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WECO: A COMPUTER PROGRAM FOR CALCULATING THERMODYNAMIC PARAMETERS OF SIMPLE WEAK COMPLEXES. TEMPERATURE AND IONIC STRENGTH DEPENDENCE OF THE IONIC PRODUCT OF WATER AND OF HYDROLYSIS CONSTANTS OF Na^+ AND Ca^{2+}

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ABSTRACT

A method and a computer program (WECO) for the calculation of the formation constants of weak complexes from pH-metric measurements is reported.

The determination of hydrolysis constants of Na^+ and Ca^{2+} was performed by calculating the ionic product of water in mixtures of NaCl, $CaCl_2$ and tetraethylammonium iodide, in the ionic strength range $0.04 \leq I \leq 0.9$ mol dm^{-3} and at 10, 25 and 45°C.

The results obtained were compared with literature findings.

INTRODUCTION

A series of recent papers [1–15] has indicated the importance of weak complexes both in the study of model systems for natural fluids and for the correct interpretation of the ionic strength dependence of stability constants.

In this paper we report a simple method for the simultaneous calculation of formation constants for weak complexes and the parameters that define their dependence on temperature and on ionic strength.

Furthermore, the ionic product of water in different media and at different ionic strengths and temperatures is relevant for equilibrium studies (primarily in the calibration of glass electrodes both for complexometric measurements and for routine analysis). It is also relevant for the interactions between OH^- and widespread naturally occurring cations, such as Na^+ and Ca^{2+}, in studying model systems of natural fluids. For these reasons we believed it interesting to investigate experimentally the systems OH^-–H^+, Na^+, Ca^{2+}, and compare our results with those reported in the literature [16–26].

EXPERIMENTAL

The NaCl, $CaCl_2$ and $(C_2H_5)_4NI$ were commercially available products (Fluka, Merck and C. Erba) of high purity (> 99.8%). Tetraethylammonium iodide was recrystallized from methanol. NaOH stock solutions, CO_2-free, were prepared by diluting concentrated ampoules (Fluka or BDH). HCl stock solution was prepared by diluting concentrated reagent. Twice distilled water was always used. All concentration values were corrected for the change in volume at the different temperatures; thus, all the thermodynamic parameters reported in this paper are in the molar scale.

The potentiometer used was a Metrohm E 600 equipped with glass–calomel (or silver–silver chloride) electrodes, supplied by the same firm. Several electrode couples were used during the investigations.

25–50 cm^3 of the solution under study, containing 10 mmol dm^{-3} HCl and NaCl, $CaCl_2$, Et_4NI, were titrated with 0.1 mol dm^{-3} NaOH (~ 40 titration points) up to pH 11–12. The titrant was delivered by an AMEL mod. 232 dispenser (minimum reading 0.001 cm^3). The measuring cells were thermostated at $t \pm 0.2°C$. Magnetic stirrers were used. All the titrations were performed with purified N_2 bubbling into the solutions.

In the calculations the formation of the $[Ca(Cl)]^+$ ion pair was always taken into account [16–18,27–29]. Throughout the paper the reported errors are the standard deviations of the parameters.

CALCULATIONS

Electrode couple standardization and pK'_w *calculation*

The calculation of the pH values (pH = $-\log[H]$) for each point of the titration requires the knowledge of E^0 and E_j in the equation

$$E = E^0 + \frac{RT}{S} \ln 10 \text{ pH} + E_j$$

E_j (junction potential) is negligible under our experimental conditions. E^0 can be calculated directly from the strong acid–base titrations in two ways: (a) by using the points in the acid range only for the calculations of slope and intercept (and using the points in alkaline range for calculating pK'_w); (b) by using a least squares computer program for calculating simultaneously E^0 and pK'_w (we denote with primes the pK_w values calculated without allowing for the hydrolysis of Na^+ and Ca^{2+}). The calculations of method (b) were performed with the program ES1AB1 [30], similar to the computer program ACBA [31], which can refine all parameters in an acid–base titration (the HCl concentration was also always checked in the calculations) by minimizing the sum of squared errors in the titrant volume or in the e.m.f.

TABLE 1

pK'_w values in various media at $t = 10$, 25 and 45°C

$t = 10°C$					$t = 25°C$					$t = 45°C$				
c_{Na} [a]	c_{Et_4N} [a]	c_{Ca} [a]	I [b]	pK'_w	c_{Na} [a]	c_{Et_4N} [a]	c_{Ca} [a]	I [b]	pK'_w	c_{Na} [a]	c_{Et_4N} [a]	c_{Ca} [a]	I [b]	pK'_w
13		9	0.040	14.313 [c]	13		8	0.037	13.831 [d]	13		9	0.039	13.163 [e]
72		18	0.126	14.254	72		16	0.121	13.752	72		17	0.124	13.081
13	59	18	0.126	14.266	13	59	16	0.121	13.772	13	59	17	0.124	13.101
205		18	0.259	14.227	205		16	0.253	13.732	203		17	0.255	13.053
13	192	18	0.259	14.278	13	192	16	0.253	13.253	13	190	17	0.255	13.111
125		45	0.259	14.188	124		40	0.246	13.682	123		44	0.254	12.992
13	112	45	0.259	14.214	13	111	40	0.246	13.710	13	111	44	0.254	13.022
187	279	18	0.521	14.285	187	279	16	0.514	13.781	186	277	17	0.515	13.104
275	164	27	0.519	14.237	274	164	24	0.511	13.732	272	163	26	0.513	13.051
229	157	45	0.521	14.216	229	157	40	0.507	13.700	227	156	44	0.514	13.001
177	157	63	0.522	14.188	177	157	57	0.503	13.669	175	156	61	0.514	12.967
711		45	0.845	14.167	710		40	0.831	13.647	705		44	0.835	12.951
13	698	45	0.845	14.324	13	697	40	0.831	13.817	13	692	44	0.835	13.121
606		89	0.875	14.114	605		81	0.848	13.587	601		87	0.862	12.871
13	594	89	0.875	14.224	13	592	81	0.848	13.705	13	588	87	0.862	12.980
362		179	0.899	14.024	361		162	0.847	13.495	359		174	0.881	12.749
13	349	179	0.899	14.074	13	348	162	0.847	13.546	13	346	174	0.881	12.789
222		224	0.893	13.993	222		202	0.829	13.457	220		218	0.873	12.696
13	209	224	0.893	14.013	13	209	202	0.829	13.478	13	208	218	0.873	12.719
537	323	9	0.886	14.284	535	322	8	0.882	13.777	532	320	9	0.878	13.107
537	297	18	0.887	14.262	535	296	16	0.880	13.757	532	294	17	0.878	13.081
537	271	27	0.888	14.242	535	270	24	0.878	13.739	532	268	26	0.878	13.051

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

[b] Ionic strength in mol dm^{-3}.

[c] ±0.005.

[d] ±0.004.

[e] ±0.005.

We used in the calculations both minimization methods

$$U=\sum w_i(v_i-v_{i,\mathrm{calc}})^2$$

$$U=\sum w_i(E_i-E_{i,\mathrm{calc}})^2$$

in the first case with $w_i = 1$ and in the latter with

$$\frac{1}{w_i}=\sigma_E^2+\left(\frac{\partial E}{\partial v}\right)^2\sigma_v^2$$

In Table 1 the values of pK'_{w} calculated with the first minimization method are reported. The mean differences in the values calculated by the two methods are 0.0035, 0.0027 and 0.0025 at 10, 25 and 45°C, respectively. Since these differences are lower than the standard deviations, the two methods, at least for simple systems, are equivalent *.

Formation constants for [Na(OH)]^0 and [Ca(OH)]$^+$

When weak complexes are formed by the anion of a weak acid, a simple equation can be used

$$\log K^{\mathrm{H}'}=\log K^{\mathrm{H}}+\log\Bigl(1+\sum_i K^{\mathrm{M}_i}[\mathrm{M}_i]\Bigr) \tag{1}$$

where $\log K^{\mathrm{H}}$ = protonation constant **, $\log K^{\mathrm{H}'}$ = protonation constant calculated without allowing for M$_i$-complexes and K^{M_i} = formation constants of M$_i$-complexes. The same, obviously, holds for pK_{w} and pK'_{w}.

Moreover, when the measurements are performed at different temperatures and ionic strengths, the following expressions

$$\log K_t=\log K_\vartheta+\sum a_i(t-\vartheta)^i \tag{2}$$

$$\log K^I=\log K^{I'}-z^*F(I,I')+L(I,I') \tag{3}$$

take into account the temperature and the ionic strength dependence [32–34] of stability constants. Equations (2) and (3) are discussed in Appendix I.

The protonation constants and the M$_i$-formation constants, together with the parameters which define their dependence on temperature and ionic

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* In principle, the use of $w_i \neq 1$ is preferred, but in practice it is very difficult to find a realistic value of $\sigma_E^2(w_i=1/\sigma_E^2)$. The method used in ES1AB1 is based on the assumption that the points in the buffered region are more accurate. This assumption is valid when only stability parameters are refined; if concentration parameters are also to be refined, the weighting scheme should be more complicated.

** In this work, as in previous investigations [2,5,7–13], tetraethylammonium cation is assumed not to form complexes with OH$^-$. Since it is known that Et$_4$NOH is one of the strongest bases, the assumption should be valid.

TABLE 2

Results of WECO calculations. The thermodynamic parameters are calculated at $I = 0.15$ mol dm^{-3} and $t = 25°\text{C}$

$\text{p}K_w = 13.834 \pm 0.002$
$\partial \text{p}K_w/\partial T = -0.0325 \pm 0.0001$
$\Delta H = -13.23 \pm 0.04$
$\log K^{\text{Na}} = -0.094 \pm 0.007$
$\partial \log K^{\text{Na}}/\partial T = 0.0028 \pm 0.0003$
$\Delta H = 1.14 \pm 0.12$
$\log K^{\text{Ca}} = 0.935 \pm 0.010$
$\partial \log K^{\text{Ca}}/\partial T = 0.0065 \pm 0.0002$
$\Delta H = 2.65 \pm 0.08$
$c_0 = 0.098 \pm 0.003$
$c_1 = 0.221 \pm 0.011 \quad \partial c_1/\partial T = -(1.8 \pm 0.8) \times 10^{-3}$
$d = -0.110 \pm 0.012 \quad \partial d/\partial T = (2.0 \pm 0.8) \times 10^{-3}$

strength, were calculated using a non-linear least-squares technique that minimizes the error squares sum

$$U = \sum \left(\log K^{\text{H}\prime}_{\text{exp}} - \log K^{\text{H}\prime}_{\text{calc}}\right)^2 \tag{4}$$

The computer program WECO (WEak COmplexes) is written in standard FORTRAN IV *. The data of Table 1 were analyzed with WECO and the results are reported in Table 2.

RESULTS AND DISCUSSION

The program WECO

The program WECO has been used for analyzing several systems [9–13]. It is quite simple to use (it does not require any particular experience with computers) and does not show divergence problems. WECO can work with medium-sized computers and is fast. The possibility of calculating simultaneously $\log K$, $\partial \log K/\partial T$ (ΔH), $\partial^2 \log K/\partial T^2$ (ΔC_p) and the dependence of $\log K$ on ionic strength makes this program very useful. A BASIC version, that can be used on personal computers, is in preparation *.

The ionic product of water

The great number of $\text{p}K_w$ values reported in the literature have been analyzed, using eqn. (2), and

$$\text{p}K_w = 13.999 - 3.295 \times 10^{-2}(t-25) + 1.8 \times 10^{-4}(t-25)^2 - 7.7 \times 10^{-7}(t-25)^3 \tag{6}$$

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* The listing of the FORTRAN IV and the BASIC version can be obtained from the authors on request.

was obtained at zero ionic strength, in the molar scale (the literature values were converted from molal to molar scale, when necessary). In Table 3 we report our data under different conditions, compared with those reported in the literature. The agreement is good and, in particular, the accordance between data obtained from glass electrode measurements and those obtained from hydrogen electrode measurements ensures that the alkaline error is, for our experimental conditions, negligible.

For pK_w values at infinite dilution, those obtained from eqn. (6) are obviously preferable. In particular, the dependence on temperature obtained from eqn. (6) is accurate and the ΔH_w value calculated (-13.40) is very close to that found from calorimetric measurements (-13.345) [36].

Hydrolysis of Na^+ and Ca^{2+}

The stability constants relative to the formation of hydrolytic species $[Na(OH)]^0$ and $[Ca(OH)]^+$, in different conditions, are reported in Table 4, together with some literature data. The agreement in this case is also good, but the comparison can be made only for $I = 0$, since in the literature only extrapolated values are reported. In some cases partial results are also reported and we considered the relative values in calculating the recom-

TABLE 3

Ionic product of water at various ionic strengths and at $t = 10$, 25 and 45°C

I (mol dm^{-3})	$t = 10$°C		$t = 25$°C		$t = 45$°C	
	pK_w	pK'_w [a]	pK_w	pK'_w [a]	pK_w	pK'_w [a]
→ 0	14.48		14.00		13.36	
	14.54 [d]		14.00 [d]		13.41 [d]	
0.05	14.34	14.33	13.86	13.84	13.22	13.20
0.10	14.33	14.29	13.84	13.80	13.20	13.16
		14.23 [b]		13.73 [b]		13.05 [b]
				13.78 [c]		
0.15	14.32	14.27	13.83	13.78	13.19	13.13
		14.19 [b]		13.68 [b]		12.99 [b]
0.25	14.33	14.25	13.84	13.76	13.20	13.10
0.50	14.38	14.24	13.89	13.74	13.25	13.07
				13.74 [c]		
0.75	14.44	14.23	13.95	13.73	13.32	13.06
1.00	14.49	14.22	14.01	13.72	13.39	13.04
				13.80 [c]		

[a] In NaCl medium, without allowing for $[Na(OH)]^0$ formation.

[b] In $CaCl_2$ medium, without allowing for $[Ca(OH)]^+$ formation.

[c] In $NaClO_4$ medium, without allowing for $[Na(OH)]^0$ formation, Fischer and Byé [35] from hydrogen electrode measurements.

[d] Equation (6).

TABLE 4

Formation constants of the hydrolytic species $[Na(OH)]^0$ and $[Ca(OH)]^+$ at various ionic strengths and at $t = 10$, 25 and 45°C

I (mol dm^{-3})	log K^{Na}			log K^{Ca}		
	$t = 10$	$t = 25$	$t = 45$	$t = 10$	$t = 25$	$t = 45$
→ 0	0.04	0.08 (-0.18 ± 0.25) [c]	0.15	1.20	1.30 1.29 [a] 1.15 [c]	1.45
0.05	−0.11	−0.06	−0.00	0.91	1.01 0.92 [a]	1.15
0.10	−0.13	-0.08_5	−0.03	0.86	0.96 1.01 [f]	1.09
0.15	−0.14	−0.09	−0.04 0.10 [b]	0.84	0.93_5	1.06_5
0.25	−0.14	-0.09_5	−0.04	0.83	0.92	1.05
0.50	−0.11	−0.07	−0.01	0.86	0.95	1.08
0.75	−0.08	−0.03	0.03	0.90	1.00 1.10 [f]	1.14
1.00	−0.05	0.00	0.07	0.93	1.04_5 1.26 [f]	1.20

0.31	log $K^{Ca} = 1.13 + 0.0040\ (t - 25)$	$10 \le t \le 40$ [e]
0.25	log $K^{Ca} = 1.07 + 0.0057\ (t - 25)$	$10 \le t \le 50$ [f]
→ 0	log $K^{Ca} = 1.32 + 0.0070\ (t - 25)$	$10 \le t \le 40$ [g]
→ 0	log $K^{Ca} = 1.25 + 0.0065\ (t - 25)$	$0 \le t \le 40$ [h]
→ 0	log $K^{Ca} = 1.42 + 0.0026\ (t - 25)$	$0 \le t \le 40$ [i]
→ 0	log $K^{Ca} = 1.37 + 0.0030\ (t - 25)$	$15 \le t \le 35$ [l]
→ 0	log $K^{Ca} = 1.30 \pm 0.0071\ (t - 25)$	$10 \le t \le 40$ this work

[a] Bell and Prue [21]. [b] Daniele et al. [15], 37°C. [c] Baes and Mesmer [24]. [d] Daniele et al. [13]. [e] Daniele et al. [12], KCl + $CaCl_2$ medium. [f] Daniele et al. [12], NaCl + $CaCl_2$ medium. [g] Bates et al. [26], in $Ca(OH)_2$–KCl mixtures. [h] Bates et al. [26], in $Ca(OH)_2$–$CaCl_2$ mixtures. [i] Bell and George [20]. [l] Gimblett and Monk [19].

mended values (see Table 6). The value reported by Baes and Mesmer [24] for the species $[Na(OH)]^0$ is affected by a large error; for this type of weak complexes, there is unfortunately no way to obtain accurate formation constants and our value, though not very precise (see below), is tentatively the most reliable reported till now.

Ionic strength and temperature dependence of formation constants

In Fig. 1 we report pK_w (pK'_w) vs. $\sqrt{I}$, in Et_4NI, NaCl and $CaCl_2$. As one can see, the curves are markedly separated and indicate clearly the hydrolysis of Na^+ and Ca^{2+}.

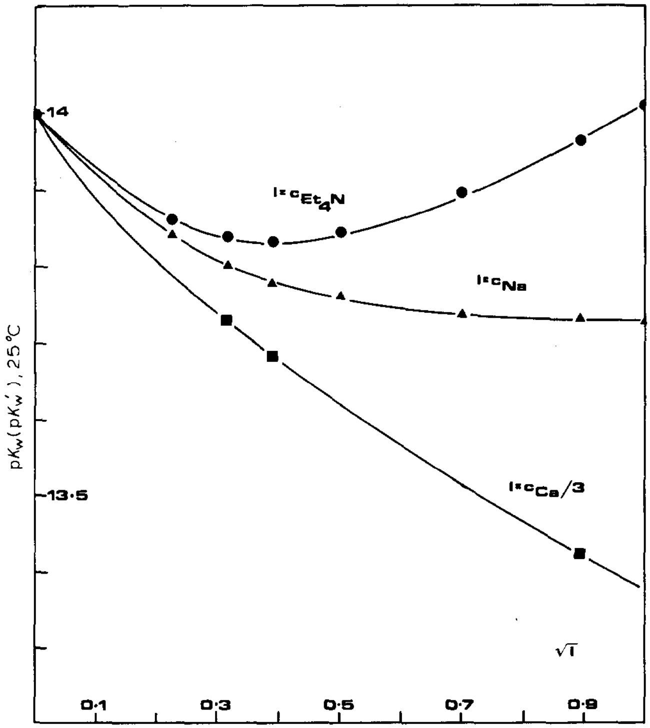

Fig. 1. pK_w (pK'_w) values vs. $\sqrt{I}$ in different ionic media, at 25°C.

The ionic strength dependence of pK_w, $\log K^{Na}$ and $\log K^{Ca}$ can be treated, using the equations of Appendix I, in the same manner, and the fit thus obtained by WECO is very satisfactory. The dependence on temperature for both $\log K^{Ca}$ and $\log K^{Na}$ can be expressed by a simple straight line and the values of $\partial \log K^{M}/\partial T$ are comparable to those found in the literature (see Table 4). Furthermore, it is interesting to investigate the dependence of $\partial \log K^{M}/\partial T$ on ionic strength. In Table 5 we report the temperature dependence coefficients together with the ΔH values for the formation of $[Na(OH)]^0$ and $[Ca(OH)]^+$ at various ionic strengths. The trend observed is the same as $\log K^{M}$, in agreement with previous findings [11].

TABLE 5

Temperature coefficients and ΔH values for $[Na(OH)]^0$ and $[Ca(OH)]^+$ formation at various ionic strengths

I (mol dm^{-3})	$\partial \log K^{Na}/\partial T$ ($\times 10^3$)	ΔH^{Na}	$\partial \log K^{Ca}/\partial T$ ($\times 10^3$)	ΔH^{Ca}
→ 0	3.16	1.3	7.2	2.9
0.05	3.14	1.3	6.9	2.8
0.15	2.84	1.15	6.4	2.6
0.50	2.86	1.2	6.3	2.6
1.0	3.43	1.4	7.7	3.1

Tentatively, the ionic strength dependence of ΔH values can be expressed by the equation

$$\Delta H = \Delta H(I = 0) - z^{*}0.73\, I + 0.81\, I^{3/2} z^{*} \tag{7}$$

with a minimum value at $I \cong 0.4$. This result seems in contrast with most literature findings, where the ΔH values are generally always decreasing with increasing ionic strength. However, if we consider (i) that generally the ionic strength is kept constant by using alkali-metal salts; (ii) that alkali-metal ions form weak complexes with a great number of ligands; (iii) that ΔH values for the weak interactions are generally > 0 and (iv) that eqn. (8)

$$\Delta H = \Delta H' - \Delta H^{\mathrm{M}} \frac{K^{\mathrm{M}} c_{\mathrm{M}}}{1 + K^{\mathrm{M}} c_{\mathrm{M}}} \tag{8}$$

is valid for weak complexes [7], then it follows that the real value of ΔH (for $\Delta H^{\mathrm{M}} > 0$) must be greater than the value calculated without allowing for the formation of weak complexes.

Error Analysis

In order to examine rigorously the parameters obtained it is of primary importance to look carefully at the sources of error. The most important of these are:

(a) If the temperature is kept constant at ±0.2°C, the error arising from this uncertainty in $\mathrm{p}K_{\mathrm{w}}$ is $\cong 0.007$, whereas in $\log K^{\mathrm{M}}$ it is negligible.

(b) The error in $\mathrm{p}K_{\mathrm{w}}$ due to an error of ±0.2% in HCl and NaOH is $\cong 0.003$.

(c) The error in K^{M}, due to the error in the concentrations, can be calculated by the equation

$$\varepsilon(K^{\mathrm{M}}) = \left(\frac{K^{\mathrm{M}}}{c_{\mathrm{M}}}\right) \varepsilon(c_{\mathrm{M}}) \tag{9}$$

TABLE 6

Recommended values at 25°C

I (mol dm^{-3})	$\log K^{\mathrm{Ca}}$	ΔH^{Ca} (Kcal mol^{-1})	$\mathrm{p}K_{\mathrm{w}}$	$\mathrm{p}K'_{\mathrm{w}}$
→ 0	1.35 ± 0.05 [a]	2.1 ± 0.3	13.999 ± 0.002	
0.05	1.00 ± 0.06			
0.10	0.95 ± 0.06		(13.84)	13.78 ± 0.03
1.0			(14.01)	13.76 ± 0.05

[a] > 95% confidence intervals.

(d) The error due to the uncertainties in the ionic strength can be calculated by the equation

$$\varepsilon(\log K) = \left\{ \frac{-z^*}{\sqrt{I}\,(2 + 3\sqrt{I})^2} + C + \frac{3}{2} D\sqrt{I} \right\} \varepsilon(I) \qquad (10)$$

On the basis of the results reported in Tables 3 and 4, looking critically at the literature data and considering the error sources (a)–(d), we select some recommended values for $\mathrm{p}K'_\mathrm{w}$ ($\mathrm{p}K_\mathrm{w}$) and $\log K^{\mathrm{Ca}}$, reported in Table 6.

CONCLUSIONS

The main conclusions to be drawn from this work are that (i) it is possible, using a simple approach for the ionic strength dependence (Appendix I), to obtain the formation constants for weak complexes without resorting to complicated methods, (ii) the calculation method, used by the computer program WECO works well and allows the simultaneous determination of formation constants as well as their dependence on temperature and ionic strength, and (iii) the simple model of Appendix I and eqn. (7) for the dependence on ionic strength of $\log K$ (and ΔH) can be used in a general manner in the range $0 \leqslant I \leqslant 1$.

REFERENCES

1 G. Arena, R. Calì, M. Grasso, S. Musumeci, C. Rigano and S. Sammartano, Thermochim. Acta, 36 (1980) 329.
2 P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 70 (1980) 119.
3 P.G. Daniele, C. Rigano and S. Sammartano, Thermochim. Acta, 46 (1981) 103.
4 R. Calì, S. Musumeci, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 56 (1981) L11.
5 V. Cucinotta, P.G. Daniele, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 56 (1981) L45.
6 P. Amico, P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 71 (1981) 659.
7 P. Amico, P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 72 (1982) 1.
8 P.G. Daniele and M. Marangella, Ann. Chim. (Rome), 72 (1982) 26.
9 P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 72 (1982) 341.
10 P.G. Daniele, C. Rigano and S. Sammartano, Inorg. Chim. Acta, 63 (1982) 267.
11 P.G. Daniele, C. Rigano and S. Sammartano, Thermochim. Acta, 62 (1983) 101.
12 P.G. Daniele, A. De Robertis, S. Sammartano and C. Rigano, Thermochim. Acta, 72 (1983) 305.
13 P.G. Daniele, A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 73 (1983) 619.
14 A. De Robertis, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 74 (1984) in press.
15 P.G. Daniele, M. Grasso, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 73 (1983) 495.

16 L.G. Sillen and A.E. Martell, Stability Constants, Chem. Soc. Spec. Publ. 17, London, 1964; Idem, 25, London, 1971.
17 E. Hoegfeldt, Stability Constants, Inorganic Ligands, Pergamon, Oxford, 1982.
18 R.M. Smith and A.E. Martell, Critical Stability Constants, Inorganic Complexes, Vol. 4, Plenum, New York, 1976.
19 F.G.R. Gimblett and C.B. Monk, Trans. Faraday Soc., 50 (1954) 965.
20 R.P. Bell and J.H.B. George, Trans. Faraday Soc., 49 (1953) 619.
21 R.P. Bell and J.E. Prue, J. Chem. Soc., (1949) 362.
22 R.P. Bell and M.H. Pankharst, J. Chem. Soc., (1956) 2836.
23 C.W. Davies and B.E. Hoyle, J. Chem. Soc., (1951) 233.
24 C.F. Baes, Jr. and R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976.
25 G. Kilde, Z. Anorg. Allg. Chem., 218 (1934) 113.
26 R.G. Bates, V.E. Bower, R.G. Canham and J.E. Prue, Trans. Faraday Soc., 55 (1959) 2062.
27 V. Majer and K. Stulik, Talanta, 29 (1982) 145.
28 L. Sucha, J. Cardek, K. Hrabek and J. Vesely, Coll. Czech. Chem. Commun., 40 (1975) 2020.
29 S.K. Patil and H.D. Sharma, Can. J. Chem., 47 (1969) 3851.
30 M. Grasso, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 74 (1984) in press.
31 G. Arena, E. Rizzarelli, S. Sammartano and C. Rigano, Talanta, 26 (1979) 1.
32 P.G. Daniele, C. Rigano and S. Sammartano, Talanta, 30 (1983) 81.
33 P.G. Daniele, C. Rigano and S. Sammartano, Transition Met. Chem., 7 (1982) 29.
34 P.G. Daniele, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 73 (1983) 741.
35 R. Fischer and J. Byé, Bull. Soc. Chim. Fr., (1964) 2920.
36 Nat. Bur. Stand., Tech. Note 270-3, Selected Values of Chemical Thermodynamic Properties, U.S. Govt. Printing Off., Washington, DC, U.S.A., 1968.
37 C.W. Davies, Ion Association, Butterworths, Washington, 1962.
38 E.J. King, Acid Base Equilibria, The International Encyclopedia of Physical Chemistry and Chemical Physics, Pergamon, New York, 1965.
39 E.C.W. Clarke and D.N. Glew, Trans. Faraday Soc., 62 (1966) 539.

APPENDIX I

Ionic strength dependence of formation constants

According to the Debye–Hückel theory, the dependence of activity coefficients on ionic strength can be expressed by the equation

$$-\log f_z = Az^2 \frac{\sqrt{I}}{1 + \mathring{a}B\sqrt{I}} - L(I) \tag{11}$$

where A and B are coefficients dependent on the temperature and on the solvent, $\mathring{a}$ is an empirical parameter (dependent on the effective radius of the ion), and $L(I)$ is an empirical linear term. For a general reaction

$$\sum p_{i,j} A_i^{z_i} = S_j^{z_j} \tag{12}$$

with an equilibrium constant

$$\beta_j = [S_j]\left(\prod_i [A_i]^{p_{i,j}}\right)^{-1}$$

the dependence on ionic strength can be expressed, according to eqns. (11) and (12), by the equation

$$\log \beta_j = \log {}^T\beta_j - A z_j^* \frac{\sqrt{I}}{1 + B_j\sqrt{I}} + \{L(I)\}_j \tag{13}$$

where ${}^T\beta_j$ is the formation constant at infinite dilution, $B_j = \bar{å}B$ ($\bar{å}$ is a mean value of $å_i$), $\{L(I)\}_j$ is a combination of the linear terms of the components and $z_j^* = \Sigma p_{i,j} z_i^2 - z_j^2$. If we consider that (i) $A \sim 0.5$ and $B \sim 0.3$, (ii) $å = 5$ is a good mean value for small ions and (iii) the errors in A, B and $å$ are absorbed in the linear term, then eqn. (13) can be rewritten as

$$\log \beta_j = \log {}^T\beta_j - \frac{z^*\sqrt{I}}{2 + 3\sqrt{I}} + \{L(I)\}_j \tag{14}$$

It has been shown in previous works [13,32–34] that the linear term can be expressed as

$$\{L(I)\}_j = C_j I + D_j I^{3/2} \tag{15}$$

where

$$C_j = p_j c_0 + z_j^* c_1 \tag{16}$$

$$D_j = z_j^* d$$

with $p_j = \Sigma p_{i,j} - 1$ (eqn. 12); for a stepwise formation constant $p_j = 1$ (for the water formation $p_j = 2$, since H_2O is the solvent). Note that the $p_j c_0$ term also takes into account the dependence on ionic strength of cationic acids.

c_1 and d are linearly temperature dependent

$$\left.\begin{aligned} c_1 &= (c_1)_{25°} + \partial c_1/\partial T(t - 25) \\ d &= d_{25°} + \partial d/\partial T(t - 25) \end{aligned}\right\} \tag{17}$$

(c_0 should also be temperature dependent, but since few data on cationic acids are available [32] at this stage of our investigation we prefer to keep c_0 constant).

In some cases it is more convenient to choose a reference ionic strength, not equal to zero, and then eqns. (14) and (15) become

$$\log \beta_j = \log \beta_j(I') - z^*\left\{\frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}}\right\} + C_j(I - I') + D_j(I^{3/2} - I'^{3/2}) \tag{18}$$

equivalent to eqn. (3). Equations (14) and (18), with the coefficients (16) for the linear term, allow the computation of ionic strength dependence of formation constants, in a more accurate way than the well known Davies' equation [37] does, as already reported [32].

Temperature dependence of formation constants

For the dependence of formation constants on temperature several equations have been proposed [38,39]. Despite efforts to find the "best" equation for the temperature dependence, the simple Taylor expression

$$\log \beta = \log \beta_\vartheta + \sum_i \frac{1}{i!} (\partial^i \log \beta / \partial T^i)_\vartheta (t - \vartheta)^i \tag{19}$$

or

$$\log \beta = \log \beta_\vartheta + \sum a_i (t - \vartheta)^i \tag{20}$$

is, in our opinion, to be preferred, and thus we used equation (20) in the program WECO.