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Salt effects on the protonation of oxalate in aqueous NaCl, KCl and tetraethylammonium iodide solution at $5 \leq T \leq 50°C$ and $0 \leq I \leq 1$ mol dm^{-3}

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Abstract

Protonation constants of oxalate (ox^{2-}) were obtained, by potentiometric measurements, in NaCl, KCl and tetraethylammonium iodide aqueous solutions in the ranges $5 \leq T \leq 50°C$ and $0 \leq I \leq 1$ mol dm^{-3}. The differences in protonation constant values were explained by a complex formation model assuming the formation of $M(ox)^-$ and $MH(ox)^0$ ($M = Na^+, K^+$) complexes. From the dependence on temperature of the protonation and formation constants, $\Delta H°$ values were calculated. The dependence on ionic strength of the formation thermodynamic parameters was obtained for each species. Consideration is given to the use of different concentration scales, and comparison is made with literature findings. Recommended values are given. Simulated protonation constants in sea water conditions are reported.

INTRODUCTION

In the last decade we have dedicated much work to the study of the protonation of low molecular weight ligands [1–4] in different salt media with the aim of building up a simple model for the dependence of protonation constants on ionic strength. It was found that differences in protonation constants obtained in different media can be explained by assuming the formation of weak complexes of the type O-ligand–alkali metal ion [1,5] or N-ligand (protonated)–inorganic anion [6,7] (ClO_4^-, NO_3^-, Cl^-, I^-). In this work we report a potentiometric study on the protonation of oxalate in NaCl, KCl and tetraethylammonium iodide aqueous solution at different temperatures and salt concentrations.

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Protonation constants of oxalate have been widely studied [8–10], but their dependence on ionic strength and on media has been investigated only at certain temperatures or ionic strengths. Here we give a full picture of salt effects on protonation in the range $0 \leq I \leq 1$ mol dm^{-3} and $5 \leq T \leq 50$°C in NaCl and KCl aqueous solution.

Particular attention has been paid to the possibility of using formation thermodynamic parameters in the speciation of natural fluids.

EXPERIMENTAL

Reagents

Oxalic acid dihydrate (Fluka, biochemika) was used as received. Its purity, as checked by alkalimetric measurements, was $> 99.8\%$. Sodium chloride and KCl (Fluka, biochemika) were dried in an oven at 110°C. Tetraethylammonium iodide (Et_4NI) and tetramethylammonium hydroxide (Me_4NOH) (Fluka, puriss.) were purified as described by Perrin et al. [11]. Solutions of NaOH, KOH and Me_4NOH were standardized against biphthalate, and HCl solution against sodium carbonate; cross titrations were performed as a check. Twice distilled water and grade A glassware were used to prepare all solutions. Thermal expansion of solutions was always taken into account so as to calculate correct molar and molal concentrations.

Apparatus

Three different sets of potentiometric equipment were employed: (1) a Metrohm model E600 with manual addition of titrant; (2) a semiautomatic homemade potentiometer built with Mosteck logic circuits, an Analog Devices potentiometer and a Printel printer; this apparatus adds a pre-established volume of titrant and prints the corresponding e.m.f. value; (3) a Metrohm model E654 coupled with a Metrohm Dosimat 665 and with appropriate software for fully computerized titrations. The potentiometers were coupled with a variety of glass reference electrodes (Orion, Metrohm, Ingold). The use of different equipment ensured the avoidance of systematic errors. In systems (1) and (2), the titrant solution was delivered by an Amel model 882 dispenser with a minimum reading of 0.001 ml. In all cases the instrumental resolution was ± 0.1 mV. The electrode couples were calibrated in $pH = -\log[H^+]$ units by titrating HCl (5 mmol dm^{-3}) with standard hydroxide (NaOH, KOH or Me_4NOH for NaCl, KCl and Et_4NI media, respectively) under the same conditions (temperature, concentration and ionic strength) as for the solution under study. The titration cells (50 ml) were thermostatted at $T \pm 0.1$°C. Purified nitrogen was bubbled into the solutions during the titration and magnetic stirring was employed.

Procedure

A volume of 25–50 ml containing oxalic acid (5–10 mmol dm^{-3}) and the necessary quantity of alkali chloride or Et_4NI to give the required ionic strength value ($0 < I \leq 1.00$ mol dm^{-3}) was titrated with standard NaOH, KOH or Me_4NOH (0.2–0.4 mol dm^{-3}) to neutralization (35–40 experimental points). An excess of HCl (5–10 mmol dm^{-3}) was also added to all solutions in order to complete the protonation of the oxalate anion and to calculate directly the internal standard electrode potential E°_{int} (we denote by E°_{ext} the corresponding value calculated by separate calibration); if $|E^\circ_{\text{int}} - E^\circ_{\text{ext}}| > 1$ mV, the titration was rejected. The reproducibility of potentiometric systems (1) and (2) was ± 0.005 pH unit; that of system (3) was ± 0.003 pH unit. The junction potential E_j was always considered when the pH was < 3.

Calculations

Calculations relating to the determination of oxalate purity, to the evaluation of E° and E_j and to standardizing the sodium, potassium and tetramethylammonium hydroxide solutions were carried out by means of the computer program ESAB2M [12]. For the evaluation of protonation and stability constants, the computer programs STACO [13] and ES2WC [14] were used. Distribution diagrams were calculated by the program ES4EC [15].

As regards the ionic strength, since Cl^- associates weakly with Na^+ and K^+, we considered in the calculations the effective ionic strength I_e by using the following degrees of dissociation (C = salt concentration)

$$\alpha = 1 - C^{1/2}_{\text{NaCl}}[0.033 - 9 \times 10^{-4}(T - 25)] - C_{\text{NaCl}}[0.219 - 4 \times 10^{-4}(T - 25)] + 0.079C^{3/2}_{\text{NaCl}}$$

$$\alpha = 1 - C^{1/2}_{\text{KCl}}[0.027 - 5 \times 10^{-4}(T - 25)] - C_{\text{KCl}}[0.246 - 1.5 \times 10^{-4}(T - 25)] + 0.059C^{3/2}_{\text{KCl}}$$

These degrees of dissociation were obtained in previous work [16] from a careful analysis of literature data; the error arising from the use of α in calculating the real ionic strength is about $0.05C$. The ionic strength, calculated by considering this association, was indicated by I_e, i.e. the effective ionic strength. Protonation and formation constants are expressed as (charges omitted)

$$K^{\text{H}}_j = [\text{H}_j(\text{ox})]/\{[\text{H}][\text{H}_{j-1}(\text{ox})]\}$$

$$\beta^{\text{H}}_j = \pi K^{\text{H}}_j$$

$$K^{\text{M}}_j = [\text{MH}_{j-1}(\text{ox})]/\{[\text{M}][\text{H}]^{j-1}[\text{ox}]\} \qquad \beta^{\text{M}}_i = K^{\text{M}}_i K^{\text{H}}_i$$

$$({}^{T}K, {}^{T}\beta) = \lim_{I \to 0}(K, \beta)$$

TABLE 1

Apparent protonation constants of oxalate [a] in NaCl and KCl aqueous solutions

Salt	T (°C)	I_c	I_m	$I_{e;c}$	$I_{e,m}$	log K'^H_{1c}	log K'^H_{1m}	log β'^H_{2c}	log β'^H_{2m}
NaCl	10	0.04	0.04	0.04	0.04	3.91 [b]	3.91 [b]	5.05 [c]	5.05 [c]
	10	0.17	0.17	0.16	0.16	3.73	3.73	4.81	4.81
	10	0.40	0.40	0.36	0.36	3.62	3.62	4.68	4.67
	10	0.75	0.76	0.64	0.65	3.55	3.55	4.59	4.59
	10	1.23	1.25	1.00	1.02	3.51	3.50	4.53	4.52
	25	0.04	0.04	0.04	0.04	3.95	3.95	5.12	5.12
	25	0.17	0.17	0.16	0.16	3.76	3.76	4.87	4.87
	25	0.39	0.39	0.36	0.36	3.65	3.65	4.74	4.73
	25	0.73	0.74	0.64	0.65	3.59	3.58	4.65	4.64
	25	1.20	1.23	1.00	1.03	3.55	3.54	4.59	4.58
	37	0.04	0.04	0.04	0.04	4.00	4.00	5.19	5.19
	37	0.17	0.17	0.16	0.16	3.81	3.80	4.93	4.93
	37	0.39	0.40	0.36	0.37	3.69	3.69	4.78	4.78
	37	0.73	0.74	0.64	0.65	3.62	3.61	4.70	4.68
	37	1.19	1.22	1.00	1.03	3.57	3.57	4.63	4.62
	45	0.04	0.04	0.04	0.04	4.05	4.04	5.25	5.25
	45	0.16	0.16	0.16	0.16	3.84	3.84	4.98	4.98
	45	0.39	0.40	0.36	0.37	3.72	3.72	4.84	4.83
	45	0.73	0.75	0.64	0.66	3.64	3.63	4.75	4.74
	45	1.17	1.21	1.00	1.04	3.60	3.59	4.70	4.68

KCl	10	0.04	0.04	0.04	0.04	3.93	3.93	5.08	5.08
	10	0.17	0.17	0.16	0.16	3.79	3.78	4.88	4.88
	10	0.40	0.40	0.36	0.36	3.71	3.71	4.79	4.79
	10	0.76	0.77	0.64	0.65	3.67	3.67	4.76	4.74
	10	1.28	1.32	1.00	1.04	3.65	3.63	4.72	4.70
	25	0.04	0.04	0.04	0.04	3.96	3.96	5.14	5.14
	25	0.17	0.17	0.16	0.16	3.80	3.80	4.92	4.92
	25	0.40	0.41	0.36	0.37	3.71	3.71	4.82	4.81
	25	0.75	0.77	0.64	0.66	3.66	3.65	4.76	4.75
	25	1.26	1.30	1.00	1.04	3.63	3.61	4.73	4.70
	37	0.04	0.04	0.04	0.04	4.01	4.01	5.20	5.20
	37	0.17	0.17	0.16	0.16	3.83	3.83	4.96	4.96
	37	0.40	0.41	0.36	0.37	3.72	3.72	4.84	4.83
	37	0.75	0.77	0.64	0.66	3.65	3.64	4.77	4.75
	37	1.25	1.30	1.00	1.05	3.60	3.59	4.72	4.69
	45	0.04	0.04	0.04	0.04	4.05	4.05	5.26	5.26
	45	0.17	0.17	0.16	0.16	3.86	3.85	5.01	5.00
	45	0.39	0.40	0.36	0.37	3.73	3.73	4.87	4.86
	45	0.74	0.76	0.64	0.66	3.65	3.64	4.80	4.78
	45	1.24	1.29	1.00	1.05	3.60	3.59	4.75	4.72

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[a] For the symbols used in this table, see the section entitled calculations.

[b] $3s(\log K_1'^{H}) = 0.005–0.01$.

[c] $3s(\log \beta_2'^{H}) = 0.05–0.1$.

TABLE 2

Thermodynamic parameters for the protonation of oxalate [a]

j	T (°C)	$\log {}^{T}\beta^{H}_{j,c}$	$\log {}^{T}\beta^{H}_{j,m}$	$\Delta G°$	$\Delta H°$	$\Delta S°$	$\Delta C°_p$
1	5	4.224 [b]	4.224 [b]	−22.49	1.1 [b]	85	0.25 [b]
	10	4.230	4.230	−22.93	2.4	90	0.27
	15	4.240	4.240	−23.39	3.8	94	0.28
	20	4.255	4.254	−23.88	5.2	99	0.30
	25	4.273	4.272	−24.38	6.8	105	0.32
	30	4.296	4.294	−24.92	8.4	110	0.34
	35	4.322	4.319	−25.48	10.2	116	0.36
	40	4.353	4.350	−26.07	12.1	122	0.38
	45	4.388	4.384	−26.69	14.0	128	0.40
	50	4.427	4.422	−27.36	16.1	134	0.42
2	5	5.49 [c]	5.49 [c]	−29.25	5 [c]	124	0.2 [c]
	10	5.51	5.51	−29.88	6	128	0.2
	15	5.54	5.54	−30.53	8	132	0.3
	20	5.56	5.56	−31.21	9	137	0.3
	25	5.59	5.59	−31.89	10	141	0.3
	30	5.62	5.62	−32.62	12	146	0.3
	35	5.66	5.65	−33.35	13	151	0.3
	40	5.70	5.69	−34.13	15	156	0.3
	45	5.74	5.73	−34.92	17	162	0.4
	50	5.78	5.78	−35.74	18	167	0.4

[a] For the symbols used in this table, see the section entitled Calculations. Units: $\Delta G°$ and $\Delta H°$ kJ mol^{-1}; $\Delta S°$ J K^{-1} mol^{-1}; $\Delta C°_p$ kJ K^{-1} mol^{-1}.

[b] $3s(\log {}^{T}\beta^{H}_{1}) = 0.002\text{–}0.005$; $3s(\Delta H°_1) = 0.15\text{–}0.4$; $3s(\Delta C°_{p_1}) = 0.01\text{–}0.02$.

[c] $3s(\log {}^{T}\beta^{H}_{2}) = 0.04\text{–}0.07$; $3s(\Delta H°_2) = 3\text{–}5$; $3s(\Delta C°_{p_2}) = 0.1\text{–}0.2$.

In this paper, subscripts c and m indicate molar and molal scales, respectively, and primes indicate apparent or conditional quantities. Throughout the paper the uncertainties in the parameters are three times the standard deviation.

RESULTS AND DISCUSSION

In Table 1 we report the apparent protonation constants of oxalate in aqueous NaCl and KCl media. A series of experiments was performed also at $I < 0.04$ mol dm^{-3} in order to obtain protonation constants at infinite dilution, which are reported in Table 2. Protonation constants in tetraethylammonium iodide solutions are reported in Table 3. In these tables the protonation constant values are given on both the molar and the molal scale, in order to calculate the correct thermodynamic parameters [18]. From the dependence of $\log K^{H}$ on T, the thermodynamic parameters

$\Delta H°$, $\Delta S°$ and $\Delta C°_p$ were calculated using the equation proposed by Clarke and Glew [17]

$$\log K^{\mathrm{H}}_{(T)} = \log K^{\mathrm{H}}_{(\theta)} + \left[\Delta H°_{(\theta)}\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta C°_{p(\theta)}\left(\frac{\theta}{T} + \ln\frac{T}{\theta} - 1\right)\right] \times (R \ln 10)^{-1} \qquad (1)$$

Protonation constants show the trend (see Fig. 1) $Et_4NI \gg KCL \geq NaCl$, which can be explained, as done already [1,9,10,19], by assuming that Et_4N^+ (or Me_4N^+, arising from the titrant) does not form any complex species with oxalate and that Na^+ and K^+ form weak complexes. For both alkali metal ions the species $M(ox)^-$ and $MH(ox)^0$ can be hypothesized. Calculations performed with the computer programs ES2WC and STACO showed that this hypothesis is very consistant with experimental data. In Table 4 we report the formation thermodynamic parameters for $Na(ox)^-$, $NaH(ox)^0$, $K(ox)^-$ and $KH(ox)^0$ species. In Fig. 2, a distribution diagram for the Na^+–H^+–ox^{2-} system is reported. In Table 5 we report some comparisons with literature findings. The protonation of oxalate has been widely studied and thermodynamic parameters have been obtained by potentiometry (glass and hydrogen electrode, with or without liquid junction) and by calorimetry. Reported $\log K^{\mathrm{H}}_j$ and $\Delta H°_j$ values are generally in good agreement with our findings for $j = 1$, but for $j = 2$ the literature data seem to be quite inaccurate. As concerns sodium and potassium unprotonated complexes, few data are available; by considering that for

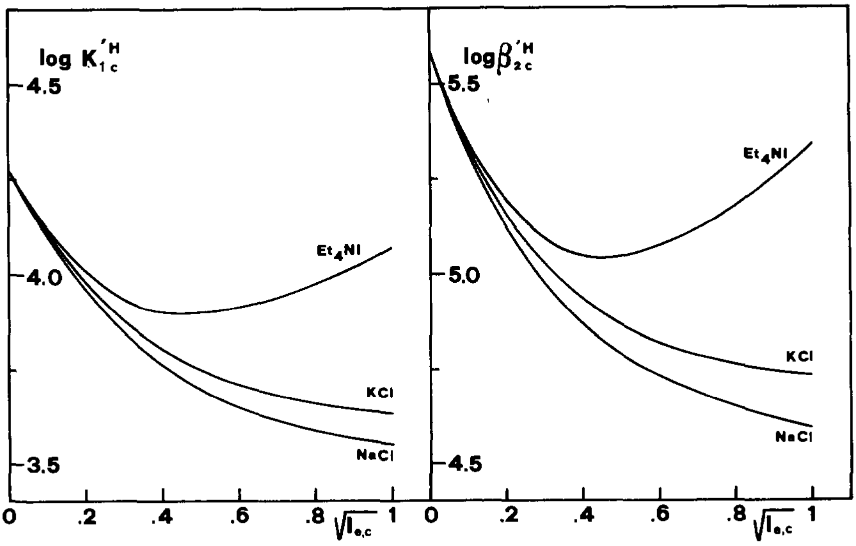

Fig. 1. Ionic strength dependence of protonation constants.

TABLE 3

Thermodynamic parameters for the protonation of oxalate in aqueous tetraethylammonium iodide solutions [a]

j	I_c	I_m	T (°C)	$\log \beta'^{H}_{j,c}$	$\log \beta'^{H}_{j,m}$	$\Delta G°$	$\Delta H°$	$\Delta S°$	$\Delta C°_p$
1	0.04	0.04	10	3.96 [b]	3.96 [b]	−16.5	2 [b]	84	0.3 [b]
	0.04	0.04	25	4.00	3.93	−22.8	7	100	0.3
	0.04	0.04	37	4.06	4.06	−24.1	11	114	0.4
	0.04	0.04	45	4.11	4.11	−25.1	14	124	0.4
	0.16	0.16	10	3.87	3.87	−21.0	2	82	0.3
	0.16	0.17	25	3.90	3.90	−22.3	8	97	0.3
	0.16	0.17	37	3.96	3.96	−23.5	11	111	0.4
	0.16	0.17	45	4.02	4.01	−24.4	14	121	0.4
	0.36	0.39	10	3.87	3.87	−20.9	2	82	0.3
	0.36	0.39	25	3.91	3.91	−22.3	7	98	0.3
	0.36	0.39	37	3.97	3.96	−23.5	11	112	0.4
	0.36	0.39	45	4.03	4.01	−24.4	14	122	0.4
	0.64	0.73	10	3.93	3.92	−21.2	3	86	0.3
	0.64	0.73	25	3.98	3.96	−22.6	7	101	0.3
	0.64	0.73	37	4.04	4.03	−23.9	11	116	0.4
	0.64	0.73	45	4.10	4.07	−24.8	15	126	0.4
	1.00	1.22	10	4.01	3.98	−21.6	4	93	0.3
	1.00	1.23	25	4.07	4.04	−23.0	9	109	0.3
	1.00	1.24	37	4.15	4.12	−24.4	13	123	0.4
	1.00	1.24	45	4.21	4.16	−25.4	17	134	0.4

2	0.04	0.04	10	5.11 [c]	5.05 [c]	−27.4	6 c	120	0.2 [c]
	0.04	0.04	25	5.18	5.13	−29.2	10	133	0.3
	0.04	0.04	37	5.26	5.20	−30.9	13	145	0.3
	0.04	0.04	45	5.33	5.24	−32.0	16	154	0.3
	0.16	0.16	10	4.98	4.89	−26.5	5	116	0.2
	0.16	0.17	25	5.05	4.95	−28.3	9	129	0.3
	0.16	0.17	37	5.12	5.03	−29.9	13	141	0.3
	0.16	0.17	45	5.19	5.19	−26.6	16	150	0.4
	0.36	0.39	10	5.00	4.92	−27.1	6	115	0.2
	0.36	0.39	25	5.07	5.07	−28.9	10	129	0.3
	0.36	0.39	37	5.14	5.14	−30.5	13	141	0.3
	0.36	0.39	45	5.20	5.20	−31.7	16	150	0.4
	0.64	0.73	10	5.11	5.11	−27.7	8	120	0.2
	0.64	0.73	25	5.18	5.18	−29.6	10	133	0.3
	0.64	0.73	37	5.26	5.26	−31.2	14	145	0.3
	0.64	0.73	45	5.32	5.32	−32.4	16	154	0.3
	1.00	1.22	10	5.25	5.24	−28.4	8	128	0.2
	1.00	1.23	25	5.34	5.33	−30.4	12	143	0.3
	1.00	1.24	37	5.43	5.41	−32.1	16	155	0.3
	1.00	1.24	45	5.51	5.48	−33.4	19	165	0.3

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[a] For the symbols used in this table see the section entitled Calculations. Units: $\Delta G°$ and $\Delta H°$ kJ mol^{-1}; $\Delta S°$ J K^{-1} mol^{-1}; $\Delta C°_p$ kJ K^{-1} mol^{-1}.

[b] $3s(\log \beta_1^{\mathrm{H}}) = 0.005$–$0.01$; $3s(\Delta H°_1) = 0.5$–1; large uncertainties in $\Delta C°_p$.

[c] $3s(\log \beta_2^{\mathrm{H}}) = 0.04$–$0.08$; $3s(\Delta H°_2) = 3.5$–7; large uncertainties in $\Delta C°_p$.

TABLE 4

Thermodynamic parameters for the formation of Na^+ and K^+-oxalate complexes [a]

Species	I_e (NaCl)	T (°C)	log β_c^M	log β_m^M	$\Delta G°$	$\Delta H°$	$\Delta S°$	$\Delta C°_p$
$Na(ox)^-$	0.04	10	0.57 [b]	0.57	−3.1	1 [b]	16	0.2 [b]
	0.04	25	0.60	0.60	−3.4	5	27	0.2
	0.04	37	0.64	0.64	−3.8	8	37	0.3
	0.04	45	0.68	0.68	−4.1	10	44	0.3
	0.16	10	0.48	0.48	−2.6	1	14	0.2
	0.16	25	0.50	0.50	−2.9	4	24	0.2
	0.16	37	0.54	0.54	−3.2	7	34	0.3
	0.16	45	0.58	0.58	−3.5	10	41	0.3
	0.36	10	0.48	0.48	−2.6	1	14	0.2
	0.36	25	0.51	0.51	−2.9	5	25	0.2
	0.36	37	0.55	0.55	−3.3	7	35	0.3
	0.36	45	0.59	0.58	−3.5	10	41	0.3
	0.64	10	0.54	0.54	−2.9	2	18	0.2
	0.64	25	0.57	0.57	−3.3	5	28	0.2
	0.64	37	0.62	0.62	−3.7	8	38	0.3
	0.64	45	0.66	0.66	−4.0	10	45	0.3
	1.00	10	0.62	0.61	−3.3	4	24	0.2
	1.00	25	0.67	0.66	−3.8	7	36	0.2
	1.00	37	0.73	0.72	−4.3	10	46	0.3
	1.00	45	0.78	0.77	−4.7	12	53	0.3
$NaH(ox)^0$	0.04	10	3.68 [c]	3.68	−19.9	7 [c]	94	
	0.04	25	3.74	3.74	−21.4	7	96	
	0.04	37	3.80	3.80	−22.5	8	98	
	0.04	45	3.83	3.83	−23.3	8	99	
	0.16	10	3.55	3.54	−19.2	6	90	
	0.16	25	3.61	3.61	−20.6	7	92	
	0.16	37	3.66	3.65	−21.7	7	94	
	0.16	45	3.69	3.68	−22.4	8	95	
	0.36	10	3.57	3.56	−19.3	6	90	
	0.36	25	3.63	3.62	−20.7	7	92	
	0.36	37	3.67	3.67	−21.8	7	93	
	0.36	45	3.71	3.70	−22.5	7	94	
	0.64	10	3.67	3.67	−19.9	7	94	
	0.64	25	3.74	3.73	−21.3	7	96	
	0.64	37	3.79	3.78	−22.5	8	98	
	0.64	45	3.83	3.82	−23.2	8	99	
	1.00	10	3.82	3.81	−20.6	8	102	
	1.00	25	3.90	3.89	−22.2	9	105	
	1.00	37	3.97	3.95	−23.5	10	107	
	1.00	45	4.01	3.99	−24.3	10	109	

TABLE 4 (continued)

Species	I_e (KCl)	T (°C)	log β_c^M	log β_m^M	$\Delta G°$	$\Delta H°$	$\Delta S°$	$\Delta C°_p$
K(ox)$^-$	0.04	10	0.32 [d]	0.32	−1.7	10 [d]	42	0.3 [d]
	0.04	25	0.43	0.43	−2.5	14	56	0.3
	0.04	37	0.54	0.54	−3.2	18	68	0.3
	0.04	45	0.62	0.62	−3.8	21	77	0.4
	0.16	10	0.22	0.22	−1.2	10	40	0.3
	0.16	25	0.33	0.33	−1.9	14	54	0.3
	0.16	37	0.44	0.44	−2.6	18	66	0.3
K(ox)$^-$	0.16	45	0.52	0.52	−3.2	21	75	0.4
	0.36	10	0.23	0.22	−1.2	10	40	0.3
	0.36	25	0.34	0.33	−1.9	14	54	0.3
	0.36	37	0.45	0.44	−2.6	18	66	0.3
	0.36	45	0.53	0.53	−3.2	21	75	0.4
	0.64	10	0.29	0.28	−1.5	11	43	0.3
	0.64	25	0.41	0.40	−2.3	15	58	0.3
	0.64	37	0.52	0.51	−3.0	19	70	0.3
	0.64	45	0.61	0.60	−3.6	21	79	0.4
	1.00	10	0.37	0.36	−1.9	12	50	0.3
	1.00	25	0.50	0.49	−2.8	17	65	0.3
	1.00	37	0.63	0.61	−3.6	21	78	0.3
	1.00	45	0.72	0.71	−4.3	23	87	0.4
KH(ox)^0	0.04	10	3.52 [e]	3.52	−19.1	7 [e]	94	
	0.04	25	3.60	3.59	−20.5	8	96	
	0.04	37	3.65	3.65	−21.7	9	98	
	0.04	45	3.69	3.69	−22.5	9	100	
	0.16	10	3.39	3.38	−18.3	7	90	
	0.16	25	3.46	3.45	−19.7	8	92	
	0.16	37	3.51	3.51	−20.8	8	94	
	0.16	45	3.55	3.54	−21.6	9	95	
	0.36	10	3.41	3.40	−18.4	7	90	
	0.36	25	3.48	3.47	−19.8	8	92	
	0.36	37	3.53	3.52	−20.9	8	94	
	0.36	45	3.57	3.56	−21.7	8	95	
	0.64	10	3.52	3.50	−19.0	7	93	
	0.64	25	3.59	3.57	−20.4	8	96	
	0.64	37	3.65	3.63	−21.6	9	98	
	0.64	45	3.69	3.67	−22.4	9	99	
	1.00	10	3.66	3.64	−19.7	9	102	
	1.00	25	3.75	3.73	−21.3	10	105	
	1.00	37	3.82	3.80	−22.5	11	108	
	1.00	45	3.87	3.84	−23.4	11	109	

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[a] For the symbols used in this table see the section entitled Calculations. Units: $\Delta G°$ and $\Delta H°$ kJ mol^{-1}; $\Delta S°$ J K^{-1} mol^{-1}; $\Delta C°_p$ kJ K^{-1} mol^{-1}.

[b] $3s(\log \beta_{01}^M) = 0.025–0.07$; $3s(\Delta H°) = 2–5$.

[c] $3s(\log \beta_{11}^M) = 0.1–0.2$.

[d] $3s(\log \beta_{01}^M) = 0.04–0.08$; $3s(\Delta H°) = 3.5–7$.

[e] $3s(\log \beta_{11}^M) = 0.1–0.3$.

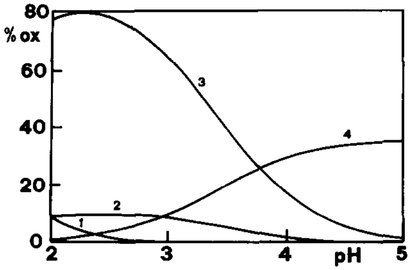

Fig. 2. Distribution of species, vs. pH, in the system H^+-Na^+-ox^{2-}. $T = 37°C$; $C_{Na} = I = 0.36$ mol dm^{-3}; $C_{ox} = 0.001$ mol dm^{-3}. Curve 1, $H_2(ox)^0$; curve 2, $NaH(ox)^0$; curve 3, $H(ox)^-$; curve 4, $Na(ox)^-$.

TABLE 5

Comparison with literature findings

T	I	$\log K_1^H$	$\log K_2^H$	Notes
25	0	4.284 ± 0.017 (m) [a]	1.29 ± 0.05	Average literature value, ref. 8
25	0	4.266 (m)		Pinching and Bates, ref. 20
25	0	4.272 ± 0.001 (m)	1.317 ± 0.015 (m)	This work
25	0.1 ($NaClO_4$)	3.83 ± 0.02 (c) [a]	1.2 ± 0.2 (c)	Average literature value, ref. 8
25	1 ($NaClO_4$)	3.56 ± 0.01 (c)	1.05 ± 0.04 (c)	Average literature value, ref. 8
25	1 (Na^+)	3.60 ± 0.01 (c)	1.10 ± 0.05 (c)	This work
37	0	4.34 ± 0.01 (c)		Average literature value
T	I	$\Delta H°_1$	$\Delta H°_2$	Notes
25	0	6.55 ± 0.28		Average literature value, ref. 8
25	0	6.49 ± 0.17	3.3 ± 1	Daniele et al., ref. 9
25	0	6.8 ± 0.1	3.4 ± 1	This work
T	I	$\log K^{Na}$ [b]	$\log K^{K}$ [b]	Notes
18	0		0.8	Banks et al., ref. 21
25	0	0.86		Daniele et al., from a literature analysis, ref. 9
35	0	0.91		
37	0.1	0.53	0.43	Daniele et al., ref. 9
25	0	0.88	0.71	This work
37	0	0.92	0.83	This work
38	0	1.12		Finlayson et al., ref. 22
25	0	$\Delta H° = 4.4$		Daniele et al., from a literature analysis, ref. 9
25	0.25	$\Delta H° = 4.4$	14.2	This work
25	0	$\Delta H° = 1$		This work
25	0	$\Delta H° = 1.7$		Daniele et al., from a literature analysis, ref. 23

[a] (m) = molal scale; (c) = molar scale; $\Delta H°$ in kJ mol^{-1}.

[b] Formation constants in the molar scale.

these species the error must be higher with respect to protonation, the agreement is satisfactory; no data are available for protonated complexes.

The dependence on ionic strength of the protonation constants and formation constants was calculated according to the equation

$$\log K(I) = \log K(0.25) - z^{*}A\left[\sqrt{I}/(1+B\sqrt{I}) - \sqrt{0.25}/(1+B\sqrt{0.25})\right] + C(I-0.25) + D(I^{3/2}-0.25^{3/2}) \quad (2)$$

$$z^{*} = \Sigma z^{2}_{\text{reactants}} - \Sigma z^{2}_{\text{products}}$$

$$A = 0.5115 + 7.2 \times 10^{-4}(T-25) + 9.5 \times 10^{-6}(T-25)^{2} \text{ (molar scale)}$$

$$A = 0.5108 + 7.1 \times 10^{-4}(T-25) + 6.9 \times 10^{-6}(T-25)^{2} \text{ (molal scale)}$$

where B, C and D are empirical parameters, and A is the Debye–Hückel parameter.

In Table 6 we report these parameters calculated from experimental data. As one can see, the parameters C and D (eqn. (2)) which define the dependence on ionic strength show different values for apparent protonation constants, whilst having the same value for protonation constants obtained in Et_4NI and for formation constants of Na^+ and K^+ complexes.

Errors reported for all the thermodynamic parameters are quite low and allow us to estimate the concentrations of various species with an accuracy compatible with a correct speciation of natural fluids containing oxalate in the investigated I,T range. As an example, in Table 7 we report some percentages of formation together with the errors arising from uncertainties in formation parameters. As one can see, errors in percentages for the main species are quite low, and the picture of solutions containing sodium and potassium species is satisfactory.

In Table 8, some recommended formation thermodynamic parameters values are reported for protonated and Na^+ complex species only, for which comparisons with literature findings can be made.

Thermodynamic formation values from this work can be used to simulate the conditions of all natural fluids containing oxalate and alkali metal ions. By using sufficiently accurate Ca^{2+} and Mg^{2+}–oxalate formation constants and Na^+, K^+–oxalate formation data here reported we were able to simulate also the protonation constants of oxalate in synthetic sea water, as reported in Table 9.

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TABLE 6

Parameters for the dependence on ionic strength of thermodynamic parameters of H^+, Na^+ and K^+ oxalate complex formation

Medium	$\log K$ [a]	ΔH^* [b]	ΔC_p^* [b]	B [c]	C [c]	$\partial C/\partial T$ [c]	D [c]	$\partial D/\partial T$ [c]	Notes
NaCl	3.71	4.9	150	1.000	0.603	−0.0025	−0.295	0.0019	$\log K'^{H}_{1c}$ vs. I_c
	3.71	5.0	146	1.606	0.080	−0.0005			
	3.70	5.0	157	1.000	0.563	−0.0026	−0.275	0.0022	$\log K'^{H}_{1c}$ vs. $I_{e,c}$
	3.70	5.1	151	1.470	0.106	−0.0005			
	3.71	4.7	144	1.000	0.598	−0.0024	−0.296	0.0020	$\log K'^{H}_{1m}$ vs. I_m
	3.71	4.9	148	1.633	0.069	−0.0004			
	3.70	4.8	158	1.000	0.566	−0.0024	−0.283	0.0022	$\log K'^{H}_{1m}$ vs. $I_{e,m}$
	3.70	5.0	155	1.504	0.091	−0.0004			
	4.79	7.5	233	1.000	1.221	−0.0012	−0.661	0.0016	$\log \beta'^{H}_{2c}$ vs. I_c
	4.81	7.8	223	2.030	0.068	0.0000			
	4.78	7.6	237	1.000	1.223	−0.0026	−0.694	0.0030	$\log \beta'^{H}_{2c}$ vs. $I_{e,c}$
	4.79	8.0	229	1.895	0.091	0.0000			
	4.79	7.6	223	1.000	1.186	−0.0012	−0.638	0.0012	$\log \beta'^{H}_{2m}$ vs. I_m
	4.80	7.8	225	1.997	0.067	−0.0002			
	4.78	7.7	230	1.000	1.181	−0.0020	−0.662	0.0022	$\log \beta'^{H}_{2m}$ vs. $I_{e,m}$
	4.79	8.0	233	1.871	0.088	−0.0002			
KCl	3.75	2.3	135	1.000	0.794	−0.0098	−0.414	0.0057	$\log K'^{H}_{1c}$ vs. I_c
	3.76	2.6	146	1.950	0.066	−0.0034			
	3.75	2.0	135	1.000	0.803	−0.0115	−0.444	0.0072	$\log K'^{H}_{1c}$ vs. $I_{e,c}$
	3.75	2.5	152	1.808	0.087	−0.0044			
	3.75	2.3	132	1.000	0.803	−0.0108	−0.429	0.0067	$\log K'^{H}_{1m}$ vs. I_m
	3.76	2.7	115	2.002	0.047	−0.0031			
	3.75	2.0	135	1.000	0.815	−0.0125	−0.465	0.0085	$\log K'^{H}_{1m}$ vs. $I_{e,m}$
	3.75	2.6	124	1.880	0.061	−0.0040			
	4.85	4.9	211	1.000	1.480	−0.0090	−0.799	0.0056	$\log \beta'^{H}_{2c}$ vs. I_c
	4.87	5.3	194	2.346	0.097	−0.0028			

	4.85	4.6	211	1.000	1.532	−0.0110	−0.879	0.0078	log β'^{H}_{2c} vs. $I_{e,c}$
	4.86	5.2	202	2.171	0.135	−0.0036			
	4.85	4.7	206	1.000	1.440	−0.0090	−0.781	0.0056	log β'^{H}_{2m} vs. I_m
	4.87	5.1	185	2.366	0.071	−0.0028			
	4.85	4.4	205	1.000	1.500	−0.0114	−0.870	0.0080	log β'^{H}_{2m} vs. $I_{e,m}$
	4.86	5.0	195	2.212	0.096	−0.0036			
Et_4NI	3.90	6.7	361	1.500	1.031	0.0011	−0.418	0.0011	log K^{H}_{1c} vs. $I_{e,c}$
	3.89	6.4	359	1.500	1.077	−0.0013	−0.518	0.0023	log K^{H}_{1m} vs. $I_{e,m}$
	5.04	9.2	312	1.500	1.602	−0.0030	−0.629	0.0050	log β^{H}_{2c} vs. $I_{e,c}$
	4.99	11.5	261	1.500	1.849	0.0088	−0.859	−0.0070	log β^{H}_{2m} vs. $I_{e,m}$
NaCl	0.49	4.5	260	1.500	1.006	−0.0004	−0.394	0.0026	log K^{Na}_{1c} vs. $I_{e,c}$
	0.49	4.4	247	1.500	1.033	−0.0015	−0.436	0.0034	log K^{Na}_{1m} vs. $I_{e,m}$
	3.60	6.7	60	1.500	1.584	−0.0010	−0.614	0.0034	log β^{Na}_{2c} vs. $I_{e,c}$
	3.60	6.7	30	1.500	1.567	−0.0006	−0.620	0.0022	log β^{Na}_{2m} vs. $I_{e,m}$
KCl	0.33	14.1	309	1.500	1.026	0.0003	−0.411	0.0019	log K^{K}_{1c} vs. $I_{e,c}$
	0.32	14.2	329	1.500	0.988	0.0013	−0.398	0.0006	log K^{K}_{1m} vs. $I_{e,m}$
	3.45	7.5	53	1.500	1.603	−0.0008	−0.633	0.0030	log β^{K}_{2c} vs. $I_{e,c}$
	3.44	7.6	46	1.500	1.563	−0.0008	−0.631	0.0024	log β^{K}_{2m} vs. $I_{e,m}$

z^*	p^*	$\bar{C}$	$\bar{D}$	$\partial C/\partial T$	$\partial D/\partial T$
4	1	1.021	−0.408	≈ 0	0.0019
6	2	1.596	−0.625	−0.0008	0.0038

$c_0 = 0.129$ $c_1 = 0.233$ $d = -0.103$ (at 25°C)
($C = c_0 p^* + c_1 z^*$; $D = z^* d$; see ref. 5)

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[a] Formation constant at $I = 0.25$.

[b] $\Delta H^* = RT^2(\partial \ln K/\partial T)$; $\Delta C_p^* = \partial \Delta H^*/\partial T$; ΔH^*, $\Delta C_p^* = \Delta H°$, $\Delta C°_p$ when K is in the molal scale.

[c] Eqn. (2).

TABLE 7

Formation percentages and errors ($\% \pm 3s$ [a])

pH	$H(ox)^-$	$H_2(ox)^0$	$Na(ox)^-$	$NaH(ox)^0$
1.5	60.4 ± 2.5	27.6 ± 2.4	–	11.4 ± 2.4
2	73.5 ± 2.5	10.6 ± 1.1	–	13.9 ± 2.8
2.5	75.8 ± 2.5	3.5 ± 0.4	3.4 ± 0.3	14.3 ± 2.8
3	68.0 ± 2.1	–	9.7 ± 0.7	12.8 ± 2.6
3.5	49.1 ± 1.3	–	22.2 ± 1.3	9.3 ± 1.9
4	26.0 ± 0.8	–	37.2 ± 1.7	4.9 ± 1.1
4.5	10.4 ± 0.4	–	47.1 ± 1.7	–

[a] Errors in percentages were calculated assuming that $3s(\log \beta_1^H) = 1.2\%$; $3s(\log \beta_2^H) = 12\%$; $3s(\log K_1^{Na}) = 7\%$; $3s(\log \beta_2^{Na}) = 23\%$; $3s(C_{Na}) = 3s(C_{ox}) = 0.1\%$.

TABLE 8

Some recommended values

T	I	Recommended value	
25	0	$\log K_{1m}^H = 4.270 \pm 0.005$	$\Delta H°_1 = 6.65 \pm 0.2$
		$\log K_{2m}^H = 1.31 \pm 0.02$	$\Delta H°_2 = 3.4 \pm 1$
37	0.16 (Et_4NI)	$\log K_{1c}^H = 3.96 \pm 0.02$	
37	0	$\log K_{1c}^H = 4.34 \pm 0.01$	
25	0	$\log K_{1c}^{Na} = 0.88 \pm 0.05$	
37	0	$\log K_{1c}^{Na} = 0.95 \pm 0.1$	

TABLE 9

Protonation constants of oxalate at 25°C in synthetic sea water (20%, 35% and 45%)

	20%	35%	45%
$\log K_{1c}^H$	2.86 ± 0.05	2.73 ± 0.05	2.68 ± 0.07
$\log \beta_{2c}^H$	3.9 ± 0.1	3.8 ± 0.1	3.7 ± 0.2

Mg^{2+} and Ca^{2+} formation constants used in the simulation

$\log K_{1c}^{Ca} = 2.99 \pm 0.1 + f(I, T)$ [a]
$\log K_{2c}^{Ca} = 1.0 \pm 0.2 + g(I)$ [b]
$\log K_{1c}^{Mg} = 3.46 \pm 0.07 + f(I, T)$ [a]
$\log K_{2c}^{Mg} = 1.0 \pm 0.2 + g(I)$ [b]

$f(I, T) = -8\sqrt{I}/(2 + 3\sqrt{I}) + 1.94I - 0.80I^{3/2} + 0.005(T - 25)$
$g(I) = -4\sqrt{I}/(2 + 3\sqrt{I}) + 1.0I - 0.4I^{3/2}$

[a] $\log K_{1c}^M$ has the same dependence on temperature for both Ca^{2+} and Mg^{2+}.
[b] $\log K_{2c}^M$ is fairly independent of temperature.

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