Thermochimica Acta, 62 (1983) 101–112
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE FORMATION OF PROTON AND ALKALI METAL COMPLEXES WITH LIGANDS OF BIOLOGICAL INTEREST IN AQUEOUS SOLUTION. THERMODYNAMICS OF Li^+, Na^+ AND K^+-DICARBOXYLATE COMPLEX FORMATION

PIER G. DANIELE

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

CARMELO RIGANO

Seminario Matematico, Università di Catania, 95125 Catania (Italy)

SILVIO SAMMARTANO

Istituto di Chimica Analitica, Università di Messina, 98100 Messina (Italy)

(Received 13 August 1982)

ABSTRACT

The formation and stability of Li^+, Na^+ and K^+ complexes with oxalate, malonate, succinate, maleate, DL-malate and phthalate were studied potentiometrically at various ionic strengths. From the data thus obtained, as well as from several literature data on the protonation of the above-mentioned ligands in various ionic media and at various temperatures, the dependence of Na^+ and K^+ complex formation on temperature was determined. The dependence on ionic strength, both for the protonation and the complex formation, is also discussed.

INTRODUCTION

Although it has long been well known that several ligands form weak complexes with alkali metal ions [1], few data concerning the thermodynamic parameters of these complexes are found in the literature [2]. The authors have recently published some papers [3–9] forming part of a series dedicated to the formation of alkali metal complexes and their relative thermodynamic parameters, and referring especially to those ligands of biological interest or, more generally, to those that may be helpful for the speciation of natural fluids and for the construction of model systems (as in the case of urine speciation [10]).

This paper examines Li^+, Na^+ and K^+ complexes with oxalate (ox^{2-}),

0040-6031/83/0000–0000/$03.00

malonate (mal^{2-}), succinate ($succ^{2-}$), maleate ($male^{2-}$), DL-malate ($mala^{2-}$) (only potassium complexes), and phthalate (pht^{2-}). All the above-mentioned dicarboxylate compounds are important model ligands, while some of them are also of biological interest. For these ligands, the literature provides a great number of data concerning the protonation at various temperatures and ionic strengths, so that it can be observed that the protonation constants obtained in different background salts follow, almost invariably, the trend $K^+ > Na^+ > Li^+$, suggesting that weak complexes, according to an $Li^+ > Na^+ > K^+$ order, are formed.

In order to check this hypothesis the protonation of the above-mentioned ligands in various background salts was studied systematically. Moreover, use was made of all thermodynamic data available in the literature to determine the enthalpy and entropy of K^+ and Na^+ complex formation (the data relating to Li^+ are too few to permit any appreciable analysis).

EXPERIMENTAL

Chemicals

Dicarboxylic acids, tetraethylammonium iodide and alkali metal nitrates (Fluka) were used without further purification. The purity of the acids, checked alkalimetrically, was always > 99%. Potassium hydroxide and nitric acid stock solutions were prepared by diluting concentrated ampoules (Merck). Twice distilled water was employed for all solutions. Grade A glassware was used.

Potentiometric measurements

The measurements were carried out potentiometrically by alkalimetric titrations of the acids. A model E 600 Metrohm potentiometer equipped with glass and calomel reference electrodes supplied by the same firm was employed. Calibration of the glass electrode, in $-\log c_H$ units (c_H is the free proton concentration), was achieved by titrating $H[NO_3]$ (5 mmole dm^{-3}) in $M[NO_3]$ (M^+ is the alkali metal ion) at the same concentration as the solution under study, with standard carbonate free $K[OH]$ (1 mole dm^{-3}). All the measurements were carried out at 37 ± 0.2°C.

Calculations

All the calculations were performed using the least-squares computer programs ACBA [11] and MINIQUAD 76A [12], both modified in order to

TABLE 1

Some experimental details of potentiometric measurements at 37°C. The statistical parameters are calculated by the computer program ACBA [11]

L^{2-}	M^+	n [a]	$\sigma(\log K_1^H)$ [b]	$\sigma(\log K_2^H)$ [b]	$R\%$ [b,c]	$\sigma_v \times 10^3$ [b,d]	C_L [e]	$\sigma(C_L)\%$ [b,f]
mal	Li	7	0.0034	0.0049	0.56	1.92	4.0–7.4	0.09
	Na	10	0.0037	0.0029	0.22	0.71	4.0–6.1	0.11
	K	9	0.0025	0.0019	0.16	0.53	4.0–6.7	0.08
succ	Li	5	0.0009	0.0009	0.16	0.40	4.0–5.1	0.04
	Na	10	0.0017	0.0008	0.11	0.33	3.9–5.5	0.06
	K	8	0.0025	0.0012	0.19	0.62	4.0–6.8	0.08
ox	Li	8	0.0095		0.81	2.05	3.6–4.0	0.24
	Na	9	0.0056		0.39	1.06	3.6–4.1	0.15
	K	9	0.0058		0.30	0.99	3.6–4.0	0.13
pht	Li	5	0.0032	0.0038	0.53	0.78	2.3–2.4	0.08
	Na	9	0.0026	0.0032	0.48	0.68	2.0–2.4	0.08
	K	7	0.0030	0.0046	0.57	0.83	2.3–2.4	0.08
male	Li	5	0.0036		0.59	1.38	3.9–4.1	0.09
	Na	8	0.0035		0.44	1.03	4.0–4.1	0.06
	K	8	0.0028		0.47	1.08	3.9–4.0	0.07
mala	K	7	0.0044	0.0038	0.83	2.11	4.1–7.5	0.21

[a] No. of independent measurements.

[b] Average values for n measurements.

[c] Hamilton factor, see ref. 11.

[d] Standard deviation in titre (cm^3).

[e] Analytical concentration of the acids in mmole dm^{-3}; $V_0 = 50$ cm^3; titrant K[OH] 1 mole dm^{-3}.

[f] Standard deviation in the analytical concentrations of the acids.

TABLE 2

Protonation constants of dicarboxylic acids (without allowing for M^+ complexes) and formation constants for M^+–L^{2-} systems, calculated using eqn. (2), at 37°C

L^{2-}	M^+	$\log K_1^H$ ($I = 0.15$)	B' [a]	C	$-D$	$\log K_1^M$ ($I = 0.15$)	$\log K_2^H$	B'	C	$-D$	K_2^M ($I = 0.15$)	$\log K_2^M$ ($I = 0.15$)
ox	Li	3.70(3) [b]	1.0	0.23	0.30	0.80(7)						
	Na	3.82(2)	1.0	0.63	0.35	0.50(8)						
	K	3.84(2)	1.0	0.70	0.37	0.44(9)						
	Et_4N	3.99	1.5	1.12	0.43							
mal	Li	5.16	1.0	0.35	0.30	0.67(9)	2.56(4)	1.0	0.18	0.15	3.0(9)	0.48(13)
	Na	5.25(1)	1.0	0.59	0.30	0.40(8)	2.61(1)	1.0	0.41	0.15	1.9(4)	0.28(9)
	K	5.23(1)	1.0	0.67	0.32	0.47(9)	2.62(2)	1.0	0.32	0.15	1.7(5)	0.23(13)
	Et_4N	5.39	1.5	1.02	0.30		2.72	1.5	0.47	0.15		
male	Li	5.76(2)	1.0	0.36	0.24	0.74(7)						
	Na	5.79(2)	1.0	0.58	0.30	0.67(9)						
	K	5.86(3)	1.0	0.44	0.30	0.47(12)						
	Et_4N	6.02	1.5	1.35	0.39							
succ	Li	5.14(2)	1.0	0.60	0.30	0.44(9)	3.94(5)	1.0	0.22	0.15	1.5(8)	0.18(23)
	Na	5.22(2)	1.0	0.66	0.30	0.07(15)	3.97(2)	1.0	0.32	0.15	1.0(4)	0.00(17)
	K	5.20(3)	1.0	0.86	0.38	0.2(2)	3.97(2)	1.0	0.30	0.07	1.0(4)	0.00(17)

	Et_4N	5.29	1.5	0.92	0.35		4.03	1.5	0.64	0.15		
mala	K	4.67(3)	1.5	0.39	0.2	0.2(2)	3.21(3)	1.5	0.29	0.1	0.8(5)	−0.10(27)
	Et_4N	4.76	1.5	1.06	0.44		3.26	1.5	0.62	0.20		
pht	Li	4.87(2)	1.0	0.47	0.30	0.64(7)	2.74(2)	1.0	0.31	0.04	1.0(4)	0.00(17)
	Na	4.92(2)	1.0	0.56	0.30	0.50(8)	2.75(2)	1.0	0.40	0.15	0.8(4)	−0.10(22)
	K	4.96(3)	1.0	0.52	0.30	0.37(12)	2.76(3)	1.0	0.16	0.05	0.6(5)	−0.22(36)
	Et_4N	5.09	1.5	1.35	0.37		2.80	1.5	0.66	0.10		
mal [c]	Na(Cl)	5.20	1.0	0.30	0.05		2.62	1.0	0.23	0.03		
	K(Cl)	5.25	1.0	0.36	0.06		2.63	1.0	0.24_5	0.03		
male [c]	Na(Cl)	5.81	1.0	0.19	0.01							
	K(Cl)	5.80	1.0	0.24	0.01							
succ [c]	Na(Cl)	5.23	1.0	0.44	0.09		3.99	1.0	0.22	0.02		
	K(Cl)	5.22	1.0	0.50_5	0.11		4.00	1.0	0.24	0.02		
pht [d]	$Na[ClO_4]$	4.88	1.0	0.65	0.25	0.52	2.69	1.0	0.62	0.24		

---

[a] For these data (for which the formation of alkali metal complexes is not taken into account) a value $B' < B$ was used in order to have a better fit of the data.

[b] 3σ in parentheses.

[c] Ref. 14, 18°C, $I = 0.1$–3 mole dm^{-3}.

[d] ref. 15, 35°C, $I = 0.05$–2 mole dm^{-3}.

calculate the parameters for the dependence on ionic strength of the formation and protonation constants [13] *.

Some experimental details of potentiometric measurements are reported in Table 1. The protonation constants in tetraethylammonium iodide background salt were studied previously [13].

RESULTS AND DISCUSSION

Table 2 gives the protonation constants calculated without allowing for alkali metal complexes. The equation **

$$\log K_j^{\mathrm{H}}(I) = \log K_j^{\mathrm{H}}(I') - A z_j^* G(I,I') + C_j(I - I') + D_j(I^{3/2} - I'^{3/2}) \qquad (1)$$

was used in order to fit the protonation constants at different ionic strengths ($0 \leqslant I \leqslant 1$ mole dm^{-3}). Table 2 also shows the values of log K_i^{M} at $I = I'$, calculated by means of the equation **

$$K_i^M = (10^{\Delta \log K_j^{\mathrm{H}}} - 1)\, c_{\mathrm{M}}^{-1} \qquad (i = j) \qquad (2)$$

Figure 1 shows the dependence of protonation constants on I (when alkali metal complexes are neglected) for oxalate. The protonation of malonate, maleate and succinate was studied by Adell [14] in NaCl and KCl ($0.1 \leqslant I \leqslant 3$ mole dm^{-3}) at 18°C, while the protonation of phthalate was studied by Lumme and Kari [15] in Na[ClO$_4$] ($0.05 \leqslant I \leqslant 2$ mole dm^{-3}) at different temperatures. Some of these data were fitted by eqn. (1) and the calculated

---

* Potassium nitrate is not completely dissociated; its degree of dissociation (using literature data, see ref. 5 and refs. therein) can be expressed by the equation

$\alpha = 1 - 0.35\ C_{\mathrm{KNO_3}} + 0.003\ C_{\mathrm{KNO_3}} t$

The formation of undissociated $[\mathrm{K(NO_3)}]^0$ was taken into account in the calculations.

** Symbols I = Ionic strength in mole dm^{-3}

I' = reference ionic strength, chosen in the range experimentally studied

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

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

$G(I,I') = [\sqrt{I}/(1 + B\sqrt{I}) - \sqrt{I'}/(1 + B\sqrt{I'})]$

$A = 0.511 + 8.89\ 10^{-4}(t - 25) + 2.95\ 10^{-6}(t - 25)^2$
$B = 1.489 + 8.77\ 10^{-4}(t - 25) + 4.69\ 10^{-6}(t - 25)^2$
$z^*_j = 2(1 - z - j)$; z is the charge of anion
C_j and D_j are empirical parameters to be determined
c = free concentrations, C = analytical concentrations (in mole dm^{-3}).

$\Delta \log K_j^{\mathrm{H}} = \log K_j^{\mathrm{H}} - \log K_j^{\mathrm{H}\prime}$

log $K_j^{\mathrm{H}\prime}$ is the conditional protonation constant calculated without allowing for alkali metal complex formation. The use of eqns. (1) and (2) was carefully discussed in previous papers [8,11].

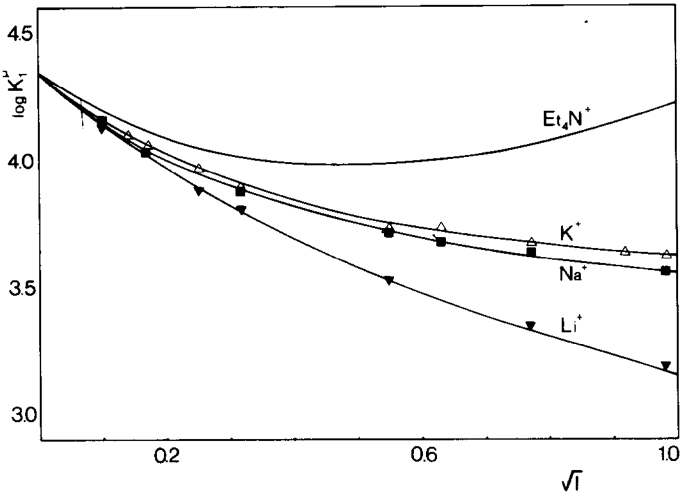

Fig. 1. Protonation constant values ($\log K_1^H$) of oxalic acid, in Et_4N^+, K^+, Na^+ and Li^+, vs. $\sqrt{I}$. △, ■, ▼ Experimental points.

parameters are shown in Table 2. These results are in agreement with ours.

The calculation of $\log K_i^M$ was also carried out by the computer programs ACBA and MINIQUAD 76A using primary potentiometric data. By considering all ionic strengths together, the parameters for the dependence on I were obtained. Table 3 shows $\log K_1^M$ (at $I' = 0.15$ mole dm^{-3}), C_1 and D_1 values for the alkali metal–dicarboxylate complexes, together with some values at fixed ionic strengths. Although a reliable, even if only approximate, value can be calculated for $\log K_2^M$ *, its dependence on ionic strength cannot be obtained due to the low formation percentages.

The literature provides a number of data pertaining to protonation at various ionic strengths and temperatures, obtained in ionic media containing Na^+ and K^+ ions [2, 14–20]. These have enabled us to obtain the constants K_1^{Na} and K_1^K, for the ligands studied here, at various temperatures. The formation constants were fitted by the equation

$$\begin{aligned}\log K_1^M(I,t) = {} & \log K_1^M(0.15, 25) - 4A\left(\sqrt{I}/(1+B\sqrt{I}) - 0.39/(1+0.39B)\right)\\ & + C_1(I-0.15) + D_1(I^{3/2} - 0.06)\\ & + a_1(t-25) + a_2(t-25)^2 \end{aligned} \tag{3}$$

where

$$a_1 = \left[\frac{\partial \log K_1^M}{\partial T}\right]_{I=0.15,t=25}, \quad a_2 = \left[\frac{\partial^2 \log K_1^M}{\partial T^2}\right]_{I=0.15,t=25}$$

---

* Although the values of $\log K_2^M$ are very low, it can be affirmed that these complexes are formed, even if in low percentages, since $3\sigma(K_2^M) < K_2^M$.

TABLE 3

Formation constants for the Li$^+$, Na$^+$ and K$^+$-dicarboxylate complexes and parameters for the dependence on the ionic strength, at 37°C. Values of log K_1^M at fixed ionic strengths

L^{2-}	M^+	log K_1^M ($I=0.15$)	C	$-D$	σ_{lin}[b]	L^{2-}	M^+	log K_1^M ($I=0.15$)	C	$-D$	σ_{lin}
ox	Li	0.79(1)[a]	0.97	0.33	0.05	pht	Li	0.65(2)	1.21	0.38	0.07
	Na	0.46(3)	0.83	0.28	0.06		Na	0.51(2)	1.14	0.31	0.10
	K	0.41(3)	0.87	0.34	0.06		K	0.41(3)	1.14	0.21	0.12
mal	Li	0.67(2)	0.98	0.32	0.04	male	Li	0.72(2)	1.11	0.30	0.06
	Na	0.40(3)	0.73	0.14	0.06		Na	0.61(3)	1.04	0.27	0.08
	K	0.44(4)	0.82	0.28	0.08		K	0.48(2)	1.17	0.29	0.10
succ	Li	0.42(3)	0.76	0.37	0.04	mala	K	0.11(4)	1.25	0.35	0.15
	Na	0.06(3)	0.94	0.37	0.06						
	K	0.11(5)	0.73	0.35	0.10						

I	Oxalate			Malonate			Succinate			Phthalate			Maleate			Malate
	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	K	K
0.0	1.17	0.87	0.81	1.05	0.81	0.85	0.84	0.46	0.53	1.00	0.87	0.76	1.08	0.98	0.83	0.45
0.2	0.78	0.45	0.40	0.66	0.38	0.43	0.40	0.05	0.09	0.65	0.51	0.41	0.72	0.60	0.48	0.11
0.4	0.80	0.45	0.40	0.68	0.39	0.43	0.37	0.06	0.06	0.71	0.57	0.48	0.77	0.65	0.55	0.18
0.6	0.85	0.48	0.43	0.74	0.43	0.46	0.37	0.10	0.06	0.80	0.66	0.60	0.86	0.73	0.65	0.29
0.8	0.91	0.53	0.47	0.80	0.50	0.50	0.38	0.14	0.07	0.90	0.76	0.72	0.96	0.82	0.76	0.40
1.0	0.97	0.58	0.51	0.87	0.56	0.55	0.39	0.19	0.08	1.00	0.86	0.86	1.06	0.91	0.87	0.51

[a] 3σ in parentheses.

[b] > 95% Confidence limits for the term $[L(I)/(I-0.15)]$ where $L(I)$ is the linear term in eqn. (1).

From (3) it is possible to obtain the values of ΔG, ΔH, ΔS and ΔC_p as a function of t and I. Table 4 shows some of these values.

By developing eqn. (2) for several alkali metal ions, once the M^+-dicarboxylate ligand formation constants are known, for any mixture of alkali metal ions and tetraethylammonium salts, the conditional protonation constant can be obtained through the relation

$$\log K^{H\prime} = \log K^H - \log\left(1 + K^{Li}c_{Li} + K^{Na}c_{Na} + K^K c_K\right) \qquad (4)$$

We have experimentally verified the validity of this equation by measuring the protonation constant $\log K_1^{H\prime}$ of oxalate for two different mixtures:

(a) $C_{Li} = C_{Na} = C_K = 0.2, \quad C_{Et_4N} = 0.1, \quad I = 0.7$ mole dm^{-3}

(b) $C_{Li} = C_{Na} = C_K = 0.3, \quad C_{Et_4N} = 0.1, \quad I = 1$ mole dm^{-3}

The protonation constants obtained are

(a) $\log K_1^{H\prime} = 3.59 \pm 0.01, \quad \Delta \log K_1^H = 0.53 \pm 0.02$

(b) $\log K_1^{H\prime} = 3.54 \pm 0.01, \quad \Delta \log K_1^H = 0.68 \pm 0.03$

Using eqn. (4) one obtains (also considering the formation of undissociated [K(NO$_3$)])

(a) $\Delta \log K_1^H = 0.54 \pm 0.05$

(b) $\Delta \log K_1^H = 0.71 \pm 0.07$

The agreement between the two groups of values can be considered very good, provided the high ionic strengths investigated are taken into account, and confirms the reliability of the chemical model here proposed.

From the results obtained in our study we can observe the following.

Stability of complexes

The stability of the alkali metal complexes with dicarboxylate ligands is:
with respect to the metal $Li^+ > Na^+ \gg K^+$;
with respect to the ligand $C_5 \simeq C_6 > C_7$.
(C_k indicates the size of the chelate ring). The stability in relation to the metal is that obtained so far in the case of all organic ligands [1]. As previously suggested [4], the order in relation to the ligand may indicate a probable chelation.

ΔH, ΔS, ΔC_p *values*

For both Na^+ and K^+ complexes, the values of ΔH at 25°C and $I = 0$ are all slightly endothermic (~ 1 kcal mole^{-1}), and are all practically equal (taking into account the errors). The values of ΔS, all of which are positive, show that these complexes are mainly stabilized entropically. The values of ΔC_p (20–40 cal mole^{-1} deg^{-1}) are similar to those relating to the protonation [20].

TABLE 4

ΔH, ΔS and ΔC_p values for the formation of Na^+ and K^+-dicarboxylate complexes at various temperatures and ionic strengths

t	I	ΔH^a	ΔS^b	$\Delta C_p{}^c$	ΔH	ΔS	ΔC_p	ΔH	ΔS	ΔC_p	ΔH	ΔS	ΔC_p
		[Na(ox)]			[K(ox)]			[Na(mal)]			[K(mal)]		
0	0.0	0.4	5.1	28	0.3	4.5	25	0.0	3.6	25	0.3	4.7	25
	0.1	0.3	2.8	24	0.1	2.3	21	−0.1	1.3	22	0.1	2.4	21
	0.2	0.2	2.5	24	0.1	1.9	21	−0.2	1.0	21	0.1	2.1	21
	0.5	0.2	2.5	23	0.0	1.9	20	−0.2	1.0	20	0.0	2.0	20
	1.0	0.1	2.9	22	0.0	2.2	19	−0.3	1.6	20	0.0	2.4	19
25	0.0	1.2	7.9	37	1.0	7.0	34	0.8	6.2	35	1.0	7.2	34
	0.1	1.0	5.4	33	0.8	4.5	30	0.5	3.6	31	0.8	4.6	30
	0.2	0.9	5.0	32	0.7	4.1	29	0.5	3.2	30	0.7	4.2	29
	0.5	0.8	4.8	31	0.6	3.9	27	0.4	3.1	29	0.6	4.0	27
	1.0	0.8	5.2	30	0.6	4.2	26	0.3	3.7	28	0.6	4.4	26
50	0.0	2.3	11.4	49	2.0	10.2	44	1.8	9.5	46	2.0	10.3	44
	0.1	1.9	8.4	44	1.6	7.2	39	1.4	6.6	41	1.6	7.4	39
	0.2	1.9	8.0	42	1.5	6.7	38	1.3	6.1	40	1.5	6.9	38
	0.5	1.7	7.7	41	1.4	6.4	36	1.2	5.8	39	1.4	6.6	36
	1.0	1.7	8.0	40	1.3	6.6	35	1.2	6.3	38	1.3	6.8	35
		[Na(succ)]			[K(succ)]			[Na(pht)]			[K(pht)]		
0	0.0	0.6	3.7	25	0.3	3.2	25	0.3	4.7	25	0.3	4.4	19
	0.1	0.4	1.5	21	0.1	0.9	21	0.1	2.6	21	0.2	2.3	15
	0.2	0.4	1.2	21	0.1	0.6	21	0.1	2.4	21	0.1	2.1	15
	0.5	0.3	1.2	20	0.0	0.3	20	0.0	2.8	20	0.1	2.6	14
	1.0	0.3	1.6	19	0.0	0.3	19	0.0	3.8	19	0.0	3.9	13

25	0.0	1.3	6.2	33	1.0	5.8	34	1.0	7.3	34	0.9	6.3	25
	0.1	1.0	3.7	29	0.8	3.2	30	0.8	4.8	30	0.6	3.9	21
	0.2	1.0	3.3	28	0.7	2.7	29	0.7	4.6	29	0.6	3.6	20
	0.5	0.9	3.2	27	0.6	2.3	27	0.6	4.8	27	0.5	4.0	19
	1.0	0.8	3.5	26	0.6	2.2	26	0.6	5.8	26	0.4	5.3	18
50	0.0	2.2	9.2	42	2.0	8.9	44	2.0	10.4	44	1.6	8.6	33
	0.1	1.8	6.3	37	1.6	5.9	39	1.6	7.6	39	1.2	5.8	28
	0.2	1.8	5.9	36	1.5	5.4	38	1.5	7.2	38	1.1	5.5	26
	0.5	1.6	5.6	34	1.4	4.8	36	1.4	7.4	36	1.0	5.8	25
	1.0	1.6	5.9	33	1.3	4.7	35	1.3	8.2	35	0.9	7.0	24
		[Na(male)]			[K(male)]			[K(mala)]					
0	0.0	0.3	5.3	25	0.3	4.6	25	0.3	2.9	25			
	0.1	0.1	3.1	21	0.1	2.5	21	0.1	0.8	21			
	0.2	0.1	2.9	21	0.1	2.3	21	0.1	0.7	21			
	0.5	0.0	3.1	20	0.0	2.7	20	0.0	1.1	20			
	1.0	0.0	4.1	19	0.0	3.9	19	0.0	2.3	19			
25	0.0	1.0	7.8	34	1.0	7.1	34	1.0	5.4	34			
	0.1	0.8	5.4	30	0.8	4.7	30	0.8	3.0	30			
	0.2	0.7	5.1	29	0.7	4.5	29	0.7	2.8	29			
	0.5	0.6	5.2	27	0.6	4.8	27	0.6	3.1	27			
	1.0	0.6	6.1	26	0.6	5.9	26	0.6	4.2	26			
50	0.0	2.0	10.9	44	2.0	10.2	44	2.0	8.5	44			
	0.1	1.6	8.1	39	1.6	7.4	39	1.6	5.8	39			
	0.2	1.5	7.7	38	1.5	7.1	38	1.5	5.5	38			
	0.5	1.4	7.7	36	1.4	7.3	36	1.4	5.7	36			
	1.0	1.3	8.5	35	1.3	8.3	35	1.3	6.7	35			

[a] ΔH in kcal mole^{-1}, ±0.3; [b] ΔS in cal mole^{-1} deg^{-1}, ±1; [c] cal mole^{-1} deg^{-1}, ±10.

Dependence on ionic strength

As can be seen from Table 3, the parameters relating to the dependence on ionic strength (i.e. C and D) show closely similar values. The average values of C_1 and D_1 are 0.98 and -0.3, respectively, with a mean error of ± 0.09 in the term C_1 ($>95\%$ confidence limits), in the range $0 \leqslant I \leqslant 1$ mole dm^{-3}. This confirms that, having taken into account all interactions among the components of the solution, the dependence on ionic strength is the same when the same charges are involved in the formation reaction, for $I \leqslant 1$ mole dm^{-3}, as previously reported for other systems [7,8,13].

REFERENCES

1 D. Midgeley, Chem. Soc. Rev., 4 (1975) 549 and refs. therein.
2 L.G. Sillen and A.E. Martell, Stability Constants, Chem. Soc. Spec. Publ., London, No. 17 (1964), No. 25 (1971).
D.D. Perrin, Stability Constants, Organic Ligands, IUPAC Chem. Data, Series No. 22, Pergamon, Oxford, 1979.
J.J. Christensen, L.D. Hansen and R.M. Izatt, Handbook of Proton Ionization Heats, Wiley, New York, 1976.
3 G. Arena, R. Calì, M. Grasso, S. Musumeci, C. Rigano and S. Sammartano, Thermochim. Acta, 36 (1980) 329.
4 P.G. Daniele, C. Rigano and S. Sammartano, Thermochim. Acta, 46 (1981) 103.
5 P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim., 70 (1980) 119.
6 R. Calì, S. Musumeci, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 56 (1981) L11.
7 V. Cucinotta, P.G. Daniele, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 56 (1981) L45.
8 P.G. Daniele, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 63 (1982) 267.
9 P. Amico, P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim., 71 (1981) 659.
10 P.G. Daniele and M. Marangella, Ann. Chim., 72 (1982) 25.
11 G. Arena, E. Rizzarelli, S. Sammartano and C. Rigano, Talanta, 26 (1979) 1.
12 A. Sabatini, A. Vacca and P. Gans, Talanta, 21 (1974) 53; Inorg. Chim. Acta, 18 (1976) 237.
13 P.G. Daniele, C. Rigano and S. Sammartano, Talanta, in press.
14 B. Adell, Z. Phys. Chem., Abt. A, 185 (1939) 161.
15 P. Lumme and E. Kari, Acta Chem. Scand., 29 (1975) 117.
16 M. Eden and R.G. Bates, J. Res. Natl. Bur. Stand., 62 (1959) 161.
17 W.J. Hamer and S.F. Acree, J. Res. Natl. Bur. Stand., 35 (1945) 381.
18 W.J. Hamer, J.O. Burton and S.F. Acree, J. Res. Natl. Bur. Stand., 24 (1940) 269.
19 G.D. Pinching and R.G. Bates, J. Res. Natl. Bur. Stand., 40 (1948) 405.
20 G.D. Pinching and R.G. Bates, J. Res. Natl. Bur. Stand., 45 (1950) 322.
21 E.J. King, Acid–Base Equilibria, McMillan, New York, 1965.