Thermochimica Acta, 46 (1981) 103—116
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THE FORMATION OF PROTON AND ALKALI-METAL COMPLEXES WITH LIGANDS OF BIOLOGICAL INTEREST IN AQUEOUS SOLUTION. THERMODYNAMICS OF H^+, Na^+ AND K^+—OXALATE COMPLEXES

PIER G. DANIELE

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

CARMELO RIGANO

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

SILVIO SAMMARTANO

Istituto Dipartimentale di Chimica e Chimica Industriale dell 'Università, Viale A. Doria 6, 95125 Catania (Italy)

(Received 20 November 1980)

ABSTRACT

The protonation constants of oxalic acid were determined potentiometrically at 37°C in different media — $NaNO_3$, KNO_3 and Et_4NI, $0.03 \leqslant I \leqslant 0.3$. From these data it was possible to determine the formation of the complexes $[Na(ox)]^-$ and $[K(ox)]^-$, and to calculate their stability constants. Simultaneous analysis of potentionmetric and calorimetric data (this work and literature) enabled the temperature and ionic strength dependendence of the equilibrium parameters to be obtained for the protonation of oxalate. Recalculation of some literature data gave the ΔH value for the formation of the $[Na(ox)]^-$ complex. The thermodynamic parameters obtained allowed us to confirm the hypothesis that dicarboxylate anions chelate with alkali-metal ions and that these complexes are mainly entropically stabilized.

INTRODUCTION

Many authors [1—23] have widely investigated the protonation of oxalate (ox^{2-}) and reported the values of thermodynamic functions at different temperatures and ionic strengths. Banks et al. [24] found association between potassium ion and oxalate by conductometric measurements, while Finlayson et al. [25] reported the stability constant for the $[Na(ox)]^-$ complex, obtained from solubility studies on the calcium—oxalate system. No other author has considered the complex formation of oxalate with alkali-metal ions, while such complexes have been studied to some extent for several bi- and tricarboxylic acids [26—30].

Oxalate is present in all natural fluids. Its concentration is 1.4—2.8 mg dm^{-3} in blood and 30 mg/24 h in urine [31]. Many foods contain oxalate

0 040-6031/81/0000—0000/$02.50 © Elsevier Scientific Publishing Company

(e.g. in oranges there are 24 mg/100 g of oxalate) [31]. Further, it is well known that the concentration of Na^+ and K^+ ions in biofluids and natural waters is generally relevant (e.g. in blood plasma, $C_{Na} = 130$—150 mmole dm^{-3} and $C_K = 4$—5 mmole dm^{-3}). Therefore, even weak interactions, at pH values of biofluids and natural waters generally >5, may signify a high degree of complex formation with respect to oxalate, when alkali-metal ion/oxalate ratios are very high.

From all this comes our interest in carefully investigating (also by analyzing the literature data) the protonation of oxalate and the complex formation between alkali-metal ions and oxalate.

EXPERIMENTAL

Chemicals, apparatus and procedure were as described elsewhere [29,30, 32,33]. The calculations relative to E^0 determination and to the standardization of oxalic acid stock solutions were performed by means of the least-squares computer program ACBA [34]. The stability constants and their dependence on ionic strength were calculated by the least-squares computer program MINIQUAD 76A [35]. Hamilton's statistical test was used [36,37]. Throughout the paper the errors reported are three times the standard deviation.

RESULTS AND DISCUSSION

The data of the alkalimetric titrations of oxalic acid were first elaborated (by taking into account the points above pH = 3) with the ACBA program, which can refine both the first protonation constant and the analytical concentration of the acid. Some results derived from this calculation are collected in Table 1. It must be noticed that the simultaneous refinement of log K_1^H and C_{ox} gives excellent fits, even with very small differences in this value, whilst the statistical parameters become considerably worse when taking a fixed value of C_{ox}.

It can be observed from Table 1 that the values of protonation constants, at the same ionic strength, follow the trend $Et_4N^+ > K^+ > Na^+$. This cannot be due to the differences of the activity coefficients in the different ionic media (see ref. 30 and refs. therein), but it is a clear indication of complex formation between oxalate and alkali-metal ions, while the interaction between oxalate and tetraethylammonium cation may be considered negligible [30]. From ΔpK values (differences between the values of pK_1^H obtained in tetraethylammonium iodide and those in the presence of alkali-metal nitrates) the stability constants of M^+—ox^- complexes (M^+ = alkali-metal ion) can be calculated from the equation

$$K_M = (10^{\Delta pK} - 1)C_M^{-1} \qquad (1)$$

where C_M is the analytical concentration of the alkali-metal ion. This equation, although valid only for $C_M >> C_{ox}$, gives good results. In general, the

TABLE 1

Experimental details of potentiometric measurements and log K_1 values calculated by means of the ACBA computer program without allowing for alkali-metal complex formation, at 37°C and $0.03 \leqslant I \leqslant 0.3$ mole dm^{-3}

M	C_M [a]	log K_1 (3σ)	C_{ox} (3σ) × 10^3	$\sigma_v \times 10^3$ [b]	$R \times 10^3$ [c]	No. of points (at pH > 3)
Et_4N^+ [d]	0.03	4.078 (12)	2.198 (6)	0.40	2.37	18
	0.03	4.062 (12)	3.303 (8)	0.62	2.32	20
	0.03	4.057 (18)	4.404 (20)	0.93	2.64	15
	0.1	3.961 (8)	3.171 (5)	0.41	1.61	20
	0.1	3.970 (18)	2.620 (11)	0.61	2.94	17
	0.1	3.992 (18)	6.582 (29)	1.62	3.09	20
	0.1	4.002 (20)	5.511 (29)	1.21	2.66	15
	0.1	3.977 (14)	2.104 (8)	0.40	2.92	15
	0.3	3.977 (6)	5.472 (8)	0.46	1.00	16
	0.3	3.976 (3)	6.520 (5)	0.31	0.60	21
	0.3	3.974 (3)	4.424 (6)	0.19	0.54	16
	0.3	3.964 (6)	6.718 (9)	0.51	0.95	21
	0.3	3.984 (11)	2.145 (6)	0.30	1.80	15
Na^+	0.03	4.018 (15)	2.181 (8)	0.64	2.26	16
	0.03	3.998 (26)	3.340 (22)	0.97	3.79	18
	0.03	4.002 (23)	4.440 (29)	0.92	2.68	14
	0.1	3.871 (15)	6.531 (23)	1.41	2.67	20
	0.1	3.879 (11)	4.359 (14)	0.67	1.96	16
	0.1	3.835 (9)	2.244 (6)	0.21	1.22	17
	0.1	3.852 (3)	3.301 (3)	0.20	0.76	18
	0.282	3.732 (3)	6.432 (3)	0.23	0.45	20
	0.3	3.697 (5)	4.442 (8)	0.45	1.23	17
	0.3	3.697 (8)	2.117 (5)	0.22	1.31	15
K^+	0.03	4.027 (25)	2.149 (17)	0.59	3.78	15
	0.03	4.009 (6)	3.306 (7)	0.35	1.34	20
	0.03	4.037 (17)	4.654 (21)	1.04	2.86	16
	0.1	3.884 (17)	2.089 (12)	0.47	3.03	15
	0.1	3.892 (25)	2.541 (21)	0.94	4.64	16
	0.282	3,726 (11)	6.467 (21)	1.12	2.17	20
	0.3	3.739 (6)	4.324 (5)	0.25	0.72	15
	0.3	3.712 (29)	2.117 (21)	0.78	4.80	14

[a] Concentrations in mole dm^{-3}; the log K_1 values and the analytical concentrations of the oxalate were refined simultaneously.

[b] Standard deviation in titre (cm^3), see ref. 34; the titrant was KOH 1 mole dm^{-3} and the initial volume 50 cm^3.

[c] $R = [\Sigma(\delta v)^2/\Sigma v^2]^{1/2}$, see refs. 36 and 37.

[d] The salts used were Et_4NI, $NaNO_3$ and KNO_3.

equation

$$\log K_1^H = \log K_1^{H'} + \sum_j \log(1 + K_{M_j} c_{M_j}) \tag{1a}$$

is valid (c_M is the free concentration of the alkali-metal ion and primes indicates the protonation constants determined in alkali-metal medium). If $C_M \sim c_M$ and only one metal ion is present (it must also be remembered that

TABLE 2

log K values for the formation of sodium and potassium—oxalate complexes at 37°C

Equilibrium	log K		
	$I = 0.03$	$I = 0.1$	$I = 0.3$
$Na^+ + ox^{2-} \rightleftharpoons [Na(ox)]^-$	0.9	0.57	0.47 [a]
	0.7	0.52	0.46 [b]
		0.53	[c]
	0.64	0.53	0.49 [d]
$K^+ + ox^{2-} \rightleftharpoons [K(ox)]^-$	0.7	0.42	0.42 [a]
	0.5	0.46	0.43 [b]
		0.43	[c]
	0.53	0.43	0.43 [d]

[a] Calculated using eqn. (1).
[b] Calculated using MINIQUAD program; considering each ionic strength separately.
[c] Calculated using eqn. (1) and the protonation constant of eqn. (4), see Table 3.
[d] Calculated using MINIQUAD program; considering all ionic strengths together, see Table 3.

with Et_4N^+ or Na^+ as background the K^+ ion is always present too, deriving from the potassium hydroxyde used as titrant), eqn. (1a) becomes again (1). In Table 2 the values of log K_M obtained from eqn. (1) and those calculated with computer refinement are reported.

The data for the different ionic strengths can be simultaneously analyzed by using the least-squares computer program MINIQUAD 76A [35], modified in such a way to allow for the changes in ionic strengths. The stability constants as a function of the ionic strength can be expressed by a semiempirical equation of the type

$$\log \beta_{pqr} = \log \beta^{0}_{pqr} - A z^{*}_{pqr} \frac{\sqrt{I}}{1 + B_{pqr}\sqrt{I}} + C_{pqr} I \qquad (2)$$

where A is the Debye—Hückel coefficient ($A = 0.523$ at 37°C), the indexes pqr refer to the reaction

$$p\,M^+ + q\,ox^{2-} + r\,H^+ \rightleftharpoons [M_p(ox)_q H_r]^{p+r-2q} \qquad (3)$$

and $z^* = p + 4q + r - (p + r - 2q)^2$. If instead of considering the zero ionic strength as reference, we choose another reference ionic strength, namely I', eqn. (2) can be rewritten

$$\log \beta^{I}_{pqr} = \log \beta^{I'}_{pqr} - A z^{*} \left(\frac{\sqrt{I}}{1 + B_{pqr}\sqrt{I}} - \frac{\sqrt{I'}}{1 + B_{pqr}\sqrt{I'}} \right) + C_{pqr}(I - I') \qquad (4)$$

The potentiometric data, obtained at different ionic strengths, were elaborated: (i) by taking into account the changes in ionic strength but neglecting the complex formation with alkali-metal ions; (ii) by considering both the changes in ionic strengths and the complex formation M^+—ox^{2-} *. In

---

* Previously it was pointed out [30] that ($K^+NO_3^-$) ion pair formation may be important when weak complexes are investigated; here it was not considered because with $C_{KNO_3} \leqslant$ 0.3 mole dm^{-3} the ion pair formation is fairly negligible.

TABLE 3

$\log\beta_{pqr}$, B_{pqr} and C_{pqr} values (see text) for the protonation of oxalate and for Na^+, K^+—oxalate complexes at 37°C ($I' = 0.1$ mole dm^{-3})

p	q	r	$\log\beta_{pqr}(3\sigma)$	B_{pqr}	$C_{pqr}(3\sigma)$	Medium
0	1	1	3.89 (1)	1.0	0.39 (3)	KNO_3 [a]
0	1	1	3.86 (1)	1.0	0.35 (4)	$NaNO_3$ [a]
0	1	1	3.999 (8)	1.5	1.00 (5)	KNO_3, $NaNO_3$, Et_4NI
1	1	0 ($M = K^+$)	0.43 (5)	1.5	0.9 (2)	KNO_3, Et_4NI
1	1	0 ($M = Na^+$)	0.53 (3)	1.5	0.7 (1)	$NaNO_3$, Et_4NI

[a] Without allowing for M—ox complexes.

Table 3 the values of β_{pqr}, B_{pqr} and C_{pqr} for the complexes H^+—oxalate, Na^+—oxalate and K^+—oxalate are shown. In Fig. 1 the values of $\log K_M$ ($=\log \beta_{110}$) are plotted vs. $\sqrt{I}$. It was also ascertained that no protonated species is formed in M^+—ox^{2-} systems.

The points of alkalimetric titrations below pH = 3 were analyzed separately and gave an approximate value of $\log K_2^H$ (the mean protonation degree reaches a maximum value of 1.1 when an excess of strong acid is not added to oxalic acid).

The large amount of literature data on the protonation of oxalate was then examined. In Table 4 both the protonation constants taken from the literature and those found in this work are collected for the first protonation step; the agreement is generally good. In Fig. 2 the values of $\log K_1^H$ are plotted vs. $\sqrt{I}$ (our values at 37°C and those reported by other authors at

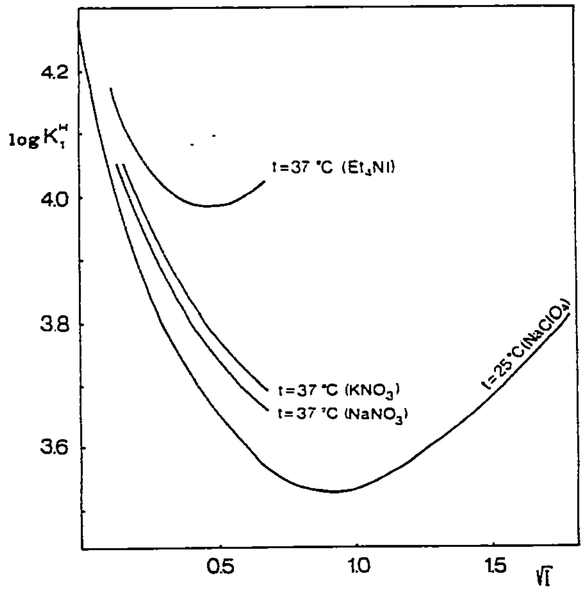

Fig. 1. Dependence of the first protonation constant of oxalate on ionic strength; t = 37°C.

TABLE 4

First protonation constant for oxalate at various temperatures and ionic strengths

t (°C)	I (mole dm^{-3})	log K_1^H		Ref.	t (°C)	I (mole dm^{-3})	log K_1^H		Ref.
25	0	4.300 [a]		1	27.4	2.5 ($NaNO_3$)	3.66 [b]		6
25	0	4.267 [f]		1	32	1 (KNO_3)	3.68		5
0	0	4.228		2	25	1 (KNO_3)	3.62		14
5	0	4.235		2	25	0.1 (KNO_3)	3.82		18
10	0	4.244		2	25	0.5 ($LiClO_4$)	3.50		16
15	0	4.255		2	37	0.03 (Et_4NI)	4.07 (2) [c]	4.097 [d]	This work
20	0	4.268		2	37	0.1 (Et_4NI)	3.98 (2)	3.993	This work
25	0	4.286		2	37	0.3 (Et_4NI)	3.98 (2)	3.982	This work
25	0	4.267 [f]		2	37	0.03 ($NaNO_3$)	4.01 (2)	4.003	This work
30	0	4.308		2	37	0.1 ($NaNO_3$)	3.86 (3)	3.857	This work
35	0	4.331		2	37	0.3 ($NaNO_3$)	3.71 (1)	3.705	This work
40	0	4.356		2	37	0.03 (KNO_3)	4.02 (2)	4.031	This work
45	0	4.388		2	37	0.1 (KNO_3)	3.89 (1)	3.892	This work
50	0	4.417		2	37	0.3 (KNO_3)	3.73 (2)	3.728	This work
0	0	4.201	4.201 [b]	3	37	0	4.34 (1) [e]		This work
5	0	4.207	4.207	3	37	0.1	3.999 (8) [e]		This work
10	0	4.218	4.218	3					

15	0	4.231	4.231	3
20	0	4.247	4.248	3
25	0	4.266	4.268	3
30	0	4.287	4.289	3
35	0	4.312	4.315	3
40	0	4.338	4.341	3
45	0	4.369	4.373	3
50	0	4.399	4.404	3
25	0.1 ($NaClO_4$)	3.81		7
25	0.1 ($NaClO_4$)	3.85		11
25	0.5 ($NaClO_4$)	3.51		12
25	1 ($NaClO_4$)	3.57		10
25	1 ($NaClO_4$)	3.554		13
20	1 ($NaClO_4$)	3.550		17
25	0.1 ($NaClO_4$)	3.817		23
25	3 ($NaClO_4$)	3.801		13

---

[a] Molal scale.

[b] Molar scale.

[c] Values calculated by the program ACBA, see Table 1 (3σ in parentheses).

[d] Values corrected for the presence of K^+ of the titrant KOH.

[e] Calculated from eqn. (4) with $B = 1.5$ and $C = 1.00$.

[f] Recalculated by Pinching and Bates (see ref. 3).

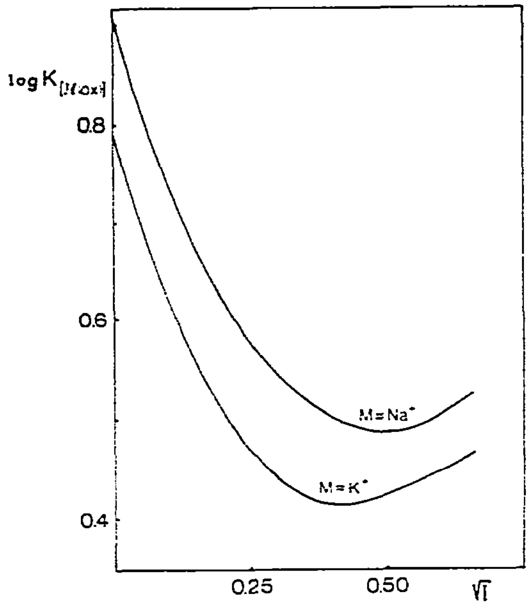

Fig. 2. Dependence of the formation constants of Na$^+$ and K$^+$—oxalate complexes on ionic strength.

25°C). The literature data (obtained in NaClO$_4$) are fitted by the equation

$$\log K_1^H(\pm 0.05) = 4.27 - \frac{2.05\sqrt{I}}{1+\sqrt{I}} + 0.28I \qquad (5)$$

at 25°C and $0 \leqslant I \leqslant 3$. The value of C_{011} (0.28) is in good agreement with our result (0.35), if we consider the different temperature and ionic medium.

Table 5 reports the stability constant values for the second protonation step. In this case the agreement between literature values and ours is not so good as was found for log K_1^H, probably owing to the difficulties in obtaining accurate pH values at $c_{H^+} > 10^{-2}$. For log K_2^H we obtained the equation

$$\log K_2^H(\pm 0.07) = 1.26 - \frac{1.02\sqrt{I}}{1+\sqrt{I}} + CI \qquad (6)$$

at 25°C and $0 \leqslant I \leqslant 3$ in NaClO$_4$. The value of C for log K_2^H is a function of the ionic strength: $C > 1$ for $I = 0.1$, $C = 0.3$ for $I = 1$ and $C = 0.2$ for $I = 3$.

In Table 6 the values of ΔH and ΔC_p for the protonation of oxalate, taken from the literature, are reported. By analyzing these data, both from calorimetric measurements and the temperature coefficient of potentiometric measurements, together with the data in Tables 4 and 5, we obtained some equations for the thermodynamic protonation properties of oxalate as a function of temperature and ionic strength (after correction from molal to molar scale of the data of Harned and Fallon [2] and Pinching and Bates [3]). Equation (7), obtained by analyzing the data in Tables 4 and 6, gives the values of log K_1^H as a function of the temperature in the range $273 \leqslant T \leqslant 323$ (K), with an error $<\pm 0.006$

$$\log K_1^H(T) = 4.268 + 1.136\,\frac{\Delta T}{T} + 7.0 \times 10^{-5}(\Delta T)^2 \qquad (7)$$

TABLE 5

Second protonation constant for oxalate at various temperatures and ionic strengths

t (°C)	I (mole dm^{-3})	log K_2^H	Ref.
0	0	1.244	8
15	0	1.252	8
25	0	1.252	8
35	0	1.286	8
45	0	1.295	8
25	0	1.30	21
30	0	1.31	21
35	0	1.32	21
40	0	1.33	21
45	0	1.34	21
50	0	1.36	21
55	0	1.36	21
25	0	1.25	2
25	0	1.36	19
25	0	1.271	15
25	0.1 ($NaClO_4$)	1.2	23
25	0.1 ($NaClO_4$)	1.13	11
25	0.1 ($NaClO_4$)	1.37	7
25	0.15 ($NaClO_4$)	1.33	9
25	1 ($NaClO_4$)	1.07	10
25	1 ($NaClO_4$)	1.08	13
20	1 ($NaClO_4$)	1.01	17
32	1 (KNO_3)	1.12	5
25	1 (KNO_3)	1.1	14
25	0.5 ($LiClO_4$)	1.00	16
37	0.1 (Na, K, Et_4N)	1.23 (6) [a]	This work

[a] 3σ in parentheses.

where $\Delta T = T(\mathrm{K}) - 298.16$. Equatiom (8), obtained from data in Table 6, gives the values of ΔH_1 as a function of the ionic strength, in the range $0 \leqslant I \leqslant 2$ mole dm^{-3} with $NaNO_3$ as background; the estimated error is $<\pm 0.04$

$$\Delta H_1 = 1.55 - 0.935I + 0.19I^2 \text{ (kcal mole}^{-1}) \tag{8}$$

Concerning the log K_2^H values, from the data in Tables 5 and 6, eqn. (9) was obtained

$$\log K_2^H(T) = 1.26 + 0.52 \frac{\Delta T}{T} + 3.5 \times 10^{-5} (\Delta T)^2 \tag{9}$$

valid in the range $273 \leqslant T \leqslant 328$ (K), with an error $< \pm 0.02$ *.

Pinching and Bates [3] performed accurate measurements, in cells without liquid junction, using NaCl as background in the range $0.05 \leqslant C_{Na} \leqslant 0.5$

---

* Equations (7) and (9) were obtained according to the method proposed by Clarke and Glew [38].

TABLE 6

Thermodynamic parameters for oxalate protonation

t (°C)	I (mole dm^{-3})	ΔH_1 (kcal mole^{-1})	ΔH_2 (kcal mole^{-1})	ΔCp_1 (cal mole^{-1} deg^{-1})	ΔCp_2 (cal mole^{-1} deg^{-1})	Ref.	Method used [a]
25	0	1.55	0.75			19, 20	C
25	0	1.50	1.02			15	C
25	0	1.551		59		2	T
25	0	1.659		55		3	T
25	0	1.658		47		22	Lit.
25	0.5 ($NaNO_3$)	1.107				20	C
25	1.0 ($NaNO_3$)	0.858				20	C
25	2.0 ($NaNO_3$)	0.394				20	C
25	0		0.6			8, this work	T
35	0		0.96			21, this work	T
25	0	1.55 (4) [b]	0.8 (2)	52 (7)	29 (16)	This work	Lit.

[a] C, Calorimetry; T, temperature dependence of potentiometric data; Lit., literature data analysis.

[b] 3σ in parentheses.

mole kg^{-1} at different temperatures $[273 \leqslant T \leqslant 323\ (K)]$. Their data were again analyzed in order to obtain values of log K_{Na} which can be compared with ours and with the aim of calculating the ΔH value for the formation of $[Na(ox)]^-$ species. The calculations were performed with the modified MINIQUAD 76A program, using the values of B and C obtained from our data (see Table 3) for eqn. (4). Since B is a function of the temperature, and bearing in mind that $B = B'\text{å}$ [30], we obtained

$$B = 1.5 + 9.45 \times 10^{-3}\,(T - 310.16)$$

The formation constant values for the sodium—oxalate complex at five temperatures are (at $I = 0$)

t(°C)	log K_{Na} ± 0.01 (molar scale)
5	0.81
15	0.84
25	0.86
35	0.91
45	0.93

From these values we were able to calculate the enthalpy change for the reaction

$$Na^+ + ox^{2-} \rightleftharpoons [Na(ox)]^-\quad \Delta H = 1.05 \pm 0.24\ \text{kcal mole}^{-1}$$

It is interesting to notice that if we extrapolate our values of log K_{Na} to $I = 0$ by using eqn. (4) and the data of Table 3, we obtain log $K_{Na} = 0.91$ (at 37°C); this value is practically the same as was obtained from the data of Pinching and Bates. Furthermore, the calculation of ΔH_I values at $I \neq 0$ from the data of Pinching and Bates gives ΔH_I ($I = 0.24$, $C_{Na} = 0.15$) = 1.31

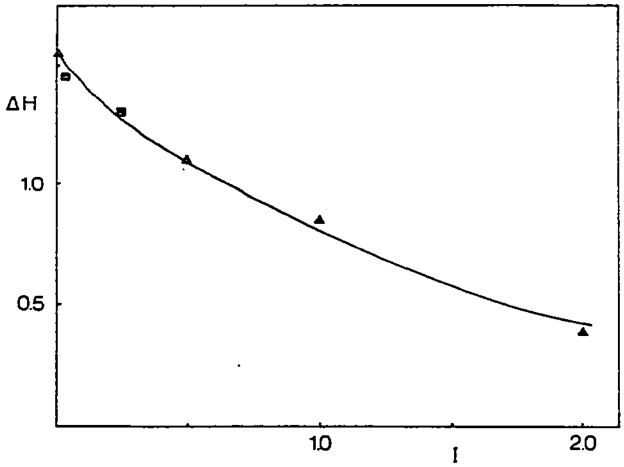

Fig. 3. ΔH ($H^+ + ox^{2-} = [H(ox)]^-$) vs. ionic strength at 25°C. ▲, Refs. 19 and 20; ■, ref. 3 and this work.

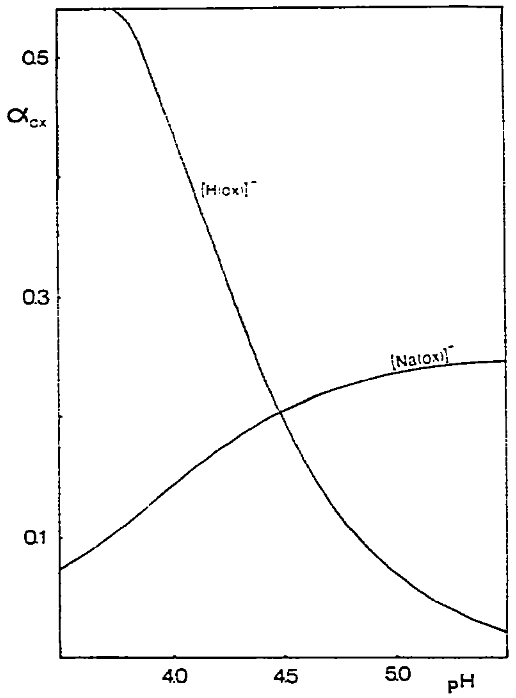

Fig. 4. Distribution diagram, α_{ox} vs. pH, for the system H—Na—ox, at 37°C. $C_{Na} = 0.1$ and $C_{ox} = 0.005$ mole dm^{-3}.

and ΔH_1 ($I = 0.032$, $C_{Na} = 0.01$) = 1.45 kcal $mole^{-1}$ at 25°C, in good agreement with the data obtained from calorimetric measurements [19,20] (the calculated values from eqn. (8) are 1.34 and 1.52 kcal $mole^{-1}$, respectively). In Fig. 3 ΔH_1 values are plotted vs. I; both calorimetric data and those calculated from temperature dependence fit eqn. (8) well.

In Fig. 4 the distribution of the species is plotted vs. pH for the system H^+—Na^+—ox^{2-}: when pH > log K_1^H the formation of the alkali-metal ion—oxalate complex is relevant; this means that in biofluids (generally at pH > 5) the amount of oxalate complexed by Na^+ (and K^+) is not negligible.

The order of stability for Na^+ and K^+—oxalate complexes is $Na^+ > K^+$, the same as was found with other carboxylic and hydroxy-carboxylic ligands

TABLE 7

Formation constants for Na^+ complexes of some carboxylic acids, at 25°C and $I = 0$

Ligand	log K_{NaL}	Ref.
Malonate	0.74	39
Phthalate	0.68	39
Maleate	0.72	39
Succinate	0.32	39
Oxalate	0.86	This work
Acetate	—0.18	40

[27—30,39,40]. In Table 7 the values are given of the stability constants concerning some carboxylic ligands [39,40]. It was proposed that chelation is necessary for the formation of the alkali-metal complexes with bicarboxylic acids [26]. Recently it was evidenced by laser Raman spectra [41] that most probably Li^+, Na^+ and K^+ form chelate complexes with oxalate, and by Raman measurements [42] it was also pointed out that oxydiacetic acid forms chelate complexes with Li^+, Na^+, K^+ and Cs^+. The order of stability that can be drawn from Table 7 is oxalate $>$ malonate $\simeq$ phthalate $>$ succinate $>$ acetate, and confirms this hypothesis on a thermodynamic basis.

Concerning the thermodynamic parameters relative to the formation of the $[Na(ox)]^-$ complex, it must be noticed that the value of $\Delta S = 7.5$ cal $mole^{-1}$ deg^{-1} confirms that these complexes are mainly stabilized entropically [26,29,30].

REFERENCES

1 H.N. Parton and R.C. Gibbons, Trans. Faraday Soc., 35 (1939) 542.
2 H.S. Harned and L.D. Fallon, J. Am. Chem. Soc., 61 (1939) 3111.
3 G.D. Pinching and R.G. Bates, J. Res. Natl. Bur. Stand., 40 (1948) 405.
4 W.C. Vosburg and J.F. Backman, J. Am. Chem. Soc., 62 (1940) 1028.
5 I.A. Duboven and A.K. Babko, Zh. Neorg. Khim., 2 (1957) 808.
6 Y. Yamane and N. Davidson, J. Am. Chem. Soc., 82 (1960) 2123.
7 A. McAuley and G.H. Nancollas, Trans. Faraday Soc., 56 (1960) 1165.
8 A. McAuley and G.H. Nancollas, J. Chem. Soc., (1961) 2215.
9 H.J. de Bruin, D. Kaitis and R.B. Temple, Aust. J. Chem., 15 (1962) 457.
10 E. Bottari and L. Ciavatta, Gazz. Chim. Ital., 95 (1965) 908.
11 K. Nagata, A. Umayahara and R. Tsuchiya, Bull. Chem. Soc. Jpn., 38 (1965) 1059.
12 S.J. Lyte and S.J. Naqui, J. Inorg. Nucl. Chem., 28 (1966) 2993.
13 E.G. Moorhead and N. Sutin, Inorg. Chem., 5 (1966) 1866.
14 K.S. Rajan and A.E. Martell, J. Inorg. Nucl. Chem., 29 (1967) 523.
15 J.J. Christensen, R.M. Izatt and L.D. Hansen, J. Am. Chem. Soc., 89 (1967) 213.
16 M. Deneux, R. Meilleur and R.L. Benoit, Can. J. Chem., 46 (1968) 1383.
17 I. Grenthe, G. Gardammar and E. Rundczantz, Acta Chem. Scand., 23 (1969) 93.
18 G.F. Condike and A.E. Martell, J. Inorg. Nucl. Chem., 31 (1969) 2455.
19 V.P. Vasilev, L.A. Kochergina and V.I. Eremenko, Russ. J. Phys. Chem., 45 (1971) 1196.
20 V.P. Vasilev, L.D. Shekhanova and L.A. Kochergina, J. Gen. Chem. U.S.S.R., 43 (1973) 967.
21 J.L. Kurz and J.M. Farrar, J. Am. Chem. Soc., 91 (1969) 6057.
22 A.K. Sinha, J.C. Ghosh and B. Prasad, J. Indian Chem. Soc., 51 (1974) 586.
23 G. Arena, R. Calì, V. Cucinotta, M. Grasso, S. Musumeci, E. Rizzarelli, S. Sammartano and G. Siracusa, Transition Met. Chem., 5 (1980) 30.
24 W.H. Banks, E.C. Righellato and C.W. Davies, Trans. Faraday Soc., 27 (1931) 621.
25 B. Finlayson, R. Roth and Lindreth Dubois, Urinary Calculi Int. Symp. Renal Stone Res., Madrid, 1972, pp. 1—7.
26 D. Midgeley, Chem. Soc. Rev., 4 (1975) 549.
27 L.G. Sillèn and A.E. Martell, Stability Constants, Chem. Soc., Spec. Publ. No. 17 (1964); No. 25 (1971).
28 A.E. Martell and R.M. Smith, Critical Stability Constants, Plenum Press, London, New York, 1977.

29 G. Arena, R. Calì, M. Grasso, S. Musumeci, S. Sammartano and C. Rigano, Thermochim. Acta, 36 (1980) 329.
30 P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Italy), 70 (1980) 119.
31 K. Diem (Ed.), Documenta Geigy Scientific Tables, Geigy, Basle, 7th edn., 1970.
32 P. Amico, V. Cucinotta, P.G. Daniele, E. Rizzarelli and S. Sammartano, Inorg. Chim. Acta, 36 (1979) 1.
33 P.G. Daniele, G. Ostacoli and V. Zelano, Ann. Chim. (Italy), 65 (1975) 455.
34 G. Arena, E. Rizzarelli, S. Sammartano and C. Rigano, Talanta, 26 (1979) 1.
35 A. Sabatini, A. Vacca and P. Gans, Talanta, 21 (1974) 53; P. Gans, A. Sabatini and A. Vacca, Inorg. Chim. Acta, 18 (1976) 237; A. Vacca, personal communication, 1976.
36 W.C. Hamilton, Statistics in Physical Sciences, Ronald Press, New York, 1964.
37 A. Vacca, A. Sabatini and M.A. Gristina, Coord. Chem. Rev., 8 (1972) 45.
38 E.C.W. Clarke and D.N. Glew, Trans. Faraday Soc., (1966) 539.
39 D.W. Archer, D.A. East and C.B. Monk, J. Chem. Soc., (1965) 720.
40 D.W. Archer and C.B. Monk, J. Chem. Soc., (1964) 3117.
41 K. Kanamori, M. Mihara and K. Kawai, Bull. Chem. Soc. Jpn., 52 (1979) 2205.
42 R.P. Oertel, Inorg. Chem., 12 (1973) 3000.