Thermochimica Acta, 72 (1984) 305–322
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALCIUM–MALONATE COMPLEXES IN AQUEOUS SOLUTION. THERMODYNAMIC PARAMETERS AND THEIR IONIC STRENGTH DEPENDENCE

PIER G. DANIELE

Istituto di Analisi Chimica Strumentale, Università di Torino, via Bidone 36, 10125 Torino (Italy)

ALESSANDRO DE ROBERTIS and SILVIO SAMMARTANO

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

CARMELO RIGANO

Seminario Matematico, Università di Catania, v.le A. Doria 6, 95125 Catania (Italy)

(Received 25 July 1983)

ABSTRACT

Formation constants of calcium complexes with malonate (mal^{2-}), in the ranges $10 \leqslant t \leqslant 50$°C and $0.05 \leqslant I \leqslant 0.9$ mol dm^{-3}, were determined by means of alkalimetric titrations in aqueous solution. The species found in this system were $[Ca(mal)]^0$ and $[Ca(Hmal)]^+$; also, the hydrolysis of Ca^{2+} was taken into account. The effect of ionic medium on the formation constants was studied by using different background salts (KNO_3, $NaNO_3$, Et_4NI and Et_4NBr); the parameters defining ionic strength dependence were calculated from the values of stability constants obtained at different ionic strengths. ΔH and ΔS values were obtained from temperature coefficients of stability constants.

A general equation, useful for correlating the formation constants in the studied temperature and ionic strength ranges, has been found. It has also been found that, by considering all the significant interactions in the solution, the formation constants are dependent on temperature and ionic strength only.

Literature data are discussed and compared with those obtained in this work.

INTRODUCTION

The calcium ion plays a fundamental role in all natural fluids, in which it is always present in more or less considerable amounts. Potassium and sodium, and in particular the latter, are also present both in biological fluids and in waters (seawater, riverwater, lakewater, etc.). Although these cations are obviously interesting from a practical point of view, the study of their complexes aroused little interest until recently [1]. This is for two reasons: (i) for a long time the interactions between these metals and ligands of different nature were explained with electrostatic models; and (ii) also, their low stability (in particular with regard to alkali metals) makes it hard to determine stability constants experimentally.

However, it is known that these metals appear in biological fluids, often as complexes, and, in most cases, the biological activity is due to the type of complex formed. Furthermore, the complexation of these cations involves a considerable lowering of the ionic strength, which may change the model systems substantially. For example, neglecting the formation of ion pairs, seawater ionic strength is $I = 0.72$ mol kg^{-1}, whilst, taking into account ionic interactions, Johnson and Pytkowicz [2] calculated $I = 0.53$ mol kg^{-1}.

The main difficulty concerning the determination of stability constants of alkali and alkaline-earth metal complexes is represented by their low stability. In fact, when dealing with weak complexes the numerical values obtained are very sensitive to the assumptions made in deriving them. In short, the problem arising from the weakness of these complexes in the experimental determination of formation constants are: (i) the high concentration of the reagents makes control of the ionic strength very difficult; (ii) when working under imperfectly constant ionic strength conditions, it is necessary to consider the junction potential each time [3]; (iii) the activity coefficients of components may be different in solutions at the same ionic strength with different ionic species; (iv) the calibration of the potentiometric system must be made systematically under the same conditions for both the ionic strength and ionic medium of the measurement solutions; and (v) the interactions between the background and the ligands under study must be taken into account. It has been shown for a large number of ligands [4–7] (EDTA, NTA, phosphate, tartrate, citrate, dicarboxylate ligands, etc.) that they form complexes with alkali metal ions; if we consider that a constant $K = 10$ mol^{-1} dm^3 for a species [Na(L)] at a metal concentration $c_{\mathrm{Na}} = 1$ mol dm^{-3} implies a log K^{H} lowering of about one unit, it is clear that these interactions must be considered.

Moreover, it is necessary to determine the temperature coefficients of formation constants for a better knowledge of the system. Other problems come from the junction potential variation with temperature and also from the necessary corrections of the concentrations due to thermic expansion *.

Bearing in mind the above-mentioned problems, we here report a potentiometric study of the complexing properties of malonic acid (H_2mal) under different experimental conditions (i.e., large ranges of temperature, ionic strength and concentration in different ionic media). Further, an accurate analysis of literature data [8–42] (Table 1) has been carried out in order to define the system H^+–Ca^{2+}–mal^{2-} in the presence of the cations

---

* A direct technique to determine the temperature coefficients is the calorimetric technique which, however, shows some difficulties as regards the accuracy of the log K values and the dilution heat, when dealing with weak complexes and high reagent concentrations.

TABLE 1

Literature data for Ca^{2+}–malonate complex formation in aqueous solution

t(°C)	I(mol dm^{-3})	Medium	log K_1^{Ca}		log K_2^{Ca}	Ref.
20	0.1	$NaClO_4$	1.85		0.80	19
25	→ 0		2.50			32
30			2.58	$\Delta H = 4.45$		
35			2.66	$\Delta C_p = 0$		
40			2.74			
25	0.16	(Na^+)	1.36			17
25	0.1	$NaClO_4$	1.51			25
25	→ 0		2.35			11
25	0.037		1.73			
25	0.2	KCl	1.46		0.47	8
25	→ 0		2.49			11
25	0.042		1.84			
15	→ 0		2.47			39
25			2.50	$\Delta H = 1.9$		
30			2.52	$\Delta C_p = 0$		
35			2.57			
25	→ 0			$\Delta H = 2.3$		39

Na^+, K^+ and Et_4N^+ (tetraethylammonium), in the temperature range $10 \leqslant t \leqslant 50$°C.

EXPERIMENTAL

Chemicals

Malonic acid (Merck p.a. or Fluka purissimum) was used without further purification. From alkalimetric titrations, we calculated a purity > 99.5%. Tetraethylammonium iodide was Fluka purissimum and Et_4NBr was C. Erba (RPS, purity > 99.5%). Calcium nitrate (Fluka) was standardized by EDTA titrations [43]. NaOH, KOH and HNO_3 stock solutions were prepared by diluting concentrated ampoules (Merck, BDH or C. Erba). Grade A glassware and twice-distilled water were employed for all solutions.

Potentiometric measurements

The free hydrogen ion concentration, c_H, was measured by means of the systems: (a) potentiometer Orion 801A with glass–saturated calomel (Metrohm) electrodes; and (b) potentiometer Metrohm E600 with the same electrode couple. The titrant was delivered by (a) an Amel dispenser (minimum reading 0.001 cm^3), and (b) a microsyringe (5000 divisions cm^{-3}). The calibration of the electrode couple, in $-\log c_H$ units, was achieved by titrating HNO_3 (5–20 mmol dm^{-3}) in the same conditions as the considered solution (i.e., in the presence of Ca^{2+}, Na^+, K^+ and Et_4N^+ at the same concentrations) with standard carbonate-free NaOH (system a) or KOH (system b). The junction potential was taken into account in all calculations. The measurement cells (50–100 cm^3) were thermostated at $t \pm 0.2$°C. Magnetic stirring was employed.

Procedure

25–50 cm^3 of the solution under study were titrated with NaOH 0.3 mol dm^{-3} (system a) or KOH 1 mol dm^{-3} (system b) up to pH 12 (35–50 experimental points). An excess of HNO_3 (10–40 mmol dm^{-3}) was added to all the solutions in order to complete the protonation of malonate, to calculate the junction potential and to calculate directly internal E^0, E^0_{int} (the value calculated by separate calibration is E^0_{ext}). If $|E^0_{int} - E^0_{ext}| > 1.5$ mV the titration was rejected. All the titrations were carried out by bubbling purified N_2 through the solutions. The pH reproducibility for both systems was ± 0.005 in the range $3 \leqslant pH \leqslant 6$ and ± 0.02 at $pH < 3$ and $pH > 10$.

Calculations

The potentiometric data were analyzed by the least-squares computer programs ACBA [44] (which refines the values of protonation constants along with other parameters, such as analytical concentrations, E^0 and the junction potential, by minimizing the error-squares sum for the volume of the added titrant) and MINIQUAD 76A [45] (which refines the values of formation constants by minimizing the error-squares sum for the analytical concentrations); a modified version of this program, which allows the simultaneous refinement of formation constants and the parameters which define the dependence on ionic strength, was used.

The formation constants are expressed as follows (L is malonate, M is Ca^{2+}, Na^+ or K^+ and c is the free concentration of the species or of the components)

$$K_j^{\mathrm{H}} = c_{\mathrm{H}_j\mathrm{L}} c_{\mathrm{H}}^{-1} c_{\mathrm{H}_{j-1}\mathrm{L}}^{-1}$$

$$K_i^{\mathrm{M}} = c_{\mathrm{MH}_{i-1}\mathrm{L}} c_{\mathrm{M}}^{-1} c_{\mathrm{H}_{i-1}\mathrm{L}}^{-1}$$

$$K_{\mathrm{M(OH)}} = c_{\mathrm{M(OH)}} c_{\mathrm{M}}^{-1} c_{\mathrm{OH}}^{-1}$$

Throughout this paper the errors associated with the parameters are $>95\%$ confidence intervals.

RESULTS

The potentiometric data obtained at different ionic strengths and temperatures, and in different ionic media, have been grouped and analyzed as follows.

$t = 25°C$ *and* $I = 0.72 \pm 0.03$ *mol dm*$^{-3}$

Under these conditions 9 (duplicate) titrations were carried out at constant malonate concentration (5 mmol dm^{-3}) and variable calcium concentration (0–0.23 mol dm^{-3}). The value $I = 0.72$ mol dm^{-3} was kept constant by adding Et_4NI. Because of the presence of Ca^{2+} (and Na^+ from the titrant), malonate protonation constants, calculated without allowing for calcium and sodium complexes, are

$$\log K_j^{H''} = \log K_j^H - \log(1 + K_i^{Ca} c_{Ca} + K_i^{Na} c_{Na}) \quad j = i \tag{1}$$

where $K_j^{H''}$ is the conditional protonation constant, or

$$K_j^{H''} = K_j^H / (1 + K_i^{Ca} c_{Ca} + K_i^{Na} c_{Na}) \tag{2}$$

The lowering due to Na^+ complexation [4] is very low; since Na formation constants and an approximate K_j^H value are known, a correction can be made by means of the equation

$$1/K_j^{H'} = (1/K_j^{H''}) - (K_i^{Na} c_{Na}/K_j^H) \tag{3}$$

Then eqns. (1) and (2) become

$$\log K_j^{H'} = \log K_j^H - \log(1 + K_i^{Ca} c_{Ca}) \tag{4}$$

$$1/K_j^{H'} = (1/K_j^H) + (K_i^{Ca} c_{Ca}/K_j^H) \tag{5}$$

In Fig. 1, $1/K_1^{H'}$ vs. c_{Ca} is reported; as can be seen the linearity is quite good. K_i^{Ca} can be calculated in two ways: (i) directly from eqn. (4), point by point; and (ii) by linear fitting of eqn. (5), which is a straight line with intercept $1/K_j^H$ and slope K_i^{Ca}/K_j^H. At pH > 10 the hydrolytic species forms: the calculation of $K_{Ca(OH)}$ is similar to the calculation of K_i^{Ca} *.

The free calcium concentration, c_{Ca}, which appears in eqns. (4) and (5) may be calculated in two ways: (i) iteratively; and (ii) from [Ca(H_{i-1}mal)] data in the literature, approximate formation constants by means of a calculation program simulating titration curves. We have chosen the latter procedure.

Some experimental and calculation details concerning this group of measurements are reported in Table 2.

---

* Baes and Mesmer [46] calculate from the data of Bates et al. [47] $K_{Ca(OH)} = 11.9$ mol^{-1} kg^3 at 0°C and $I = 0$, $K_{Ca(OH)} = 15.5$ mol^{-1} kg^3 at 40°C, and $\Delta H = 2.5$ kcal mol^{-1} at $t = 0$–40°C.

TABLE 2

Experimental details of potentiometric measurements at 25°C and $I = 0.72 \pm 0.02$ mol dm^{-3} and calculated data [a]

Run [b]	C^0_{Ca} [c]	$C^0_{Et_4N}$ [c]	$\log K_1^{H\prime}$ ± 0.01	$\log K_2^{H\prime}$ ± 0.02	$-\log K'_w$ ± 0.02	$(c_{Ca})_1$ [d] $\pm 1\%$	$(c_{Ca})_2$ [e] $\pm 1\%$	$(c_{Ca})_3$ [f] $\pm 2\%$	K_1^{Ca}	K_2^{Ca}	K_{CaOH}
1	0.0	700.0	5.55	2.73	13.95	0.0	0.0	0.0			
2	51.27	530.0	5.11	2.68	13.72	44.7	47.9	43.0	39.2	2.5	16.2
3	76.90	455.0	4.96	2.63	13.62	67.6	72.4	65.0	42.7	3.6	17.5
4	102.5	380.0	4.93	2.62	13.64	91.2	95.5	86.0	34.7	3.0	13.2
5	128.2	305.0	4.82	2.60	13.63	115.0	120.0	105.0	38.0	2.9	10.4
6	153.8	230.0	4.76	2.56	13.53	138.0	145.0	129.0	37.4	3.3	12.6
7	179.4	155.0	4.70	2.55	13.48	160.0	167.0	150.0	38.0	3.1	13.0
8	205.1	80.0	4.65	2.54	13.43	182.0	191.0	175.0	38.1	2.9	13.2
9	230.7	5.0	4.59	2.50	13.37	209.0	214.0	199.0	38.9	3.3	14.1
									38.4 ± 1.9	3.08 ± 0.28	13.8 ± 2.0
									$\log K_1^{Ca} =$	$\log K_2^{Ca} =$	$\log K_{CaOH} =$
									1.58 ± 0.02	0.49 ± 0.04	1.14 ± 0.06

$10^6/K_1^{H\prime} = 2.83 + 0.1076\,(c_{Ca})_1 \times 10^3$, $r = 0.9977$ (correlation coefficient), $t = 38.9$ [g]

$\log K_1^H = 5.548$, $K_1^{Ca} = 38.0$, $\log K_1^{Ca} = 1.58$

$10^3/K_2^{H\prime} = 1.85 + 0.00582\,(c_{Ca})_2 \times 10^3$, $r = 0.9919$, $t = 20.7$ [g]

$\log K_2^H = 2.733$, $K_2^{Ca} = 3.15$, $\log K_2^{Ca} = 0.50$

$10^{14}\,K'_w = 1.149 + 0.0147\,(c_{Ca})_3 \times 10^3$, $r = 0.9805$, $t = 13.2$ [g]

$-\log K_w = 13.940$, $K_{CaOH} = 12.8$, $\log K_{CaOH} = 1.11$

---

[a] Obtained from the linear least-squares fit (eqn. (5)).

[b] For each run 2 titrations were performed. Initial volume, v_0, = 50 cc; titrant, NaOH 0.3 mol dm^{-3}; malonate concentration, 5 mmol dm^{-3}; excess of HNO$_3$, 20 mmol dm^{-3}.

[c] Initial analytical concentrations in mmol dm^{-3}.

[d] Free concentrations at pH = 2.5.

[e] Free concentrations at pH = 5.5.

[f] Free concentrations at pH = 11.

[g] Student t.

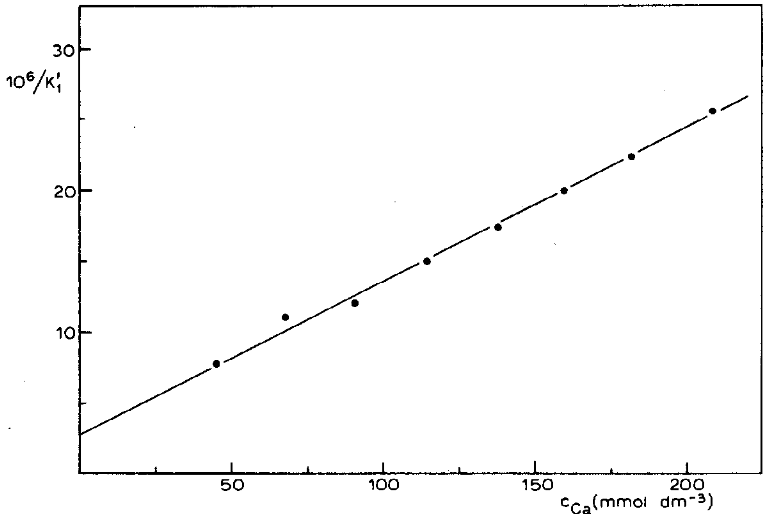

Fig. 1. $1/K_1^{H'}$ vs. c_{Ca} at $t = 25$°C and $I = 0.72$ mol dm^{-3}.

The error coming from the uncertainties about c_{Ca} and log $K_j^{H'}$, in the calculation of K_i^{Ca} using eqn. (4), may be deduced from eqn. (6)

$$\sigma^2(K^{Ca}) = \left(\frac{\partial K^{Ca}}{\partial \delta}\right)^2 \sigma_\delta^2 + \left(\frac{\partial K^{Ca}}{\partial c_{Ca}}\right)^2 \sigma_{c_{Ca}}^2 \tag{6}$$

($\delta = \log K^{H} - \log K^{H'}$) or

$$\sigma^2(K^{Ca}) = \left[\frac{\ln 10(c_{Ca}K^{Ca} + 1)}{c_{Ca}}\right]^2 \sigma_\delta^2 + \left(\frac{K^{Ca}}{c_{Ca}}\right)^2 \sigma_{c_{Ca}}^2 \tag{7}$$

From eqn. (7) it can be seen that for $\sigma_{\delta_1} = 0.02$ and $\sigma_{c_{Ca}} = 1\%\ c_{Ca}$ (maximum error in our case), $\sigma_{K_1^{Ca}} < 3$ or $\sigma(\log K_1^{Ca}) < 0.03$. This error, for a constant K of ~ 40 mol^{-1} dm^3, is quite reasonable. It can be seen (Table 2) that the value of K_1^{Ca} is constant in all mixtures of $Ca^{2+} + Et_4N^+$ and the error ± 0.02 (> 95% confidence interval) appears considerably lower than the standard deviation expected for the error propagation. Similar considerations may be made for $[Ca(Hmal)]^+$ and $[Ca(OH)]^+$ complexes. The fit for eqn. (5) seems to be good and also gives log K_j^{H}, log K_w, K_i^{Ca} and K_{CaOH} values that agree with those calculated point by point. The correlation coefficient value, r, is always > 0.898 (> 99.9% confidence interval for 7 degrees of freedom). The solutions 1–9 show quite a different composition and the activity coefficients of the components may change by changing the ionic medium. However, the constancy of K_1^{Ca}, K_2^{Ca} and K_{CaOH} calculated point by point and the highly significant correlation coefficient values show that the background has little influence on activity coefficients.

TABLE 3

Initial concentrations of reagents in experiments at 10, 25 and 40°C and $I = 0.31$ mol dm^{-3}

C^0_{K} [a]	C^0_{Ca} [a]	$C^0_{Et_4N}$ [a]	I' [b]
0	50	150	300
50	10	220	300
0	100	0	300
220	10	50	300
100	33	100	300
140	50	10	300
270	10	0	300
0	10	270	300

[a] Concentrations in mmol dm^{-3}.

[b] I': ionic strength, in mmol dm^{-3}, without considering the contribution of malonate (3–6 mmol dm^{-3}) and HNO_3 (10–20 mmol dm^{-3}) added in excess.

Therefore, all the potentiometric data have been analyzed simultaneously by the computer program MINIQUAD 76 A, giving the following results

$-\log K_w = 13.95 \pm 0.01$

$\log K_{CaOH} = 1.10 \pm 0.03$

$\log K_1^H = 5.55 \pm 0.01$ $\qquad \log K_1^{Ca} = 1.57 \pm 0.02$

$\log K_2^H = 2.74 \pm 0.02$ $\qquad \log K_2^{Ca} = 0.50 \pm 0.03$

These values agree with those obtained by the above-mentioned methods.

t = *10, 25 and 40°C and* I = *0.31 ± 0.02 mol dm*$^{-3}$

24 titrations were carried out under these conditions. The composition of the solutions was: malonate 3–6 mmol dm^{-3}; $Ca(NO_3)_2$, KNO_3 and Et_4NBr, see Table 3. The potentiometric data, analyzed as described in the preceding section, led to the results reported in Table 4. Also, the linearity of the pairs $1/K_j^{H\prime}$, c_{Ca} fitted to eqn. (5) is satisfactory. The potentiometric data concerning the alkaline region of the titrations have been elaborated only with the program MINIQUAD 76 A and have given the following results: $\log K_{Ca(OH)} = 1.07 \pm 0.02$ at 10°C, 1.12 ± 0.01 at 25°C, and 1.19 ± 0.02 at 45°C. These values may be expressed by the equation

$$\log K_{Ca(OH)} = 1.13 + 0.0040(t - 25) \tag{8}$$

t = *10, 25, 32, 40 and 50°C and* I = *0.25 mol dm*$^{-3}$

40 titrations were performed under these conditions. The solutions contained, besides the ligands, $NaNO_3$, $Ca(NO_3)_2$ and Et_4NI. Potentiometric data, analyzed as in the preceding section, gave the results reported in Table

TABLE 4

Some calculated results for experiments at $I = 0.31$ mol dm^{-3} (KNO_3, Et_4NBr) and $t = 10, 25, 40$°C

t(°C)	$(c_{Ca})_1$ [a]	$\log K_1^{H\prime}$	$(c_{Ca})_2$ [a]	$\log K_2^{H\prime}$	Calculated results
10	8.9	5.25	9.8	2.72	$10^6/K_1^{H\prime} = 4.709 + 0.1068\,(c_{Ca})_1 \times 10^3$
	9.1	5.24	9.8	2.74	$r = 0.9970$; $\log K_1^H = 5.33$; $K_1^{Ca} = 22.7$; $\log K_1^{Ca} = 1.36$; $t = 31.6$ [b]
	30.2	5.11	32.4	2.69	
	9.1	5.25	9.8	2.73	$10^3/K_2^{H\prime} = 1.837 + 0.00454\,(c_{Ca})_2 \times 10^3$
	46.8	4.99	49.0	2.68	
	46.8	5.02	49.0	2.68	$r = 0.9600$; $\log K_2^H = 2.74$; $K_2^{Ca} = 2.5$; $\log K_2^{Ca} = 0.39$; $t = 8.4$ [b]
	9.1	5.25	9.8	2.73	
	95.5	4.83	97.7	2.65	
25	46.8	5.02	49.0	2.67	$10^6/K_1^{H\prime} = 4.450 + 0.1137\,(c_{ca})_1 \times 10^3$
	9.3	5.27	9.8	2.73	$r = 0.9973$; $\log K_1^H = 5.35$; $K_1^{Ca} = 25.6$; $\log K_1^{Ca} = 1.41$; $t = 33.3$ [b]
	8.5	5.27	9.8	2.73	
	30.2	5.10	32.4	2.68	
	95.5	4.82	97.7	2.64	$10^3/K_2^{H\prime} = 1.861 + 0.00506\,(c_{Ca})_2 \times 10^3$
	9.1	5.26	9.8	2.72	$r = 0.9472$; $\log K_2^H = 2.73$; $K_2^{Ca} = 2.7$; $\log K_2^{Ca} = 0.43$; $t = 7.2$ [b]
	8.9	5.27	9.8	2.72	
	45.7	4.99	49.0	2.66	
40	45.7	5.00	49.0	2.64	$10^6/K_1^{H\prime} = 4.085 + 0.1137\,(c_{Ca})_1 \times 10^3$
	8.5	5.30	9.8	2.71	$r = 0.9961$; $\log K_1^H = 5.39$; $K_1^{Ca} = 27.8$; $\log K_1^{Ca} = 1.44$; $t = 27.7$ [b]
	93.3	4.84	97.7	2.60	
	9.1	5.30	9.8	2.70	
	29.5	5.14	32.4	2.69	$10^3/K_2^{H\prime} = 1.900 + 0.00665\,(c_{Ca})_2 \times 10^3$
	46.8	5.03	49.0	2.64	$r = 0.9732$; $\log K_2^H = 2.72$; $K_2^{Ca} = 3.5$; $\log K_2^{Ca} = 0.54$; $t = 10.4$ [b]
	8.9	5.29	9.8	2.71	
	9.1	5.30	9.8	2.71	

[a] Free concentrations of Ca^{2+}, mmol dm^{-3}.

[b] Student t: for 6 degrees of freedom, t = 3.7, 99% confidence interval.

TABLE 5

Some calculated results for experiments at $I = 0.25$ mol dm^{-3} ($NaNO_3$, Et_4NI) and $t = 10, 25, 32, 40$ and 50°C

t(°C)	$(c_{Ca})_1$ ^{a}	$\log K_1^{H\prime}$	$(c_{Ca})_2$ ^{a}	$\log K_2^{H\prime}$	Calculated results
10	1.6	5.31	1.7	2.72	
	7.2	5.25	8.5	2.70	$10^6/K_1^{H\prime} = 4.807 + 0.1032\,(c_{Ca})_1 \times 10^3$
	38.5	5.06	42.7	2.67	$r = 0.9935$; $\log K_1^H = 5.32$; $K_1^{Ca} = 21.5$; $\log K_1^{Ca} = 1.33$
	16.2	5.21	17.4	2.69	
	0.7	5.30	0.85	2.72	$10^3/K_2^{H\prime} = 1.915 + 0.00587\,(c_{Ca})_2 \times 10^3$
	53.7	4.96	63.1	2.64	
	70.8	4.93	72.4	2.63	$r = 0.9921$; $\log K_2^H = 2.72$; $K_2^{Ca} = 3.0$; $\log K_2^{Ca} = 0.48$
25	1.4	5.34	1.7	2.68	
	7.1	5.28	8.5	2.67	$10^6/K_1^{H\prime} = 4.488 + 0.1161\,(c_{Ca})_1 \times 10^3$
	38.5	5.04	43.0	2.65	$r = 0.9969$; $\log K_1^H = 5.35$; $K_1^{Ca} = 25.9$; $\log K_1^{Ca} = 1.41$
	15.9	5.20	17.4	2.65	
	0.7	5.342	0.85	2.675	$10^3/K_2^{H\prime} = 2.111 + 0.00510\,(c_{Ca})_2 \times 10^3$
	54.3	4.95	64.0	2.61	
	70.8	4.91	72.4	2.60	$r = 0.9417$; $\log K_2^H = 2.68$; $K_2^{Ca} = 2.4$; $\log K_2^{Ca} = 0.38$

32	0.75	5.36	0.85	2.665	$10^6/K_1^{H'} = 4.319 + 0.1316\,(c_{Ca})_1 \times 10^3$
	1.5	5.35	1.7	2.66	$r = 0.9993$; $\log K_1^H = 5.36_5$; $K_1^{Ca} = 30.5$; $\log K_1^{Ca} = 1.48$
	37.5	5.02	42.3	2.61	$10^3/K_2^{H'} = 2.222 + 0.00490\,(c_{Ca})_2 \times 10^3$
	3.0	5.33	4.1	2.63	$r = 0.9387$; $\log K_2^H = 2.65$; $K_2^{Ca} = 2.2$; $\log K_2^{Ca} = 0.34$
	52.5	4.95	62.0	2.60	
	70.8	4.87	72.4	2.59	
40	1.35	5.37	1.7	2.67	$10^6/K_1^{H'} = 4.046 + 0.1609\,(c_{Ca})_1 \times 10^3$
	6.8	5.29	8.3	2.66	$r = 0.99999$; $\log K_1^H = 5.39$; $K_1^{Ca} = 39.8$; $\log K_1^{Ca} = 1.60$
	15.1	5.19	16.6	2.655	$10^3/K_2^{H'} = 2.140 + 0.00485\,(c_{Ca})_2 \times 10^3$
	37.0	5.00	42.0	2.65	$r = 0.892$; $\log K_2^H = 2.67$; $K_2^{Ca} = 2.3$; $\log K_2^{Ca} = 0.36$
	0.65	5.38	0.81	2.66	
	51.3	4.91	61.7	2.60	
50	0.8	5.42	0.85	2.665	$10^6/K_1^{H'} = 3.761 + 0.1702\,(c_{Ca})_1 \times 10^3$
	1.6	5.40	1.7	2.66	$r = 0.9989$; $\log K_1^H = 5.425$; $K_1^{Ca} = 45.2$; $\log K_1^{Ca} = 1.65$
	37.5	4.99	41.7	2.62	$10^3/K_2^{H'} = 2.168 - 0.00559\,(c_{Ca})_2 \times 10^3$
	6.7	5.31	8.3	2.655	$r = 0.9993$; $\log K_2^H = 2.66$; $K_2^{Ca} = 2.6$; $\log K_2^{Ca} = 0.42$
	51.3	4.89	61.0	2.60	
	70.8	4.81	72.4	2.59	

---

[a] Free concentrations of Ca^{2+}, mmol dm^{-3}.

5. The alkaline region data, elaborated with the program MINIQUAD 76 A, gave the following results: $\log K_{Ca(OH)} = 0.99 \pm 0.02$ at 10°C, 1.07 ± 0.02 at 25°C, 1.12 ± 0.02 at 32°C, 1.15 ± 0.01 at 40°C, and 1.20 ± 0.03 at 50°C. They may be expressed by the equation

$$\log K_{Ca(OH)} = 1.07 + 0.0057(t - 25) \tag{9}$$

t = *10, 25 and 40°C and variable ionic strength*

The ionic strength dependence of formation constants may be expressed by the semi-empirical equation [48]

$$\log K = \log K^0 - Az^*[\sqrt{I}/(1 + B\sqrt{I})] + CI + DI^{3/2} \tag{10}$$

where $\log K^0$ is the constant at infinite dilution; $A = 0.5115 + 8.84 \times 10^{-4}(t - 25) + 2.95 \times 10^{-6}(t - 25)^2$; $B = 1.489 + 8.77 \times 10^{-4}(t - 25) + 4.69 \times 10^{-6}(t - 25)^2$; $z^* = \Sigma(\text{charge})^2_{\text{reagents}} - \Sigma(\text{charge})^2_{\text{products}}$; and C and D are empirical parameters to be determined experimentally. 15 solutions for each temperature were prepared in order to give the following conditions: $0.03 \leqslant I \leqslant 0.95$ mol dm^{-3}; $0.005 \leqslant C_{Ca} \leqslant 0.1$ mol dm^{-3}; $0.01 \leqslant C_{Na}$, $C_{Et_4N} \leqslant 0.4$ mol dm^{-3}; and $0.005 \leqslant C_{mal} \leqslant 0.05$ mol dm^{-3}.

The potentiometric data, analyzed with the program MINIQUAD 76 A, modified in order to calculate the parameters defining the ionic strength dependence, gave the following results.

(a) For the complex $[Ca(mal)]^0$, $D = -0.8$ (at all temperatures), $C = 1.95 \pm 0.06$ at 10°C, 2.05 ± 0.05 at 25°C, and 2.15 ± 0.07 at 40°C. These results may be expressed by the equation

$$C = 2.05 + 6.7 \times 10^{-3}(t - 25) \tag{11}$$

(b) For the complex $[Ca(Hmal)]^+$, $D = -0.4$ (at all temperatures), $C = 1.0 \pm 0.1$ at 10°C, 1.08 ± 0.07 at 25°C, and 1.14 ± 0.08 at 40°C. These results may be expressed by the equation

$$C = 1.08 + 0.004\ (t - 25) \tag{12}$$

Besides calculating the formation constants of Ca^{2+} complexes, we also tried to calculate those of potassium and sodium complexes (present in rather high concentrations in the solution with $I = 0.31$, $I = 0.25$ and variable I). As regards Na^+ complexes, the following have been found at ionic strength zero ($I \to 0$):

t	$\log K_1^{Na}$
10	0.45
25	0.58
40	0.64

$$\log K_1^{Na} = 0.56 + 0.006(t - 25) \tag{13}$$

These values agree substantially with those found previously. For the protonate complex [NaH(mal)], at $I \to 0$ and $10 \leqslant t \leqslant 40°\mathrm{C}$

$\log K_2^{\mathrm{Na}} = -0.2 \pm 0.1$

As regards potassium complexes, only the first constant may be calculated: $I = 0.31$, $t = 25°\mathrm{C}$, and $\log K_1^{\mathrm{K}} = 0.3 \pm 0.2$.

ANALYSIS OF LITERATURE DATA

Protonation constants of malonate and complexes with Na^+

Analyzing all the most important literature data [8–42] about malonic acid protonation at $I \to 0$ and at different ionic strengths in the presence of Na^+ (taking into account 63 protonation constants), the following results were obtained for the first step (at $I = 0.25$ mol dm^{-3} and $t = 25°\mathrm{C}$): $\log K_1^{\mathrm{H}} = 5.342 \pm 0.012$; $\partial \log K_1^{\mathrm{H}}/\partial T = (3.0 \pm 0.9) \times 10^{-3}$; $\partial^2 \log K_1^{\mathrm{H}}/\partial T^2 = (8.2 \pm 2.5) \times 10^{-5}$; $\log K_1^{\mathrm{Na}} = 0.26 \pm 0.06$; and $\partial \log K_1^{\mathrm{Na}}/\partial T = (5.7 \pm 2.3) \times 10^{-3}$.

As regards dependence on ionic strength, parameters C and D were found to be practically equal for $\log K_1^{\mathrm{H}}$ and $\log K_1^{\mathrm{Na}}$: $D_1 = -0.40 \pm 0.05$; $C_1 = 1.12 \pm 0.08$; and $\partial C_1/\partial T = (3.4 \pm 1.3) \times 10^{-3}$.

Literature data concerning the second step of protonation are much less accurate and it was only possible to deduce the dependence on T of the constants at $I \to 0$: $\log K_2^{\mathrm{H}} = 2.849 \pm 0.002$; $\partial \log K_2^{\mathrm{H}}/\partial T = (1.05 \pm 0.15) \times 10^{-4}$; and $\partial^2 \log K_2^{\mathrm{H}}/\partial T^2 = (6.9 \pm 1.4) \times 10^{-5}$.

Complexes of Ca^{2+} with malonate

The different values of $\log K_1^{\mathrm{Ca}}$ reported in Table 1 show the following mean values at ionic strength $I \sim 0.1$ mol dm^{-3}: $\log K_1^{\mathrm{Ca}} \sim 1.5$; and at $I \to 0$, $\log K_1^{\mathrm{Ca}} \sim 2.5$.

While the former value agrees with that found in this work, the latter is appreciably different (~ 0.3 logarithmic units). This is probably due to an incorrect treatment of ionic strength dependence. In fact, by considering our data, which are also confirmed by the findings for similar complexes previously, we obtained for the complex $[\mathrm{Ca(mal)}]^0$ at $t = 25°\mathrm{C}$, $C = 2.05$ and $D = -0.8$. Introducing these values into eqn. (10) gives

$$\log K_1^{\mathrm{Ca}}(I = 0) - \log K_1^{\mathrm{Ca}}(I = 0.1) = 0.7$$

Using Davies equation

$$\log K_1^{\mathrm{Ca}} = \log K_1^{\mathrm{Ca}}(I = 0) - 4.1\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - CI\right) \tag{14}$$

TABLE 6

Formation constants for the complexes $[Ca(mal)]^0$ and $[Ca(Hmal)]^+$ obtained under different conditions

I (mol dm^{-3})	t (°C)	$\log K_1^{Ca}$ [a]	C_1	D_1	Δ	$\log K_2^{Ca}$ [a]	C_2	D_2	Δ
0.72	25	1.58 ± 0.02			0.00	0.49 ± 0.04			0.00
0.31	10	1.36 ± 0.03			0.00	0.39 ± 0.04			−0.03
	25	1.41 ± 0.02			0.00	0.43 ± 0.03			0.01
		(1.38 ± 0.04)			(−0.03)	(0.47 ± 0.14)			(0.05)
	40	1.44 ± 0.03			−0.10	0.54 ± 0.04			0.11
0.25	10	1.33 ± 0.03			−0.02	0.48 ± 0.04			0.05
	25	1.41 ± 0.02			0.01	0.38 ± 0.03			−0.03
		(1.42 ± 0.03)			(0.02)	(0.41 ± 0.05)			(0.00)
	32	1.48 ± 0.03			0.03	0.34 ± 0.04			−0.07
	40	1.60 ± 0.03			0.08	0.36 ± 0.04			−0.06
	50	1.65 ± 0.05			0.00	0.42 ± 0.06			0.00
Variable	10	(2.10 ± 0.13, $I \to 0$)	1.95 ± 0.06	−0.8	0.03	(0.83 ± 0.20, $I \to 0$)	1.0 ± 0.1	−0.4	−0.01
(0.03–0.95)	25	(2.04 ± 0.09, $I \to 0$)	2.05 ± 0.05	−0.8	−0.08	(0.81 ± 0.15, $I \to 0$)	1.08 ± 0.07	−0.4	0.01
	40	(2.26 ± 0.11, $I \to 0$)	2.15 ± 0.07	−0.8	0.01	(0.77 ± 0.34, $I \to 0$)	1.14 ± 0.08	−0.4	0.00
					$\lvert\bar{\Delta}\rvert = 0.03$				$\lvert\bar{\Delta}\rvert = 0.03$

[a] MINIQUAD 76 A calculations in parentheses.

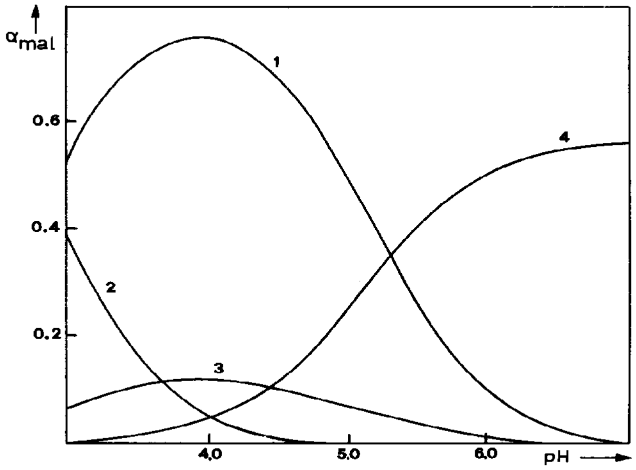

Fig. 2. Distribution of species in the system Ca^{2+}–mal^{2-}, at $t = 25$°C and $I = 0.25$ mol dm^{-3}, vs. pH. $C_{mal} = 1/3\ C_{Ca} = 2$ mmol dm^{-3}. Curve 1, $[H(mal)]^-$; Curve 2, $[H_2(mal)]^0$; Curve 3, $[Ca(Hmal)]^+$; Curve 4, $[Ca(mal)]^0$.

For $C = 0.2$ or 0.3

$$\log K_1^{Ca}(I = 0) - \log K_1^{Ca}(I = 0.1) = 0.86 - 0.90$$

(this depends on the use of either $C = 0.2$ or $C = 0.3$).

The average value of the temperature dependence for the formation constants in Table 1 is ($I = 0$, $t = 25$°C)

$$\partial \log K_1^{Ca}/\partial T = (6.2 \pm 2.1) \times 10^{-3}$$

DISCUSSION AND CONCLUSIONS

In Table 6 the values of formation constants for complexes Ca^{2+}–mal^{2-} obtained under different conditions are summarized in the following equations

$$\begin{aligned}\log K_1^{Ca} = {} & 1.40(\pm 0.03) - 8A\left[\frac{\sqrt{I}}{1 + B\sqrt{I}} - \frac{\sqrt{0.25}}{1 + B\sqrt{0.25}}\right] \\ & + [2.42 + 0.0060(t - 25)](I - 0.25) - 0.122(I^{3/2} - 0.25^{3/2}) \\ & + 0.0058(t - 25) + 1.8 \times 10^{-4}(t - 25)^2 \qquad (15)\end{aligned}$$

TABLE 7

Thermodynamic parameters[a] for the formation of $[Ca(mal)]^0$ and $[Ca(Hmal)]^+$ species, in aqueous solution at 25°C

I	$[Ca(mal)]^0$			$[Ca(Hmal)]^+$		
	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
0	2.95 ± 0.05	2.4 ± 0.6	18 ± 2	1.08 ± 0.06	-1.0 ± 0.8	0 ± 3
0.1	1.96 ± 0.04	2.2 ± 0.5	14 ± 2	0.61 ± 0.05	-0.9 ± 0.7	-1 ± 3
0.25	1.91 ± 0.04	2.4 ± 0.5	15 ± 2	0.56 ± 0.05	-0.2 ± 0.7	1 ± 3
0.5	2.03 ± 0.04	2.8 ± 0.5	16 ± 2	0.62 ± 0.05	1.0 ± 0.7	5 ± 3
0.7	2.14 ± 0.05	3.3 ± 0.6	18 ± 2	0.67 ± 0.06	1.9 ± 0.8	9 ± 3
1	2.99 ± 0.07	3.9 ± 0.8	21 ± 3	0.74 ± 0.08	3.3 ± 1.2	14 ± 5

[a] ΔG and ΔH in kcal mol^{-1}; ΔS in cal mol^{-1} deg^{-1}.

$$\begin{aligned}\log K_2^{Ca} = {} & 0.41(\pm 0.04) - 4A\left[\frac{\sqrt{I}}{1 + B\sqrt{I}} - \frac{\sqrt{0.25}}{1 + B\sqrt{0.25}}\right] \\ & + [1.07 + 0.012(t - 25)](I - 0.25) - 0.50(I^{3/2} - 0.25^{3/2}) \\ & - 3.9 \times 10^{-4}(t - 25) + 3.0 \times 10^{-5}(t - 25)^2 \qquad (16)\end{aligned}$$

In the same Table, the deviations (Δ) of the experimental values of log K_i^{Ca}, in comparison with those calculated from eqns. (15) and (16), are reported. In both cases the mean deviation is ±0.03. These rather low deviations confirm the hypothesis that, considering all the ligand interactions with the background, the dependence of the formation constants on ionic strength is the same in the presence of different salts. In Table 7 the values of the thermodynamic parameters at different ionic strengths are reported. As has been noted previously for some alkali metal complexes with dicarboxylate ligands, ΔH and ΔS follow the same behaviour as ΔG, reaching a minimum at $I \sim 0.2$–0.3 mol dm^{-3}.

In Fig. 2 the species distribution diagram vs. pH is reported. It is interesting to note that the species $[Ca(Hmal)]^+$, often neglected in previous investigations (Table 1), reaches, in not too drastic concentration conditions, a formation percentage of > 10% and it is, therefore, to be considered as a correct speciation. Further, it has been calculated that, because of the error in the constants, (±0.03 for the neutral complex constant and ±0.04 for the protonated complex), the error in the concentration is very low (at pH 6, % $[Ca(mal)]^0 = 49.4 \pm 1.3$; at pH 3.5, % $[Ca(Hmal)]^+ = 11 \pm 1$).

ACKNOWLEDGEMENT

We thank C.N.R. (Rome) for partial financial support.

REFERENCES

1 N.S. Poonia and A.V. Bajaj, Chem. Rev., 79 (1979) 389.
2 K.S. Johnson and R.M. Pytkowicz, Am. J. Sci., 278 (1978) 1428.
3 F.J.C. Rossotti and H. Rossotti, The Determination of Stability Constants, McGraw-Hill, New York, 1961, Chap. 7.
4 P.G. Daniele, C. Rigano and S. Sammartano, Thermochim. Acta, 62 (1983) 101; ibid, unpublished results.
5 P.G. Daniele, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 63 (1982) 267.
6 G. Arena, R. Cali, M. Grasso, S. Musumeci, S. Sammartano and C. Rigano, Thermochim. Acta, 36 (1980) 329.
7 C.W. Davies, Ion Association, Butterworths, Washington, 1962.
8 R.K. Kannan and A. Kibrick, J. Am. Chem. Soc., 60 (1938) 2314.
9 B. Adell, Z. Phys. Chem., Abt. A, 185 (1939) 161.
10 W.J. Hamer, J.O. Burton and S.F. Acree, J. Res. Natl. Bur. Stand., 24 (1940) 269.
11 D.I. Stock and C.W. Davies, J. Chem. Soc., (1949) 1371; R.H. Jones and D.I. Stock, ibid., (1962) 306.
12 E. Gelles and G.H. Nancollas, J. Chem. Soc., (1956) 4847.
13 K.N. Dutt and P. Bose, Z. Anorg. Chem., 295 (1958) 131.
14 M. Yasada, K. Yamasaki and H. Ohtaki, Bull. Chem. Soc. Jpn., 33 (1960) 1067.
15 V.S.K. Nair and G.H. Nancollas, J. Chem. Soc., (1961) 4367.
16 S.N. Das and D.J.G. Ives, Proc. Chem. Soc., (1961) 373.
17 J. Shubert and A. Lindenbaum, J. Chem. Soc., (1962) 306.
18 H.J. deBruin, D. Kaitis and R.B. Temple, Aust. J. Chem., 15 (1962) 457.
19 E. Campi, Ann. Chim. (Italy), 53 (1963) 96.
20 S.H. Laurie and C.B. Monck, J. Chem. Soc., (1963) 3343.
21 D.W. Archer, D.A. East and C.B. Monk, J. Chem. Soc., (1965) 720.
22 V.S.K. Nair, J. Chem. Soc., (1965) 1450.
23 V.T. Athavole, N. Mahadevan, P.K. Mathur and R.M. Sathe, J. Inorg. Nucl. Chem., 29 (1967) 1947.
24 S.K. Rajan and A.E. Martell, J. Inorg. Nucl. Chem., 29 (1967) 523.
25 G. Ostacoli, A. Vanni and E. Roletto, Ric. Sci., 38 (1968) 318.
26 M. Deneux, R. Meilleur and R.L. Benoit, Can. J. Chem., 46 (1968) 1383.
27 C.M. Ke, P.C. Kong, M.S. Cheng and N.C. Li, J. Inorg. Nucl. Chem., 30 (1968) 961.
28 J.E. Powell, J.L. Farrell, W.F.S. Neillie and R. Russell, J. Inorg. Nucl. Chem., 30 (1968) 2223.
29 M. Bonnet and V. Mikhailova, C. R. Acta Bulg. Sci., 21 (1968) 1295.
30 V. Mikhailova and M. Bonnet, Bull. Soc. Chim. Fr., (1969) 4258.
31 G. Ostacoli, A. Vanni and E. Roletto, Gazz. Chim. Ital., 100 (1970) 350.
32 R. Ghosh and V.S.K. Nair, J. Inorg. Nucl. Chem., 32 (1970) 3033.
33 D.J.G. Ives and D. Prasad, J. Chem. Soc. B, (1970) 1649.
34 F.P. Cavasino and E. Di Dio, J. Chem. Soc. A, (1971) 3176.
35 L.G. Sillén and A.E. Martell, Stability Constants, Chem. Soc., Spec. Publ. (London), 17 (1964); 25 (1971).

36 S. Ramamoortty and P.G. Manning, J. Inorg. Nucl. Chem., 35 (1973) 1571.

37 G. Ostacoli, P.G. Daniele and A. Vanni, Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat., 108 (1974) 539.

38 J.J. Christensen, D.J. Eatough and R.M. Izatt, Handbook of Metal Ligand Heats, Dekker, New York, 1975.

39 U.K. Klaning and O. Osterby, J. Chem. Soc. Faraday Trans. 1, 72 (1976) 513.

40 A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 3, Plenum, New York, 1977.

41 G. Arena, R. Cali, E. Rizzarelli and S. Sammartano, Transition Met. Chem., 3 (1978) 147.

42 D.D. Perrin, Stability Constants, Part B: Organic Ligands, IUPAC Chem. Data Series No. 22, Pergamon, Oxford, 1979.

43 H.A. Flaschka, EDTA Titrations, Pergamon, London, 1959.

44 G. Arena, E. Rizzarelli, S. Sammartano and C. Rigano, Talanta, 26 (1979) 1.

45 A. Sabatini, A. Vacca and P. Gans, Talanta, 21 (1974) 52; P. Gans, A. Sabatini and A. Vacca, Inorg. Chim. Acta, 18 (1976) 237; A. Vacca, personal communication, 1976.

46 C.F. Baes, Jr. and R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976.

47 R.G. Bates, V.E. Bower, R.G. Canbam and J.E. Prue, Trans. Faraday Soc., 55 (1959) 2062.

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