THERMODYNAMICS OF FORMATION OF MAGNESIUM(II), CALCIUM(II), STRONTIUM(II) AND BARIUM(II)–SUCCINATE COMPLEXES IN AQUEOUS SOLUTION

ALESSANDRO DE ROBERTIS, CONCETTA DE STEFANO
and ROSARIO SCARCELLA

Istituto di Chimica Analitica dell'Università, via dei Verdi, 98100 Messina (Italy)

CARMELO RIGANO

Seminario Matematico dell'Università, viale A. Doria 6, 95125 Catania (Italy)

(Received 21 March 1984)

ABSTRACT

The formation constants for the complexes Mg^{2+} –, Ca^{2+} –, Sr^{2+} – and Ba^{2+} – succinate ($succ^{2-}$) have been determined by potentiometric measurements, in aqueous solution, at different temperatures and ionic strengths. The species $[M(succ)]^0$ and $[M(succ)H]^+$ were found for all systems. For the stability constant the ionic strength dependence has been found, and general parameters for the relation $\log \beta = f(I)$ have been obtained. From the temperature dependence of stability constants ΔH values have been deduced. The procedure adopted in calculating all the thermodynamic parameters for the systems under study, where weak complexes are formed, is discussed. The stability of the complexes follows the order $Mg < Ca > Sr \approx Ba$.

INTRODUCTION

The literature data [1–10] concerning the complexes of succinate ($succ^{2-}$) with bivalent cations such as magnesium, calcium, strontium and barium (M^{2+}) are very few; in particular, the dependence of the stability constants on the temperature and ionic strength has not been studied.

By considering the remarkable role and interest that many carboxylic acids and related complexes play in natural fluids, we believed it very important to define the correct speciation of these systems in a wide range of I, T conditions.

Therefore, this paper reports a potentiometric study on the complexes of succinic acid with magnesium, calcium, strontium and barium cations at various temperatures ($t = 15$, 25, 37 and 45 °C) and ionic strengths ($I = 0.06$, 0.15, 0.45 and 1.0 mol l^{-1}) in order to calculate: (a) the protonation constants of succinate ion; (b) the complex formation constants between

TABLE 1

Some experimental conditions and protonation constants [d]

Run	$t\,(^\circ C)$	M	$C_M^{0\,e}$	$\log K_1^{H'}$	$\log K_2^{H'}$	$\bar{I}^{\,f}$	$\log K_1^{H\,g}$	$\log K_2^{H\,g}$	Potentiometric equipment [h]
1–1'	15	Mg	19.9	5.169(7)	4.013(4)	0.065	5.335(6)	4.079(5)	b
2–2'			49.8	5.061(6)	3.952(3)	0.14	5.278(5)	4.061(4)	b
3–3'			149	4.914(5)	3.862(3)	0.40	5.292(5)	4.108(4)	b
4–4'			330	4.808(4)	3.795(3)	0.88	5.430(5)	4.266(4)	b
5		Ca	19.9	5.138(9)	3.998(5)	0.065			b
6			50.5	5.029(5)	3.940(3)	0.14			b
7			150	4.878(5)	3.840(3)	0.4			b
8			330	4.771(5)	3.767(3)	0.88			b
9		Sr	19.2	5.200(6)	4.024(3)	0.065			b
10			50.6	5.079(5)	3.955(3)	0.14			b
11			150	4.941(4)	3.867(3)	0.4			b
12			330	4.861(5)	3.805(3)	0.88			b
13		Ba	20.4	5.190(6)	4.017(3)	0.065			b
14			49.4	5.083(5)	3.952(3)	0.14			b
15			150	4.952(4)	3.862(3)	0.4			b
16			330	4.879(4)	3.806(3)	0.88			b
17		Mg	19.9						
		Ca	19.9	4.996(5)	3.908(3)	0.22			b
		Sr	19.2						
		Ba	20.4						
18		Mg	83						
		Ca	82.6	4.833(5)	3.797(3)	0.88			b
		Sr	83.7						
		Ba	83.4						
19–19'	25	Mg	19.9	5.201(3)	4.006(2)	0.065	5.333(5)	4.059(3)	c
20–20'			49.7	5.073(5)	3.940(3)	0.14	5.271(4)	4.041(3)	c
21–21'			149	4.887(5)	3.829(3)	0.4	5.274(4)	4.081(3)	c
22–22'			329.5	4.811(5)	3.768(3)	0.88	5.395(4)	4.245(3)	c
23		Sr	19.1	5.214(4)	4.010(3)	0.065			c
24			50.5	5.090(3)	3.939(2)	0.14			c
25			150	4.965(4)	3.857(3)	0.4			c
26			329	4.853(3)	3.782(2)	0.88			c
27		Ba	20.4	5.209(5)	4.001(3)	0.065			c
28			49.3	5.090(4)	3.937(3)	0.14			c
29			149.5	4.946(4)	3.840(2)	0.4			c
30			329.5	4.854(3)	3.777(2)	0.88			c

[d] In all the experiments $C_{succ}^0 = C_{HCl}^0 = 5$ mmol l^{-1} (initial analytical concentrations).

[e] Initial analytical concentration of M^{2+} in mmol l^{-1}.

[f] Mean ionic strength (during the titration) in mol l^{-1}.

[g] Protonation constants determined in presence of tetraethylammonium iodide at the same temperature and ionic strength as the solutions containing M^{2+} ($C_{Et_4N} = 3\,C_M$).

[h] See Experimental section.

Run	t (°C)	M	C_M^0 [e]	$\log K_1^{H'}$	$\log K_2^{H'}$	$\bar{I}$ [f]	$\log K_1^{H}$ [g]	$\log K_2^{H}$ [g]	Potentiometric equipment [h]
	25	Mg	19.9						
31		Ca	19.8	5.001(5)	3.890(3)	0.22			c
		Sr	19.2						
		Ba	20.4						
		Mg	82.8						
32		Ca	82.4	4.825(5)	3.775(3)	0.88			c
		Sr	83.6						
		Ba	83.3						
33–33′	37	Mg	148	4.835(12)	3.803(6)	0.4	5.279(6)	4.075(4)	a
34		Ca	149	4.813(5)	3.779(3)	0.4			a
35		Sr	149	4.900(6)	3.814(3)	0.4			a
36		Ba	149	4.894(5)	3.808(3)	0.4			a
37–37′	45	Mg	19.7	5.148(12)	3.970(7)	0.065	5.360(6)	4.043(5)	b
38–38′			49.3	4.996(5)	3.890(3)	0.14	5.295(6)	4.027(4)	b
39–39′			148	4.830(12)	3.776(6)	0.4	5.278(6)	4.069(4)	b
40–40′			327	4.724(8)	3.796(5)	0.88	5.363(6)	4.227(4)	b
41		Ca	19.7	5.131(8)	3.955(4)	0.065			b
42			50.0	4.996(3)	3.888(2)	0.14			b
43			148.5	4.779(5)	3.760(3)	0.4			b
44			327	4.666(5)	3.670(3)	0.88			b
45		Sr	19.0	5.219(4)	3.989(3)	0.065			c
46			50.1	5.037(4)	3.893(3)	0.14			c
47			149	4.962(6)	3.832(4)	0.4			c
48			327	4.815(7)	3.740(4)	0.88			c
49		Ba	20.3	5.227(5)	3.978(3)	0.065			c
50			48.9	5.059(6)	3.897(3)	0.14			c
51			148.5	4.942(4)	3.810(3)	0.4			c
52			327	4.825(4)	3.744(2)	0.88			c
		Mg	19.7						
53		Ca	19.7	4.988(3)	3.863(2)	0.22			c
		Sr	19.0						
		Ba	20.3						
		Mg	82.2						
54		Ca	81.9	4.772(6)	3.719(4)	0.88			c
		Sr	83.0						
		Ba	82.7						

[g] Protonation constants determined in presence of tetraethylammonium iodide at the same temperature and ionic strength as the solutions containing M^{2+} ($C_{Et_4N} = 3\ C_M$).

[h] See Experimental section.

succ^{2-} (and Hsucc$^-$) and M^{2+} cations; (c) the dependence of these parameters on temperature and ionic strength.

EXPERIMENTAL

Materials

Succinic acid (H$_2$succ, Fluka puriss. p.a.) was used without further purification; the purity was tested by alkalimetric titrations and was found to be > 99.5%. Magnesium, calcium, strontium and barium chlorides (Fluka purum p.a.) were standardized by EDTA titrations [11]. HCl and NaOH solutions were prepared by diluting concentrated ampoules (BDH); NaOH was also standardized against potassium biphthalate (Fluka puriss. p.a.). Tetraethylammonium iodide (Et$_4$NI, Fluka puriss.) was recrystallized from methanol. All solutions were preserved from atmospheric CO$_2$ by utilizing soda lime traps. Grade A glassware and twice-distilled water were employed for all the solutions.

Apparatus

In order to measure the free concentration of the hydrogen ion, c_H, three different potentiometric systems were employed: (a) Orion potentiometer (model 801 A); (b) Metrohm potentiometer (model E 600); (c) semi-automatic home-made potentiometer built with Analog Devices millivoltmeter, Printel printer and Mostek logic circuits in order to add a preordinate volume of titrant and to print the corresponding value of potential. The use of different equipment ensured the avoidance of systematic errors. The potentiometers were coupled with glass-saturated calomel electrodes supplied by Metrohm. In all cases, the instrumental resolution was ± 0.1 mV. The titrant solution of NaOH was always delivered by an Amel dispenser (model 882; minimum reading 0.001 cm^3). The electrode couples were systematically calibrated in $-\log c_H$ units (pH) by titrating hydrochloric acid (5 mmol l^{-1}) added to any solution of M^{2+}–H$_2$succ under study [10]. In the calculations, the pK_w values of ref. 17 were used.

Procedure

A 30 cm^3 sample of the solution under study was thermostated at $t \pm 0.2°$C and a stream of purified N$_2$ was allowed to flow through the solution in order to exclude CO$_2$ and O$_2$. Magnetic stirring was employed. The solution was then titrated with standard 0.1 mol l^{-1} NaOH up to ~ 90% of the neutralization. Some experimental details are reported in Table 1. No substantial differences were noted in response between the different equip-

ment. The statistical parameters R-factor [12], standard deviation and mean deviation in the titrant volume, σ_v and ϵ_v, were as follows:

t (°C)	Equipment	$\bar{R}$ (%)	$\bar{\sigma}_v$ (10^3 cm^3)	$\bar{\epsilon}_v$ (10^3 cm^3)
15	(b)	0.073	0.0027	0.0021
25	(c)	0.055	0.0021	0.0015
37	(a)	0.091	0.0037	0.0026
45	(b)	0.088	0.0029	0.0024
45	(c)	0.075	0.0028	0.0022

CALCULATIONS AND RESULTS

The calculations were performed in two steps. (The data for the Ca^{2+}–succinate system at 25°C previously reported [10] were also taken into account.) (1) Using the computer program ESAB [13], the succinate protonation constants were calculated without allowing for M^{2+}-complex formation. The protonation constants of Et_4N^+ solution are markedly higher than those obtained from M^{2+} solutions, and this indicates complexation. In Table 1 the results of these calculations are reported. (2) The protonation constants in Et_4NI and the "conditional" protonation constants in M^{2+} chlorides were used together in minimizing the following function in order to determine the formation constants, β_{pq}

$$U = \sum \left(\bar{p}_{exp} - \bar{p}_{calcd} \right)^2 \tag{1}$$

where $\bar{p}$ = average number of protons bound to the ligand, and

$$\bar{p}_{exp} = \frac{\sum q\beta'_{0q}c_H^q}{1 + \sum \beta'_{0q}c_H^q} \tag{2}$$

where c = free concentration, β'_{0q} = protonation constant calculated without allowing for M^{2+} complex formation $\equiv K_q^{H'}$, and

$$\bar{p}_{calcd} = \frac{\sum q\beta_{pq}c_M^p c_H^q}{1 + \sum \beta_{pq}c_M^p c_H^q} \tag{3}$$

where $\beta_{pq} = c_{[M_pLH_q]}c_M^{-p}c_H^{-q}$, $\beta_{0q} = K_q^H$. The c_H values in eqns. (2) and (3) can be chosen arbitrarily, taking into account the characteristics of the titration curve. We found that for a diprotic acid that can form [ML] and [MHL] complexes the values $c_H = 1/\beta'_{01}$, $c_H = \beta'_{01}/\beta'_{02}$ and $c_H = (\beta'_{02})^{1/2}$ are sufficient. In this manner the amount of experimental data reduces to $3M$ (M = number of titrations), instead of $N \times M$ (N = number of potentiometric readings for each titration). This procedure corresponds, as a first approximation, to a preliminary smoothing of the data (calculation of β'_{0q}) and a subsequent calculation of the system parameters using a few significant smoothed values.

TABLE 2

Thermodynamic parameters for the formation of Mg^{2+} –, Ca^{2+} –, Sr^{2+} –, Ba^{2+} – succinate complexes [a]

t	I	$\log \beta_{01}$	ΔH	ΔS	$\log \beta_{02}$	ΔH	ΔS	$\log \beta_{10}$	ΔH	ΔS	$\log \beta_{11}$	ΔH	ΔS	$\log \beta_{10}$	ΔH	ΔS	$\log \beta_{11}$	ΔH	ΔS
								Magnesium						*Calcium*					
15	0	5.63	−0.2	25	9.86	−0.9	42	2.15	0.5	11	6.60	1.0	34	2.22	0.5	12	6.65	2.2	38
25		5.63	0.3	27	9.84	−0.1	45	2.18	2.4	18	6.64	2.1	37	2.26	2.3	18	6.71	2.4	39
37		5.65	0.9	29	9.85	0.9	48	2.29	5.0	27	6.72	3.7	43	2.36	4.8	26	6.79	2.7	40
45		5.67	1.4	30	9.88	1.7	51	2.39	6.9	33	6.80	4.8	46	2.46	6.7	32	6.84	3.0	41
15	0.05	5.345	−0.3	23	9.43	−1.1	39	1.56	0.2	8	6.03	0.8	30	1.64	0.2	8	6.08	2.0	35
25		5.34	0.1	25	9.41	−0.3	42	1.59	2.1	14	6.06	1.9	34	1.66	2.0	14	6.13	2.2	35
37		5.355	0.8	27	9.42	0.7	45	1.68	4.7	23	6.13	3.4	39	1.76	4.5	23	6.20	2.5	36
45		5.37	1.3	29	9.44	1.5	48	1.79	6.7	29	6.20	4.5	43	1.85	6.4	29	6.24	2.7	27
15	0.1	5.29	−0.4	23	9.36	−1.2	39	1.45	0.0	7	5.93	0.6	29	1.52	0.0	7	5.98	1.8	34
25		5.29	0.0	24	9.34	−0.5	41	1.47	1.9	13	5.95	1.7	33	1.55	1.8	13	6.02	2.0	34
37		5.30	0.7	26	9.34	0.6	44	1.56	4.5	22	6.02	3.2	38	1.63	4.3	21	6.08	2.3	35
45		5.31	1.1	28	9.35	1.3	47	1.66	6.4	28	6.09	4.3	41	1.72	6.1	27	6.12	2.4	36
15	0.25	5.27	−0.7	22	9.34	−1.5	37	1.36	−0.4	5	5.87	0.1	27	1.44	−0.4	5	5.92	1.3	32
25		5.26	−0.2	23	9.31	−0.8	40	1.38	1.4	11	5.89	1.2	31	1.45	1.3	11	5.96	1.5	32
37		5.26	0.4	25	9.30	0.2	43	1.45	4.0	19	5.94	2.6	36	1.52	3.8	19	6.01	1.7	33
45		5.27	0.9	27	9.305	0.9	45	1.54	5.9	26	6.00	3.8	39	1.60	5.6	25	6.04	1.9	34
15	0.5	5.32	−0.9	21	9.44	−1.9	37	1.41	−0.9	3	5.98	−0.4	26	1.49	−0.9	4	6.03	0.9	31
25		5.30	−0.5	23	9.40	−1.2	39	1.41	0.9	10	5.98	0.7	30	1.49	0.8	10	6.05	1.0	31
37		5.30	0.1	25	9.38	−0.2	42	1.47	3.4	18	6.02	2.1	34	1.55	3.2	17	6.09	1.2	32
45		5.305	0.6	26	9.38	0.5	44	1.55	5.3	24	6.07	3.2	38	1.62	5.0	23	6.11	1.3	32
15	1.0	5.47	−1.0	22	9.73	−2.0	37	1.61	−1.1	4	6.28	−0.5	27	1.685	−1.1	4	6.33	0.7	31
25		5.45	−0.6	23	9.68	−1.3	40	1.60	0.7	10	6.28	0.5	30	1.68	0.6	10	6.35	0.8	32
37		5.45	0.0	25	9.66	−0.4	43	1.66	3.2	18	6.32	1.9	35	1.73	3.0	18	6.38	1.0	32
45		5.45	0.5	26	9.66	0.3	45	1.73	5.1	24	6.36	3.0	39	1.80	4.8	23	6.40	1.1	33

t	I	Strontium						Barium					
		$\log \beta_{10}$	ΔH	ΔS	$\log \beta_{11}$	ΔH	ΔS	$\log \beta_{10}$	ΔH	ΔS	$\log \beta_{11}$	ΔH	ΔS
15	0	2.08	0.2	10	6.58	1.1	34	2.07	1.7	16	6.59	1.7	36
25		2.10	1.4	14	6.62	1.6	36	2.12	2.0	17	6.64	1.9	37
37		2.165	3.1	20	6.67	2.3	38	2.185	2.4	18	6.69	2.1	37
45		2.23	4.4	24	6.72	2.8	39	2.23	2.7	19	6.73	2.3	38
15	0.05	1.50	-0.1	7	6.01	0.9	31	1.49	1.5	12	6.02	1.4	33
25		1.51	1.1	11	6.04	1.4	32	1.53	1.8	13	6.06	1.6	33
37		1.56	2.8	16	6.08	2.0	34	1.58	2.1	14	6.10	1.9	34
45		1.625	4.1	20	6.12	2.5	36	1.62	2.4	15	6.14	2.0	34
15	0.1	1.38	-0.3	5	5.90	0.7	30	1.37	1.3	11	5.91	1.2	31
25		1.39	0.9	9	5.93	1.2	31	1.41	1.6	12	5.95	1.4	32
37		1.44	2.6	15	5.97	1.8	33	1.46	1.9	13	5.99	1.6	33
45		1.50	3.8	19	6.00	2.3	35	1.495	2.2	14	6.02	1.8	33
15	0.25	1.30	-0.7	3	5.85	0.3	28	1.29	0.9	9	5.86	0.8	30
25		1.295	0.4	7	5.87	0.7	29	1.31	1.1	10	5.88	0.9	30
37		1.33	2.1	13	5.89	1.3	31	1.35	1.4	11	5.91	1.1	31
45		1.38	3.3	17	5.92	1.7	32	1.38	1.6	11	5.94	1.3	31
15	0.5	1.35	-1.2	2	5.96	-0.2	27	1.34	0.4	8	5.97	0.3	28
25		1.33	-0.1	6	5.96	0.2	28	1.35	0.6	8	5.98	0.4	29
37		1.35	1.5	11	5.97	0.7	30	1.37	0.9	9	5.99	0.6	29
45		1.39	2.7	15	5.99	1.1	31	1.39	1.1	10	6.01	0.7	30
15	1.0	1.54	-1.4	2	6.26	-0.4	27	1.53	0.2	8	6.27	0.2	29
25		1.52	-0.2	6	6.26	0.0	29	1.54	0.4	8	6.28	0.2	30
37		1.54	1.3	11	6.265	0.5	30	1.56	0.7	9	6.29	0.4	30
45		1.57	2.5	15	6.28	0.9	32	1.57	0.8	10	6.29	0.5	30

a t, °C; I, mol l⁻¹; ΔH, kcal mol⁻¹; ΔS, cal mol⁻¹ K⁻¹; $3\sigma(\log \beta_{01}) = 0.008$–$0.015$; $3\sigma(\log \beta_{02}) = 0.01$–$0.02$; $3\sigma(\log \beta_{10}) = 0.015$–$0.025$; $3\sigma(\log \beta_{11}) = 0.03$–$0.05$; $3\sigma(\Delta H_{01}) = 0.2$–$0.5$; $3\sigma(\Delta H_{02}) = 0.3$–$0.7$; $3\sigma(\Delta H_{10}) = 0.3$–$0.7$; $3\sigma(\Delta H_{11}) = 0.4$–$0.8$; $3\sigma(\Delta S_{01}) = 0.6$–$1.2$; $3\sigma(\Delta S_{02}) = 1$–$2$; $3\sigma(\Delta S_{10}) = 1$–$3$; $3\sigma(\Delta S_{11}) = 2$–$4$.

As described in previous works [14–17] the dependence of formation constants on temperature and ionic strength was determined using the following equations

$$\log \beta_t = \log \beta_\theta + \left(\frac{\partial \log \beta}{\partial T} \right)_\theta (t - \theta) + \frac{1}{2} \left(\frac{\partial \log \beta}{\partial T} \right)_\theta (t - \theta)^2 \qquad (4)$$

$$\log \beta_I = \log \beta_{I'} - z^* \left(\frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}} \right) + C(I - I')$$

$$+ D(I^{3/2} - I'^{3/2}) \qquad (5)$$

where I' and θ are the reference ionic strength and temperature, respectively; C and D are empirical parameters.

All calculations were performed by the least-squares computer program ES2WC [18]. For all systems under study, we found the species $[M(succ)]^0$ and $[M(Hsucc)]^+$; the species $[M_2(succ)]^{2+}$, already proposed for similar systems, proved not to be present; species with a ratio (succinate)/(metal ion) > 1 were not present in our experimental conditions, with the C_M/C_{succ} ratio consistently being much greater than 1.

In Table 2 the thermodynamic parameters for the formation of succinate–alkaline-earth complexes are reported, at several temperatures and ionic strengths.

DISCUSSION AND CONCLUSIONS

The results reported in Table 2 were obtained by assuming that all formation constants of the species in the system have the same dependence on ionic strength according to the equation

$$\log \beta_{pq}(I) = \log \beta_{pq}(I') - z^*_{pq} G(I, I') + L(I, I') \qquad (6)$$

where

$$G(I, I') = \frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}}$$

$$z^*_{pq} = pz^2_M + z^2_L + q - (pz_M + z_L + q)^2$$

$$L(I, I') = \left(p'c_0 + c_1 z^*_{pq} \right)(I - I') + dz^*_{pq}(I^{3/2} - I'^{3/2}) \qquad (7)$$

$p' = $ (No. of reactants) $-$ (No. of products)

In this work we found

$c_0 = 0.22$

$c_1 = 0.18 - 0.0018 \, (t - 25) \qquad (8)$

$d = -0.08 + 0.0013 \, (t - 25)$

TABLE 3

Comparison between experimental and calculated pH values for some titration curves

v (cm^3)	Titration 1			Titration 30			Titration 52		
	pH$_{exp}$	pH$_{calc}$	δpH	pH$_{exp}$	pH$_{calc}$	δpH	pH$_{exp}$	pH$_{calc}$	δpH
0.3	2.377	2.376	0.001	2.378	2.375	0.003	2.380	2.376	0.004
0.6	2.490	2.489	0.001	2.488	2.483	0.005	2.488	2.483	0.005
0.9	2.634	2.634	0.000	2.623	2.614	0.009	2.621	2.613	0.008
1.2	2.825	2.826	-0.001	2.791	2.777	0.014	2.785	2.772	0.013
1.5	3.075	3.079	-0.004	2.993	2.971	0.022	2.981	2.961	0.020
1.8	3.351	3.361	-0.010	3.210	3.180	0.020	3.190	3.165	0.025
2.1	3.598	3.612	-0.014	3.415	3.382	0.033	3.391	3.364	0.027
2.4	3.809	3.824	-0.015	3.600	3.568	0.028	3.574	3.549	0.026
2.7	3.996	4.010	-0.014	3.769	3.740	0.029	3.742	3.721	0.021
3.0	4.170	4.183	-0.013	3.928	3.904	0.024	3.902	3.886	0.016
3.3	4.339	4.341	-0.002	4.081	4.063	0.018	4.057	4.048	0.009
3.6	4.506	4.514	-0.008	4.233	4.221	0.012	4.210	4.209	0.001
3.9	4.673	4.683	-0.010	4.385	4.378	0.007	4.364	4.370	-0.006
4.2	4.842	4.849	-0.007	4.539	4.530	0.009	4.519	4.526	-0.007
4.5	5.013	5.020	-0.007	4.698	4.693	0.005	4.680	4.692	-0.012
4.8	5.193	5.199	-0.006	4.868	4.866	0.002	4.850	4.865	-0.015
5.1	5.392	5.399	-0.007	5.059	5.060	-0.001	5.039	5.057	-0.018
5.4	5.634	5.642	-0.008	5.294	5.297	-0.003	5.269	5.290	-0.021
5.7	5.994	6.006	-0.012	5.648	5.653	-0.005	5.605	5.627	-0.022
		$\overline{\delta pH}$ = -0.007			$\overline{\delta pH}$ = 0.012			$\overline{\delta pH}$ = 0.004	
		$\overline{|\delta pH|}$ = 0.007			$\overline{|\delta pH|}$ = 0.013			$\overline{|\delta pH|}$ = 0.014	

Is this procedure correct? Let us examine some calculation results. (a) By analyzing simultaneously all the experimental data (including solutions containing mixtures of metal ions), the standard deviation in $\bar{p}$ is $\sigma(\bar{p}) = 0.0093$ and the mean deviation $\epsilon(\bar{p}) = 0.0056$. The values of these statistical parameters obtained in refining simple systems without ionic strength and background variations are rarely lower than the above values. (b) The comparison between primary experimental data and calculated values (pH_{exp} and pH_{calcd}), if the procedure followed is not valid, should show significant and systematic deviations in particular when considering extreme cases (experimental conditions far from the mean). Therefore, we calculated for each titration curve the pH values using the formation constants obtained by the general equation (6) with the general parameters (8). The analysis of variance applied to the residuals, δpH, showed no significant differences among the titration curves. Table 3 reports these examples, regarding extreme conditions: (1) $M = Mg$, $t = 15°C$, $I = 0.065$ mol 1^{-1}; (2) $M = Mg + Ca + Sr + Ba$, $t = 25°C$, $I = 0.88$ mol 1^{-1}; (3) $M = Ba$, $t = 45°C$, $I = 0.88$ mol 1^{-1}. As can be seen, the fit is very good and we can assert that for low molecular ligands, in the range $0 < I \leqslant 1$ mol 1^{-1}, the procedure followed here is correct.

Furthermore, a methodological consideration must be added: once we had defined the possibility of using the same equations for the ionic strength dependence of all the formation constants and of using the simple second-order Taylor expansion for the dependence on temperature, with a relatively
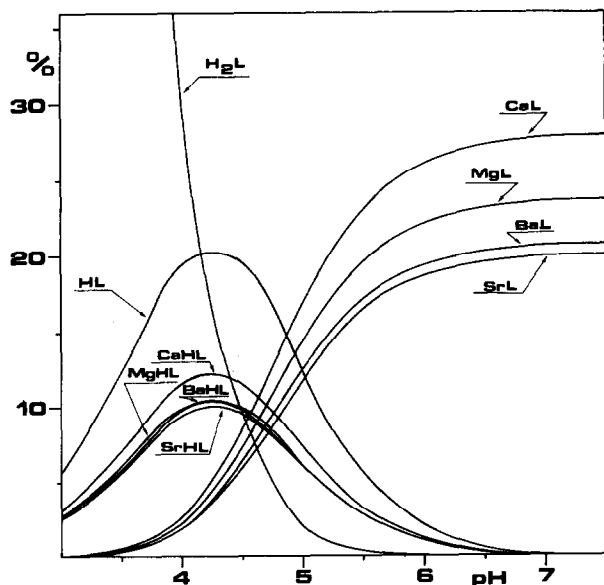

Fig. 1. Distribution of the species in the system H^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, $Ba^{2+}-succ^{2-}$ vs. pH, at $25°C$ and $I = 0.87$ mol 1^{-1}. $C_{succ} = 7.43$; $C_{Mg} = 82.8$; $C_{Ca} = 82.4$; $C_{Sr} = 83.6$; C_{Ba} 83.3 mmol 1^{-1}. The percentages are calculated with respect to the ligand.

low number of alkalimetric titrations (i.e., 63), we were able to define the stability characteristics of a 1 ligand–4 metal ions system in different temperature and ionic strength conditions. Finally, the calculation method used (eqns. 1–3), can be considered an exact method since no approximations were made in deriving the relationships.

In Fig. 1 the distribution of the species in a system containing the succinate and Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, vs. pH is reported.

The stability of the succinate–alkaline-earth metal complexes follows the order Mg < Ca > Sr ~ Ba. This order is the same shown by some hydroxy-carboxylic acids and polycarboxylic ligands. As regards ΔH and ΔS values, more systems have to be investigated in order to ascertain their structural significance.

The dependence on ionic strength of the thermodynamic parameters follows the same trend as some systems previously investigated [14–17, 19]. The comparison of the values assumed by the linear term in eqn. (7), using the general parameters (8) calculated in this work, or the parameters calculated previously [14–17], shows a very good agreement. Tentatively, the dependence on ionic strength of ΔH values can also be drawn from eqns. (6)–(8)

$$\Delta H(I) = \Delta H(I') + \ln 10RT10^{-6}\left[1.8(I - I') - 1.3(I^{3/2} - I'^{3/2})\right]$$

$$(\text{cal mol}^{-1}\,\text{K}^{-1}) \tag{9}$$

Equation (9) must be used with care, because the $\partial c_1/\partial T$ and $\partial d/\partial T$ terms are affected by a large error. Nevertheless, the trend shown by eqn. (9) is the same as that already found [20,21], and this confirms once again the validity of the proposed procedure.

REFERENCES

1 R.K. Cannan and A. Kibrick, J. Am. Chem. Soc., 60 (1938) 2314.
2 N.E. Topp and C.W. Davies, J. Chem. Soc., (1940) 87.
3 N.R. Joseph, J. Biol. Chem., 164 (1946) 529.
4 J. Schubert, J. Phys. Chem., 56 (1952) 113.
5 J.M. Peacock and J.C. James, J. Chem. Soc., (1951) 2233.
6 J. Schubert, J. Am. Chem. Soc., 76 (1954) 3442.
7 J. Schubert and A. Lindenbaum, J. Am. Chem. Soc., 74 (1952) 3529.
8 E. Gelles and R.H. Hay, J. Chem. Soc., (1958) 3673, 3684, 3689.
9 E. Campi, Ann. Chim. (Rome), 53 (1963) 96.

10 P.G. Daniele, A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 73 (1983) 619.

11 G. Schwarzenbach, Complexometric Titrations, Interscience, New York, 1957.

12 W.C. Hamilton, Statistics in Physical Science, Ronald Press, New York, 1964.

13 C. Rigano, M. Grasso and S. Sammartano, Ann. Chim. (Rome), 73 (1984) 537.

14 P.G. Daniele, C. Rigano and S. Sammartano, Talanta, 30 (1983) 81.

15 P.G. Daniele, C. Rigano and S. Sammartano, Transition Met. Chem., 7 (1982) 109.

16 P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 73 (1983) 741.

17 A. De Robertis, C. Rigano and S. Sammartano, Thermochim. Acta, 74 (1984) 343.

18 C. Rigano and S. Sammartano, work in progress.

19 P.G. Daniele, A. De Robertis, C. Rigano and S. Sammartano, work in progress.

20 P.G. Daniele, C. Rigano and S. Sammartano, Thermochim. Acta, 62 (1983) 101.

21 G. Arena, R. Purrello, S. Musumeci and S. Sammartano, Thermochim. Acta, 61 (1983) 129.