K^+	10	10	0.66(6)	1.3	0.7
			25	0.68(5)	1.2	0.5
			37	0.70(5)	1.05	0.37
			45	0.71(6)	1.0	0.2
		11	10	5.25(9)	1.9	0.9
			25	5.31(7)	1.7	0.6
			37	5.39(7)	1.6	0.56
			45	5.44(9)	1.6	0.4
Maleate	Li^+	10	37	0.91(9)	1.18	0.36
		11	37	5.9(1)	2.14	0.82
	Na^+	10	37	0.86(7)	1.20	0.38
		11	37	6.0(1)	2.10	0.78
	K^+	10	25	0.84(7)	1.23	0.38
			37	0.83(7)	1.14	0.32
		11	25	6.0(1)	2.14	0.80
			37	6.04(9)	2.12	0.80
Phthalate	Li^+	10	37	0.85(5)	1.33	0.41
		11	37	5.03(9)	1.95	0.62
	Na^+	10	10	0.73(7)	1.33	0.44
			25	0.73(5)	1.31	0.40
			37	0.74(5)	1.30	0.38
		11	10	4.96(9)	1.9	0.7
			25	4.96(7)	1.9	0.65
			37	4.98(8)	1.85	0.62
	K^+	10	10	0.83(7)	1.34	0.43
			25	0.83(6)	1.33	0.41
			37	0.84(6)	1.32	0.40
		11	10	5.15(8)	2.0	0.7
			25	5.16(6)	1.9	0.6
			37	5.18(8)	1.9	0.6
Glycinate	K^+	11	37	8.78(9)	0.75	0.2
Succinate	Li^+	10	37	0.70	0.92	0.38
		11	37	5.38	1.52	0.56
	Na^+	10	15	0.46	1.00	0.36
			25	0.47	0.92	0.30
			37	0.49	0.86	0.27
			45	0.52	0.80	0.22
		11	15	5.26	1.60	0.53
			25	5.26	1.54	0.50
			37	5.27	1.38	0.38
			45	5.29	1.28	0.31
	K^+	10	15	0.47	1.03	0.39
			25	0.48	0.93	0.31
			37	0.49	0.87	0.28
			45	0.51	0.78	0.20
		11	15	5.28	1.64	0.57
			25	5.28	1.53	0.49
			37	5.28	1.36	0.36
			45	5.29	1.33	0.36
Malate	Na^+	10	10	0.31(5)	0.95	0.46
			25	0.30(5)	1.15	0.62
			37	0.29(5)	0.88	0.41
		11	10	4.7(1)	1.50	0.59
			25	4.7(1)	1.54	0.61
			37	4.7(1)	1.41	0.62
	K^+	10	10	0.38(4)	0.98	0.49
			25	0.38(4)	1.12	0.59
			37	0.38(4)	0.87	0.40
		11	10	4.4(2)	1.53	0.62
			25	4.5(2)	1.53	0.60
			37	4.5(2)	1.38	0.59
Tartrate	Na^+	10	10	0.58(5)	0.90	0.39
			25	0.58(5)	0.80	0.37
			37	0.59(5)	0.86	0.37
		11	10	4.05(6)	1.54	0.61
			25	4.05(6)	1.36	0.59
			37	4.06(6)	1.48	0.62
Oxydiacetate	Li^+	10	12.5	0.66(3)	1.02	0.50
			25	0.70(3)	0.86	0.31
			37	0.71(4)	1.06	0.50
			48	0.82(4)	0.65	0.09
		11	12.5	3.85(6)	1.6	0.6
			25	3.91(6)	1.5	0.5
			37	3.93(7)	1.4	0.4
			48	4.08(8)	1.4	0.3
	Ni^+	10	12.5	0.33(5)	0.64	0.12
			25	0.34(4)	1.05	0.50
			37	0.51(4)	1.06	0.50
			48	0.66(5)	1.05	0.50
		11	12.5	3.6(2)	1.6	0.6
			25	3.5(2)	1.5	0.5
			37	3.8(2)	1.4	0.4
			48	4.0(1)	1.4	0.3
	K^+	10	12.5	0.22(5)	1.04	0.50
			25	0.25(4)	1.04	0.50
			37	0.31(4)	0.75	0.20
			48	0.49(5)	0.85	0.29
		11	12.5	3.5(2)	1.6	0.6
			25	3.5(2)	1.5	0.5
			37	3.5(2)	1.4	0.4
			48	3.9(2)	1.4	0.3

[a,b,c] See Table 1.

Equations (18)—(20) indicate that the activity coefficient of a single z-charged ion can be expressed, as a function of I, by equation (21). The validity of equations (18)—(20) has been discussed in previous papers mainly in connection with speciation problems,[16–20] where the possibility of calculating log β values, at the desired ionic strength using literature values, is of great importance. In this work we discuss the correctness of the current approach for the ionic strength dependence of activity

Table 3. Formation constants[a] for Ca^{2+} complexes at $I' = 0.25$ mol dm^{-3}

	pq[b]	T(°C)	log β_{pq}	C_{pq}[c]	$-D_{pq}$[c]
Acetate	10	10	0.59(4)	1.12	0.49
		25	0.57(1)	1.04	0.38
		35	0.61(1)	1.01	0.30
		45	0.70(2)	0.96	0.22
Salicylate	10	10	0.53(5)	0.99	0.42
		25	0.63(4)	0.98	0.40
		37	0.74(4)	0.98	0.39
		45	0.80(5)	0.96	0.37
Malonate	10	10	1.56(4)	1.87	0.85
		25	1.64(3)	2.01	0.85
		37	1.71(5)	2.19	0.85
		45	1.77(6)	2.1	0.8
	11	10	5.83(6)	2.12	0.90
		25	5.90(4)	2.26	0.90
		37	5.97(5)	2.4	0.90
		45	6.03(7)	2.3	0.8
Maleate	10	25	1.76(5)	2.48	0.93
	11	25	6.67(6)	2.6	1.0
Succinate	10	15	1.44(4)	1.80	0.74
		25	1.45(3)	1.82	0.80
		37	1.52(3)	1.49	0.51
		45	1.60(4)	1.37	0.43
	11	15	5.92(5)	2.18	0.90
		25	5.96(4)	2.14	0.90
		37	6.01(5)	2.09	0.90
		45	6.04(5)	2.06	0.90
Malate	10	10	1.97(4)	1.43	0.80
		25	1.95(3)	1.70	0.80
		37	1.90(4)	1.33	0.65
	11	10	5.81(6)	1.78	0.80
		25	5.72(5)	1.90	0.80
		37	5.66(6)	1.73	0.80
Tartrate	10	10	2.11(4)	1.57	0.90
		25	2.10(4)	1.49	0.85
		37	1.95(4)	1.49	0.80
	11	10	5.27(7)	1.92	0.90
		25	5.02(5)	1.72	0.85
		37	5.06(6)	1.78	0.80
Phthalate	10	25	1.71(5)	1.70	0.50
	11	25	5.70(6)	1.93	0.50
Oxydiacetate	10	12.5	3.57(4)	1.54	0.64
		25	3.46(3)	1.71	0.80
		37	3.44(3)	1.46	0.56
		48	3.41(4)	1.45	0.56
	11	12.5	6.6(1)	2.1	1.0
		25	6.38(5)	2.1	1.0
		37	6.34(6)	2.1	1.0
		48	6.38(6)	2.1	1.0
Glycinate	10	10	1.08(6)	0.61	0.37
		25	1.05(4)	0.66	0.40
		37	1.03(5)	0.55	0.40
	11	10	10.21(9)	0.58	0.16
		25	9.85(6)	0.71	0.27
		37	9.70(7)	0.58	0.20
L-Histidinate	10	10	0.88(7)	0.72	0.44
		25	0.95(7)	0.58	0.40
		37	1.0(1)	0.81	0.40
	11	10	9.80(8)	0.71	0.22
		25	9.35(8)	0.58	0.20
		37	9.2(1)	0.55	0.20
	12	10	16.1(2)	0.3	−0.2
		25	15.4(1)	0.25	−0.2
		37	15.0(2)	0.1	−0.2

[a,b,c] See Table 1.

$$\log \beta_{pq}(I) = \log \beta_{pq}(I') - z^*\left(\frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}}\right) + C_{pq}(I - I') + D_{pq}(I^{\frac{3}{2}} - I'^{\frac{3}{2}}) \quad (18)\dagger$$

$$C_{pq} = c_0 p^* + c_1 z^* \quad (19)$$

$$D_{pq} = dz^* \quad (20)$$

$$\log f = -z^2\left(\frac{\sqrt{I}}{2 + 3\sqrt{I}} - c_1 I - dI^{\frac{3}{2}}\right) + c_0 I \quad (21)$$

coefficients in connection with the rigorous determination of stability constants in systems where the constant ionic medium method cannot be followed.

Temperature Dependence of Formation Constants.—Though many equations have been proposed[26] for the dependence of formation constants on temperature, we have found[27] that the simple Taylor expansion [equation (22)] (θ = reference temperature, i = degree of the polynomial) can be used in all cases. The maximum value of i depends, of course, on the number of temperatures at which the system has been studied and on the accuracy of the log β values.

$$\log \beta_T = \log \beta_\theta + \sum_i \frac{1}{i!}(\partial^i \log \beta/\partial T^i)_\theta (T - \theta)^i \quad (22)$$

Results

Ligand Protonation and Alkali-metal Complexes.—In Table 1 the protonation constants of the ligands studied in this work are reported. The formation constants of the Na^+ and K^+ complexes (and, in some cases, the Li^+ complexes) are given in Table 2. The parameters C_{pq} and D_{pq}, for the dependence of log β on ionic strength, for each species are also reported in Tables 1 and 2. The monocarboxylate ligands form the complexes [MA] and the dicarboxylates form both $[MA]^-$ and [M(HA)]. For the amino acids glycine and histidine only the species $[K(HA)]^+$ (HA = glycine) is formed.‡ The stability of the M^+–carboxylate complexes is quite independent of the ligand. In fact, by considering log β_{10} for succinate, malonate,

† I' = reference ionic strength; $z^* = pz_M^2 + z_A^2 + q - (pz_M + z_A + q)^2$; C_{pq} and D_{pq} = adjustable parameters for each complex species; $p^* = p + q$ [in general p^* = (number of reactants) − (number of products)]; c_0, c_1, and d = adjustable parameters for all complex species.

‡ Rechnitz and Zamochnick[28] discovered the existence of a species [NaA] [A = alaninate(1−)] with $\beta_{10} = 0.2$ dm^3 mol^{-1}, but in our work we were unable to find the analogous species for glycine (either with Na^+ or K^+).

Table 4. Thermodynamic parameters[a] at 25 °C and I = 0 mol dm^{-3}

	M	pq[b]	log β_{pq}	$-\Delta G^{\circ}$	ΔH°	ΔS°
Acetate	H^+	01	4.74	27.0	0	91
	Li^+	10	0.29	1.6		
	Na^+	10	−0.11	−0.6	9	28
	K^+	10	−0.27	−1.5	5	12
	Ca^{2+}	10	0.93	5.3	3.5	30
Salicylate	H^+	01	2.93	16.7	−3	46
	Na^+	10	−0.31	−1.8		
	K^+	10	−0.31	−1.8	8	22
	Ca^{2+}	10	0.72	4.1	5	31
Malonate	H^+	01	5.70	32.5	5	126
		02	8.56	48.9	4	177
	Li^+[c]	10	1.31	7.8		
		11	6.16	36.6		
	Na^+	10	0.91	5.2	3	28
		11	5.66	32.3	9	139
	K^+	10	1.01	5.8	4	33
		11	5.82	33.2	11	148
	Ca^{2+}	10	2.39	13.6	7	69
		11	6.59	37.6	5	143
Maleate	H^+	01	6.33	36.1	4	134
		02	8.21	46.9	2	164
	Li^+[c]	10	1.23	7.3		
		11	6.32	37.6		
	Na^+[c]	10	1.18	7.0		
		11	6.43	38.2		
	K^+	10	1.15	6.6		
		11	6.42	36.6		
	Ca^{2+}	10	2.40	13.7		
		11	7.29	41.6		
Oxydiacetate	H^+	01	4.36	24.9	11	120
		02	7.33	41.8	7	164
	Li^+	10	1.10	6.3	4	35
		11	4.45	25.4	10	119
	Na^+	10	0.71	4.1	10	47
		11	4.04	23.1	19	144
	K^+	10	0.62	3.6	9	42
		11	4.04	23.1	5	94
	Ca^{2+}	10	4.28	24.4	−10	48
		11	7.12	40.7	−15	86
Succinate	H^+	01	5.64	32.2	1	111
		02	9.85	56.2	0	188
	Li^+[c]	10	1.09	6.5		
		11	5.93	35.2		
	Na^+	10	0.85	4.85	4	30
		11	5.79	33.1	4	124
	K^+	10	0.86	4.9	4	30
		11	5.82	33.2	3	121
	Ca^{2+}	10	2.24	12.8	10	76
		11	6.68	38.1	11	165
Malate	H^+	01	5.10	29.1	0	98
		02	8.57	48.9	−2	157
	Na^+	10	0.66	3.8	0	13
		11	5.25	30.0	1	104
	K^+	10	0.75	4.2	1	17
		11	5.05	28.8	3	107
	Ca^{2+}	10	2.77	15.8	−7	30
		11	6.49	37.0	−9	94
Tartrate	H^+	01	4.43	25.3	−4	71
		02	7.46	42.6	−6	123
	Na^+	10	1.00	5.7	1	22
		11	4.64	26.5	1	92
	Ca^{2+}	10	2.98	17.0	−9	27
		11	5.84	33.3	−12	71
Phthalate	H^+	01	5.40	30.8	4	117
		02	8.36	47.7	11	197
	Li^+[c]	10	1.14	6.8		
		11	5.48	32.5		
	Na^+	10	1.02	5.8	1	23
		11	5.42	31.0	2	111
	K^+	10	1.12	6.4	1	25
		11	5.62	32.1	8	134
	Ca^{2+}	10	2.49	14.2		
		11	6.42	36.7		
Glycinate	H^+	01	9.75	55.6	−41	49
		02	12.08	69.0	−44	84
	K^+[c]	11	8.90	52.8		
	Ca^{2+}	10	1.51	8.6	−2	22
		11	9.99	57.0	−31	87
L-Histidinate	H^+	01	9.27	52.9	−42	37
		02	15.24	87.0	−69	60
		03	16.69	95.2	−68	91
	K^+[c]	12	8.44	50.1		
	Ca^{2+}	10	1.43	8.1	5	44
		11	9.52	54.3	−36	61
		12	15.03	85.8	−66	66

[a] $-\Delta G^{\circ}$ and ΔH° are expressed in kJ mol^{-1}; ΔS° in J K^{-1} mol^{-1}. [b] The indexes pq refer to the reaction: $pM + A + qH \rightleftharpoons [M_pAH_q]$. [c] At 37 °C.

maleate, phthalate, oxydiacetate, tartrate, and malate (see Table 4) we obtain (at I = 0 mol dm^{-3} and T = 37 °C) the mean values of 0.95 ± 0.2, 0.93 ± 0.15, and 1.17 ± 0.15 for the K^+, Na^+, and Li^+ complexes respectively. Furthermore, by considering log $K^{M}_{M(HA)}$ {for the reaction $M^+ + HA^- \rightleftharpoons [M(HA)]$} for the dicarboxylate ligands and log β_{10} for acetate and salicylate we obtain the mean values (at I = 0 mol dm^{-3} and T = 37 °C) of 0.02 ± 0.2, 0.02 ± 0.15, and 0.18 ± 0.15 for the K^+, Na^+, and Li^+ complexes respectively. The complex species $[K(HA)]^+$ (HA = glycine) is less stable [log $K^{M}_{M(HA)} = -0.5$], due, probably, to the presence of the positive charge in the zwitterionic form of the ligand (see similar considerations for calcium complexes). This also accounts for the absence of alkali-metal complexes of histidine, since this ligand is also zwitterionic. The ΔH° and ΔS° values, reported in Table 4, show that alkali-metal complexes are stabilized entropically.

Ca^{2+} *Complexes.*—The monocarboxylate ligands form the complexes $[CaA]^+$, the dicarboxylates form [CaA] and $[Ca(HA)]^+$, and glycine and histidine form $[CaA]^+$ and $[Ca(HA)]^{2+}$ (L-histidine also forms the species $[Ca(H_2A)]^{3+}$). The formation constants (and the parameters for the dependence of log β on ionic strength) of the calcium(II) complexes are given in Table 3. The ΔH° and ΔS° values are given in Table 4.

As regards the Ca^{2+} complexes of protonated dicarboxylate ligands, the formation constants, log $K^{Ca}_{Ca(HA)}$, for the reaction $Ca^{2+} + HA^- \rightleftharpoons [Ca(HA)]^+$ are 0.89, 1.02, 0.96, and 1.04 for malonate, phthalate, maleate, and succinate respectively (at $I = 0$ mol dm^{-3} and $T = 25$ °C). These values are similar, with a mean value of 0.98 ± 0.09, and are close to the log β_{10} value of 0.93 for $[CaA]^+$ (A = acetate): this suggests that the Ca^{2+}–carboxylate binding is independent, as a first approximation, of the ligand involved. The same considerations are not true however for malate, tartrate, and oxydiacetate [log $K^{Ca}_{Ca(HA)}$ = 1.39, 1.41, and 2.76 respectively] for which other oxygen containing groups are effective in the co-ordination. The order of stability of the 1:1 Ca^{2+}–carboxylate complexes ([Ca(succinate)]^0 < [Ca(malonate)]^0 < [Ca(oxalate)]^0; log β_{10}(oxalate) = 3.27 at $I = 0$ mol dm^{-3} and $T = 37$ °C[29]) suggests a chelate effect. Furthermore, log β_{10} values of 2.39, 2.49, and 2.40 (mean 2.43 ± 0.06) for malonate, phthalate, and maleate respectively, suggest a binding independent of the ligand when the chelate ring is of the same size. The higher stability of the complexes [CaA] [A = tartrate(2−) or malate(2−)] can be attributed to the presence of OH groups, as in the complexes where the carboxylate groups are protonated. The effect of an ethereal oxygen seems to be particular in enhancing the stability of the complex [CaA] [A = oxydiacetate(2−)], probably through the formation of the two chelate rings. For the amino acids (glycine and L-histidine) log β_{10} values of 1.51 and 1.43 and log $K^{Ca}_{Ca(HA)}$ values of 0.24 and 0.25 (at $I = 0$ mol dm^{-3} and $T = 25$ °C) for glycine and L-histidine respectively, clearly indicate glycine-like co-ordination (N,O) for the 1:1 complexes $[CaA]^+$ $\{[Ca(HA)]^{2+}$ complexes are fairly destabilized with respect to the analogous complexes of dicarboxylate ligands, $[Ca(HA)]^+$, due, probably, to the positive charge on the amino acids}.

From the dependence on temperature of stability constants, estimates were obtained for ΔH° and ΔS° (Table 4). Although they are rather inaccurate due to the lack of data (three or four temperatures) and to the short temperature range studied, they indicate some interesting trends. The ΔH° values are slightly endothermic for the 1:1 complexes [CaA] where A = malonate(2−) or succinate(2−) (~8 kJ mol^{-1}) and slightly exothermic (~ −9 kJ mol^{-1}) for malate(2−), tartrate(2−), and oxydiacetate(2−). This behaviour is also found for complexes of the protonated ligands and confirms the above considerations concerning the influence of OH or ethereal-oxygen groups. For the amino acids, the ΔH° values for the complexes of the unprotonated ligands are close to zero while ΔH° values for the reaction $Ca^{2+} + HA \rightleftharpoons [Ca(HA)]^{2+}$ are slightly endothermic (~8 kJ mol^{-1}) as in the case of simple dicarboxylate ligands (~6 kJ mol^{-1}) for the same reaction, *i.e.* $Ca^{2+} + HA^- \rightleftharpoons [Ca(HA)]^+$.

On the basis of the above findings, it is possible to find general equations for the stability of a series of similar ligands. These could be of great importance in chemical modelling of large aqueous natural systems.

Ionic Strength Dependence of Thermodynamic Parameters.—The parameters C_{pq} and D_{pq} of equation (18) are reported in Tables 1—3 for each species. Since our hypothesis is that, in the range $0 < I \leqslant 1$ mol dm^{-3}, the dependence on ionic strength of activity coefficients is the same,* it should be possible to express these parameters by equations (19) and (20). By considering the values of C_{pq} and D_{pq} for the species reported here we found:† $c_0 = 0.18$, $\partial c_0/\partial T = -1.1 \times 10^{-3}$; $c_1 = 0.208 \pm 0.005$, $\partial c_1/\partial T = -0.3 \times 10^{-3}$; and $d = -0.10$, $\partial d/\partial T = 0.9 \times 10^{-3}$. Using the above values, the conversion equations (23) and (24) can be written for the thermodynamic

$$\log \beta(I) = \log \beta(I') - z^*\left(\frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}}\right) + \{[0.18 - 1.1 \times 10^{-3}(T - 25)]p^* + [0.208 - 0.3 \times 10^{-3}(T - 25)z^*]\}(I - I') - [0.1 - 0.9 \times 10^{-3}(T - 25)](I^{\frac{1}{2}} - I'^{\frac{1}{2}}) \quad (23)$$

$$\Delta H^\circ(I) = \Delta H^\circ(I') - 1.87\, p^*\,(I - I') - 0.51\, z^*(I - I') + 1.53(I^{\frac{1}{2}} - I'^{\frac{1}{2}}) \quad (24)$$

parameters. Equation (24) must be used with care, since the temperature coefficients are affected by a large error.

Discussion

We will discuss the validity of the present method of determining the stability of weak complexes on the basis of three questions. (*a*) Are the errors arising from the use of the proposed model for the ionic strength dependence of formation constants compatible with a correct calculation of thermodynamic parameters?; (*b*) are the proposed calculation methods rigorous? (*i.e.*, does the drastic reduction of experimental data from several e.m.f. values to β_{0q} values lead to further errors or not?); (*c*) are the experimental thermodynamic parameters comparable to literature values obtained using different experimental and calculation methods?

As regards question (*a*), we can rewrite equation (18) ($\sqrt{I} = J$) as either (25) or (26) [log $^T\beta$ (thermodynamic infinite dilution) is referred to $I = 0$ mol dm^{-3}]. By taking into account the errors in J and $L(J)$, variance propagation leads to equation ‡ (27), or, by taking into account equations (18)—(20), to equations (28) and (29). Since the error in J (due to small uncertainties in the analytical concentrations and to errors in calculating free concentrations from formation constants affected, in turn, by the inherent error) does not exceed 2% (*i.e.* $\sigma_J^2 = 4J^2 \times 10^{-4}$), equation (29) can be written as (30). If we

$$\log \beta = \log {}^T\beta - z^*J/(2 + 3J) + CJ^2 + DJ^3 \quad (25)$$

$$\log \beta = \log {}^T\beta - z^*J/(2 + 3J) + L(J) \quad (26)$$

$$\sigma^2_{\log \beta} = \left\{\left[\frac{-2z^*}{(2 + 3J)^2} + \frac{\partial L(J)}{\partial J}\right]^2 \sigma_J^2 + \left[\frac{\partial L(J)}{\partial C}\right]^2 \sigma_C^2 \right. \quad (27)$$

$$L(J) = (p^*c_0 + z^*c_1)J^2 + dz^*J^3 \quad (28)$$

$$\left.\sigma^2_{\log \beta} = \left\{\left[\frac{-2z^*}{(2 + 3J)^2} + 2(p^*c_0 + z^*c_1)J + 3dz^*J^2\right]^2 \sigma_J^2 + (z^*J^2)^2\, \sigma^2_{c_1}\right\} \right. \quad (29)$$

* This statement, of course, is valid only within experimental errors and assuming the correct determination of the species present in the system under study and hence of the correct calculation of the thermodynamic formation parameters (see Discussion section).

† The errors for c_0 and d are not reported because of the strong correlation among c_0, c_1, and d; in the simultaneous calculation, c_0 and d were kept constant and the error in c_1 was thus found. This procedure allows a simple discussion of the errors (see next section). A rigorous treatment of errors would imply many more calculations without obtaining substantially different results. Temperature coefficients are affected by an error of ~30—50%.

‡ The more important terms in equations (25) and (28) are C and c_1 respectively; therefore in the error propagation we considered the standard deviation on these parameters only.

Table 5. Details of six simulations

(*a*) Species and log formation constants used in simulating titration curves

	System						
	1	2	3	4	5	6	pq[a]
log β	6.00	4.00	6.00	6.00	4.00	5.00	01
	9.00	7.00	9.00	9.00	7.00	7.50	02
	0.30	0.80	0.80	1.00	2.00	1.50	10
	6.00	4.30	6.30	6.80	5.00	5.50	11
						2.00	20

(*b*) Conditional protonation constants calculated from simulated titration curves

		log β′$_{01}$					log β′$_{02}$				
	C_M =	0.04	0.16	0.36	0.64	1.	0.04	0.16	0.36	0.64	1.
System	1	5.98		5.90	5.86	5.82	8.96		8.76_5	8.64	8.52
	2	3.94	3.82	3.72	3.66	3.61	6.91	6.70	6.48_5	6.30	6.13_5
	3	5.93_5	5.82	5.72	5.65_5	5.61	8.90	8.70	8.48	8.29_5	8.13
	4	5.95	5.89	5.85	5.83		8.85	8.59	8.33_5	8.13	
	5	3.46	3.19	3.09_5	3.05	3.03_5	6.31	5.78	5.43_5	5.19	4.99_5
	6	4.67	4.25	3.93	3.69	3.50	7.12	6.57	6.10	5.71	5.38

(*c*) Log formation constants calculated from conditional protonation constants

	System						
	1	2	3	4	5	6	pq[a]
log β	6.00	4.01	6.00	6.00	4.05	4.99	01
	8.99	7.01	9.00	9.00	7.04	7.49	02
	0.29	0.81	0.81	1.00	2.03	1.48	10
	5.99	4.31	6.30	6.79	5.03	5.49	11
						1.99	20

[a] See footnote *b* of Table 1.

$$\sigma^2_{\log\beta} = J^2\left\{4 \times 10^{-4}\left[\frac{-2z^*}{(2+3J)^2} + 2(p^*c_0 + z^*c_1)J + 3z^*dJ^2\right]^2 + J^2(z^*)^2\,\sigma^2_{c_1}\right\} \quad (30)$$

accept the criterion $3\sigma_\beta \leqslant \beta$ (*i.e.* $\sigma^2_{\log\beta} \leqslant 0.02$) for which the constants, and therefore the species, are significant, from (30) we can calculate the maximum value of $\sigma^2_{c_1}$ as a function of J, z^*, and p^*. For example, for $z^* = 8$ and $p^* = 1$ (calcium complexes, [CaA], of dicarboxylate ligands), at $J = 1$ (maximum value of J for which the present model for the dependence of formation constants should be valid) we have $(\sigma_{c_1})_{\lim} \sim 2 \times 10^{-2}$. Since the value of c_1 at $T = 25$ °C found for all the complexes studied here is 0.208 ± 0.005, we can conclude that the adopted method is valid, and therefore the answer to question (*a*) is affirmative.

As regards question (*b*), we performed several calculations by simulating various conditions, as reported in Table 5. The procedure was: (*i*) calculation of the titration curve from values of β_{pq}, C_M and C_A [Table 5(*a*)] by using the computer program ES4EC;[30] (*b*) calculation of β'_{0p} by the computer program ESAB[25] [Table 5(*b*)]; (*c*) recalculation of β_{pq} from β'_{pq} values, using the program ES2WC* [Table 5(*c*)]. The method of Appendix A, using the non-linear least-squares program WECO,[31] has been tested previously[15,31] with monoprotic acids. In all cases we were able to reproduce β_{pq} values, and therefore the present calculation method is correct. Moreover it must be observed that the proposed method considerably reduces the number of data required for calculating β_{pq} and that the calculation of β'_{0q} corresponds to a preliminary smoothing of v (titrant volume)–E (e.m.f.) curve with a lowering of experimental noise.

As regards question (*c*), comparison with literature data[31] shows satisfactory agreement, even though the amount of reported thermodynamic parameters available, in particular for alkali-metal complexes, is not as large as desired.

* C. Rigano and S. Sammartano, ES2WC, a computer program based on the method described in Appendix B.

Appendix A

Equations (6)—(8) can be written by (1A), the equation of a

$$1/\beta'_{01} = 1/\beta_{01} + \beta_{10}m/\beta_{01} \quad (1A)$$

straight line, where $1/\beta_{01}$ = intercept and β_{10}/β_{01} = slope. If $C_M \gg C_A$ (*e.g.* $C_M > 100\ C_A$) we can assume that $m = C_M$ otherwise with a simple iterative method m can be calculated from an initial estimate of β_{10}. This is the simplest method for calculating β_{10} and β_{01} when dealing with monoprotic acids or with polyprotic acids with very separate protonation steps, and where only one complex species is formed.

β_{01} and β_{10} can also be calculated by using WECO,[31] a computer program that refines the formation constants, together with the parameters for the dependence on temperature and on ionic strength [see equations (18)—(20)], by minimizing the errors squares sum (2A).

$$U = \Sigma[(\log\beta'_{01})_{exp} - (\log\beta'_{01})_{calc}]^2 \quad (2A)$$

Often, the cation of the strong base (M_1) added during the titrations forms weak complexes with the ligand under study. In

these cases a correction can be made, by considering that $C_{M_1} \ll C_M$ and $\beta_{10}^{M_1} m_1 \ll 1$, using equation (3A), where

$$\log \beta'_{01} = \log \beta''_{01} + [0.43\ \beta_{10}^{M_1} m_1/(1 + \beta_{10} m)] \quad (3A)$$

β''_{01} is the protonation constant calculated without allowing for the lowering effect of both M and M_1.

Appendix B

The two sides of equation (17) can be written as (1B) and (2B),

$$\bar{p}_{exp} = \Sigma q \beta'_{0q} h^q/(1 + \Sigma \beta'_{0q} h^q) \quad (1B)$$

$$\bar{p}_{calc} = \Sigma q \beta_{pq} m^p h^q/(1 + \Sigma \beta_{pq} m^p h^q) \quad (2B)$$

where $\bar{p}$ is the average number of protons bound to the ligand. By minimizing the function (3B) we can calculate values of β_{pq}.

$$U = \Sigma(\bar{p}_{exp} - \bar{p}_{calc})^2 \quad (3B)$$

The values of h can be chosen arbitrarily. By taking into account the characteristics of the titration curves, we have chosen either (4B) or (5B) and (6B) when $\beta'_{00} = 1$. In other words, in

$$h_1 = 1/\beta'_{01},\ h_2 = (\beta'_{02})^{-\frac{1}{2}},\ h_3 = \beta'_{01}/\beta'_{02} \ldots \quad (4B)$$

$$h_k = \beta'_{0(k-1)/2}/\beta'_{0(k+1)/2} \qquad k \text{ odd} \quad (5B)$$

$$h_k = [\beta'_{0(k+2)/2}/\beta'_{0(k-2)/2}]^{-\frac{1}{2}} \qquad k \text{ even} \quad (6B)$$

calculating the differences between the protonation curves in the presence and absence of complexing metal ions we chose the maximum buffer power and inflection points, represented, approximately, by the values of (4B)—(6B). During this and other work [14,15] we investigated the possibility of using other values of h_k or the eventual need to use a greater number of h values (and therefore a greater number of $\bar{p}$ values in the calculation); invariably, the described choice has been demonstrated to be the better one by simulated experiments.

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