Thermochimica Acta, 214 (1993) 325–338
Elsevier Science Publishers B.V., Amsterdam

Protonation thermodynamics of 2,2′-bipyridyl in aqueous solution. Salt effects and weak complex formation

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(Received 4 May 1992)

Abstract

Protonation constants of 2,2′-bipyridyl (bipy) have been determined potentiometrically, using (H^+)–glass electrode, in different aqueous media (alkali and alkaline earth chlorides, tetramethylammonium chloride and tetramethylammonium iodide) at different temperatures and ionic strengths. The differences in $\log K^H$ values are explained using a complex formation model. Formation thermodynamic parameters are given.

INTRODUCTION

The complex formation of 2,2′-bipyridyl with different metal ions has been extensively studied by several authors and the stability constants and related thermodynamic parameters have been reviewed [1]. Though the paper of McBryde contains more than two hundred references (before 1976) on 2,2′-bipyridyl and 1,10-phenanthroline (and some related compounds) complexes, only two references report formation data on Ca^{2+} and Mg^{2+} complexes [2], and none report on other alkaline earth metal complexes or on salt effects on protonation constants (Näsänen [3] studied protonation constants at different ionic strengths but only in KCl aqueous solutions). Recently, Capone et al. [4] published thermodynamic data on the formation of all the alkaline earth metal complexes of 2,2′-bipyridyl at different temperatures and ionic strengths, without taking into account some secondary effects (the self-association of the background salt and the weak complex formation between protonated ligand and Cl^-).

The speciation of a ligand in natural fluids, in which different electrolytes are present in considerable amounts, needs the thermo-

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dynamic parameters for protonation and main components interactions to be known in opportune temperature and ionic strength ranges. Owing to the interesting complexing ability of 2,2′-bipyridyl towards several natural ions, and because this ligand is a complexing model molecule, we thought it interesting to investigate the thermodynamic properties of the system $bipy^0$–H^+, –Li^+, –Na^+, –K^+, –Et_4N^+, –Me_4N^+, –Mg^{2+}, –Ca^{2+}–Sr^{2+}, –Ba^{2+}, –Cl^- and –I^- (where bipy = 2,2′-bipyridyl, Et_4N^+ = tetraethylammonium cation and Me_4N^+ = tetramethylammonium cation), in the ranges $0 \leqslant I \leqslant 1$ mol l^{-1} and $5 \leqslant T \leqslant 55$°C.

EXPERIMENTAL

The ligand 2,2′-bipyridyl (Fluka puriss.) was used without further purification; its purity, determined acidimetrically, was always >99.5%. Magnesium, calcium, strontium and barium chlorides (various firms, p.a.) were standardized by EDTA titrations [5]. Me_4NCl and Et_4NI (Fluka) were recrystallized from methanol [6]. The solutions of alkali metal ions were prepared from their chloride salts (various firms, p.a.), previously dried. KOH (or NaOH) and HCl stock solutions were prepared by diluting concentrated solutions in ampoules (Carlo Erba or BDH) and standardized against potassium hydrogen phthalate and sodium carbonate, respectively. All solutions were prepared using twice distilled water and grade A glassware, and preserved from atmospheric CO_2 by soda lime traps.

Potentiometric apparatus and procedure were as reported elsewhere [7,8]. All the calculations were performed using least squares computer programs (ESAB [9], ES2WC [10]). All the concentrations are expressed in molarities. Protonation and formation constants are derived from the reactions

$$H^+ + bipy^0 = H(bipy)^+ \qquad (K^H)$$

$$H(bipy)^+ + X^- = (bipy)XH^0 \qquad (K^X)$$

$$H^+ + bipy^0 + X^- = (bipy)XH^0 \qquad (\beta^X)$$

$$M^{z+} + bipy^0 = M(bipy)^{z+} \qquad (K^M)$$

with $X^- = Cl^-$, I^- and $M^{z+} = Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}, Me_4N^+, Et_4N^+. We indicate formation constants at infinite dilution, by ${}^TK$ or ${}^T\beta$ and apparent protonation constants by K'^{H}.

RESULTS

Measurements in KCl solutions

The measurements in KCl aqueous solutions were performed at six temperatures (5–55°C) and seven ionic strength values (0.05–1.2 mol l^{-1}). Apparent protonation constants are reported in Table 1. The behaviour of

TABLE 1

Apparent protonation constant of 2,2′-bipyridyl in aqueous KCl solutions

T (°C)	I (mol l^{-1})	log K'^{H} [a]	T (°C)	I (mol l^{-1})	log K'^{H} [a]
5	0.010	4.561	35	0.010	4.275
5	0.040	4.573	35	0.040	4.287
5	0.090	4.593	35	0.090	4.306
5	0.160	4.620	35	0.160	4.331
5	0.250	4.652	35	0.250	4.362
5	0.360	4.690	35	0.360	4.398
5	0.490	4.733	35	0.490	4.438
5	0.640	4.779	35	0.640	4.481
5	0.810	4.829	35	0.810	4.527
5	1.000	4.882	35	1.000	4.575
5	1.210	4.936	35	1.210	4.624
15	0.010	4.456	45	0.010	4.200
15	0.040	4.468	45	0.040	4.212
15	0.090	4.487	45	0.090	4.230
15	0.160	4.513	45	0.160	4.255
15	0.250	4.545	45	0.250	4.286
15	0.360	4.583	45	0.360	4.321
15	0.490	4.624	45	0.490	4.359
15	0.640	4.670	45	0.640	4.402
15	0.810	4.718	45	0.810	4.446
15	1.000	4.769	55	0.010	4.135
15	1.210	4.822	55	0.040	4.147
25	0.010	4.360	55	0.090	4.165
25	0.040	4.373	55	0.160	4.189
25	0.090	4.392	55	0.250	4.219
25	0.160	4.417	55	0.360	4.253
25	0.250	4.449	55	0.490	4.291
25	0.360	4.485	55	0.640	4.332
25	0.490	4.526	55	0.810	4.376
25	0.640	4.570			
25	0.810	4.618			
25	1.000	4.667			
25	1.210	4.718			

[a] $3s(\log K'^{\mathrm{H}}) = 0.0015 - 0.01$.

log K'^{H} vs. I at different values of temperature is shown in Fig. 1. As one can see, the dependence of log K'^{H} on I is not linear, and the protonation data at 25°C fit the equation

$$\log K'^{\mathrm{H}}_{(I)} = 4.3555 + 0.4429I - 0.1300I^{3/2} \tag{1}$$

Further, the dependence on temperature is not linear and at $I = 0$, the protonation data fit the equation

$$\log K'^{\mathrm{H}}_{(T)} = 4.3555 - 0.009071(T - 25) + 0.000062(T - 25)^2 \tag{2}$$

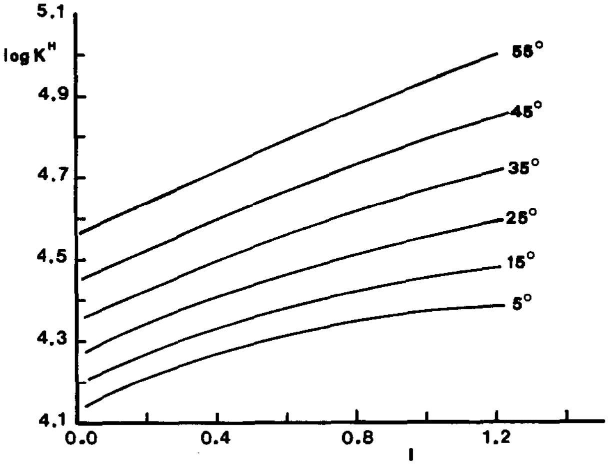

Fig. 1. Protonation constants of 2,2′-bipyridyl in aqueous KCl solution.

All the protonation constants are fitted by the general equation

$$\log K'^{\mathrm{H}}_{(I,T)} = \log K'^{\mathrm{H}}_{(0,T)} + c_0' I + d_0' I^{3/2} \tag{3}$$

with $c_0' = 0.4429 + 0.0021(t - 25)$ and $d_0' = 0.1300 + 0.0049(t - 25)$. The agreement of experimental data with the calculated data, using the eqns. (1)–(3) is very good, with $\varepsilon \approx 0.009$ (ε = mean deviation in $\log K'^{\mathrm{H}}$).

Näsänen [3] found at $T = 25$°C (KCl medium) that

$$\log K'^{\mathrm{H}}_{(I)} = 4.353 + 0.343I - 0.036I^2 \tag{4}$$

and

$$\log K'^{\mathrm{H}}_{(T)} = 1.82 + 754/(T + 273.15) \tag{5}$$

Protonation constants calculated by eqn. (4) agree quite well with those of eqn. (1): at $I = 0$ the difference is less than 0.003 (<1%) and at $I = 1$ about 0.008 log units (<2%). The agreement between eqns. (2) and (5) is also satisfactory (the differences in $\log K'^{\mathrm{H}}$ are less than 0.01), though using eqn. (5) it is assumed a linear dependence on $1/(T + 273.15)$, i.e. $\Delta C_{\mathrm{p}}^{\ominus} = 0$.

Measurements in LiCl, NaCl, Me$_4$NCl and Et$_4$NI solutions

These measurements were performed at 25°C and at seven ionic strengths (0.05–1 mol l^{-1}). Apparent protonation constants (reported in Table 2) fit the equation

$$\log K'^{\mathrm{H}}_{(I)} = 4.355 + c_0' I + d_0' I^{3/2} \tag{6}$$

The empirical parameters c_0' and d_0' are reported in Table 3.

TABLE 2

Apparent protonation constants of 2,2′-bipyridyl in aqueous LiCl, NaCl, Me_4NCl and Et_4NI solutions at 25°C

I (mol l^{-1})	log K'^{H} [a]			
	LiCl	NaCl	Me_4NCl	Et_4NI
0.05	4.38	4.38	4.37	4.37
0.10	4.40	4.40	4.38	4.37
0.15	4.42	4.43	4.38	4.37
0.25	4.46	4.47	4.38	4.35
0.50	4.55	4.56	4.37	4.29
0.80	4.64	4.66	4.36	4.23
1.00	4.70	4.72	4.37	4.21

[a] $3s(\log K'^{H}) = 0.01 - 0.02$.

TABLE 3

Empirical parameters of eqn. (6)

Salt	c_0'	d_0'	log K'^{H} [a]
LiCl	0.507	−0.164	4.698
NaCl	0.546	−0.179	4.722
Me_4NCl	0.172	−0.174	4.353
Et_4NI	0.080	−0.265	4.170
KCl	0.443	−0.130	4.668

[a] At $I = 1$ mol l^{-1}.

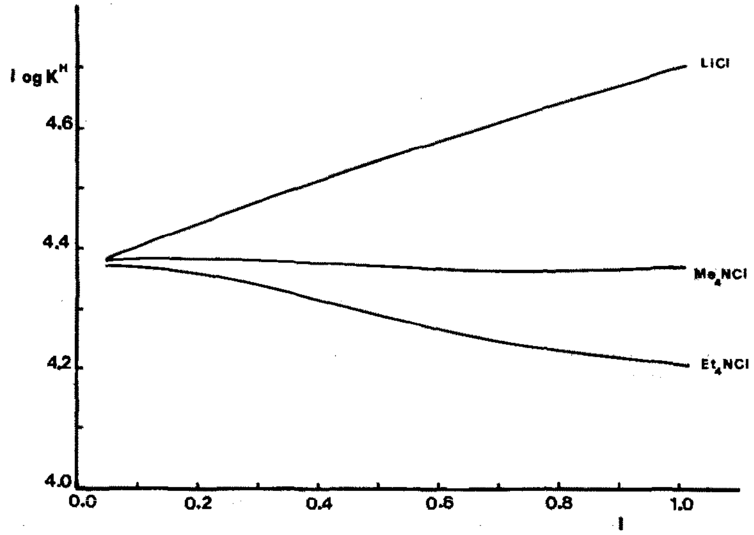

Fig. 2. Protonation constants of 2,2′-bipyridyl in various aqueous salt solutions.

Protonation constants in LiCl, NaCl and KCl are quite similar: at $I = 1$ we have a mean value $\log K'^{H}_{(1)} = 4.70 \pm 0.03$. In contrast, in Me_4NCl and Et_4NI solutions a remarkable lowering can be observed, as shown in Fig. 2.

Measurements in $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ solutions

These measurements were performed at five temperature values ($5 \leq T \leq 45$°C) and three ionic strengths ($0.21 \leq I \leq 0.93$, with $C_M = 0.07$, 0.15 and 0.31 mol l^{-1}). Apparent protonation constants (reported in

TABLE 4

Apparent protonation constants of 2,2′-bipyridyl in aqueous $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ solutions

T (°C)	I (mol l^{-1})	$\log K'^{H}$ [a]			
		$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
5	0.21	4.53	4.54	4.59	4.58
5	0.45	4.52	4.56	4.63	4.63
5	0.93	4.55	4.71	4.73	4.75
15	0.21	4.44	4.45	4.49	4.48
15	0.45	4.43	4.48	4.53	4.53
15	0.93	4.45	4.60	4.62	4.64
25	0.21	4.36	4.38	4.40	4.40
25	0.45	4.36	4.41	4.45	4.44
25	0.93	4.35	4.50	4.53	4.54
35	0.21	4.29	4.32	4.33	4.32
35	0.45	4.29	4.36	4.37	4.37
35	0.93	4.27	4.42	4.44	4.45
45	0.21	4.23	4.27	4.26	4.26
45	0.45	4.24	4.31	4.31	4.31
45	0.93	4.20	4.35	4.37	4.38

[a] $3s(\log K'^{H}) = 0.01$–0.03.

TABLE 5

Empirical parameters of eqn. (7)

Salt	c'_0	c''_0	d'_0	d''_0	$\log K'^{H}$ [a]
$MgCl_2$	0.0055	0.0128	−0.0071	−0.013	4.36
$CaCl_2$	0.056	0.0215	0.110	−0.0225	4.42
$SrCl_2$	0.244	0.0081	−0.059	−0.0084	4.46
$BaCl_2$	0.199	0.0096	0.0020	−0.0103	4.46
KCl [b]					4.53

[a] $T = 25$°C; $I = 0.5$ mol l^{-1}. [b] See eqn. (4).

Table 4) fit the equation

$$\log K'^{\mathrm{H}}_{(I,T)} = 4.355 - 0.00904(T-25) + 0.00006(T-25)^2 + c'_0 I + c''_0 I(T-25) + d'_0 I^{3/2} + d''_0 I^{3/2}(T-25) \tag{7}$$

The empirical parameters c'_0, c''_0, d'_0 and d''_0 are reported in Table 5.

Medium effects

According to a variety of experience on the ionic strength dependence of protonation constants [7, 8, 9–12], we should have

$$\log K^{\mathrm{H}} = \log {}^{\mathrm{T}}K^{\mathrm{H}} + c_0 I \tag{8}$$

with $c_0 = 0.10 \pm 0.01$ (at $T = 25$°C).

As reported in eqn. (1), the dependence of $\log K'^{\mathrm{H}}$ on I in KCl media is very different and this can be explained by the formation of the (bipy)HCl^0 species.

TABLE 6

True protonation constants of 2,2′-bipyridyl and related thermodynamics parameters [a]

I (mol l^{-1})	T (°C)	$\log K^{\mathrm{H}}$	ΔG [b]	$\Delta H'$ [c]	$\Delta S^{\ominus}$ [d]	$\Delta C'_{\mathrm{p}}$ [e]
0.00	5	4.560	−24.28	−17.02	26.1	58
0.00	15	4.451	−24.55	−16.32	28.6	81
0.00	25	4.355	−24.85	−15.39	31.7	104
0.00	35	4.270	−25.19	−14.22	35.6	130
0.00	45	4.198	−25.57	−12.78	40.2	156
0.00	55	4.139	−26.00	−11.08	45.5	184
0.10	5	4.575	−24.36	−17.40	25.0	58
0.10	15	4.464	−24.62	−16.73	27.4	81
0.10	25	4.365	−24.91	−15.83	30.5	104
0.10	35	4.278	−25.23	−14.69	34.2	130
0.10	45	4.203	−25.60	−13.28	38.7	156
0.10	55	4.141	−26.01	−11.61	43.9	184
0.50	5	4.636	−24.68	−18.93	20.7	58
0.50	15	4.514	−24.90	−18.37	22.7	81
0.50	25	4.405	−25.14	−17.59	25.3	104
0.50	35	4.308	−25.41	−16.56	28.7	130
0.50	45	4.223	−25.72	−15.29	32.8	156
0.50	55	4.150	−26.07	−13.74	37.6	184
1.00	5	4.172	−25.09	−20.84	15.3	58
1.00	15	4.577	−25.25	−20.43	16.7	81
1.00	25	4.455	−25.42	−19.79	18.9	104
1.00	35	4.345	−25.63	−18.91	21.8	130
1.00	45	4.247	−25.86	−17.79	25.4	156
1.00	55	4.161	−26.14	−16.41	29.6	184

[a] $3s(\log K^{\mathrm{H}}) = 0.002 - 0.008$. [b] kJ mol^{-1}. [c] kJ mol^{-1} (to obtain $\Delta H^{\ominus}$ see Appendix). [d] J K^{-1} mol^{-1}. [e] J K^{-1} mol^{-1} (to obtain $\Delta C^{\ominus}_{\mathrm{p}}$ see Appendix).

TABLE 7

Formation constants of the species (bipy)HCl^0 and related thermodynamics quantities[a]

I (mol l^{-1})	T (°C)	$\log \beta^{\mathrm{Cl}}$	$\Delta G^{\ominus}$ [b]	ΔH [c]	ΔS [d]	$\Delta C_p'$ [e]
0.00	5	4.547	−24.21	−11.84	44.5	115
0.00	15	4.474	−24.68	−10.56	49.0	141
0.00	25	4.414	−25.19	−9.00	54.3	169
0.00	35	4.368	−25.77	−7.15	60.4	199
0.00	45	4.336	−26.40	−5.00	67.3	230
0.00	55	4.317	−27.11	−2.53	74.9	263
0.10	5	4.400	−23.43	−12.49	39.3	115
0.10	15	4.322	−23.84	−11.25	43.7	141
0.10	25	4.258	−24.30	−9.74	48.8	169
0.10	35	4.208	−24.82	−7.95	54.8	199
0.10	45	4.171	−25.40	−5.85	61.4	230
0.10	55	4.148	−26.05	−3.44	68.9	263
0.50	5	4.545	−24.20	−18.30	21.2	115
0.50	15	4.428	−24.43	−17.49	24.1	141
0.50	25	4.325	−24.68	−16.42	27.7	169
0.50	35	4.235	−24.98	−15.08	32.1	199
0.50	45	4.159	−25.33	−13.45	37.3	230
0.50	55	4.096	−25.73	−11.52	43.3	263
1.00	5	4.836	−25.75	−29.58	−13.8	115
1.00	15	4.643	−25.61	−29.59	−13.8	141
1.00	25	4.463	−25.47	−29.38	−13.1	169
1.00	35	4.298	−25.35	−28.92	−11.1	199
1.00	45	4.145	−25.25	−28.21	−9.3	230
1.00	55	4.006	−25.17	−27.22	−6.3	263

[a] $3s(\log K^{\mathrm{H}}) = 0.002 - 0.008$. [b] kJ mol^{-1}. [c] kJ mol^{-1} (to obtain $\Delta H^{\ominus}$ see Appendix). [d] In J K^{-1} mol^{-1}. [e] J K^{-1} mol^{-1} (to obtain $\Delta C_p^{\ominus}$ see Appendix).

Assuming that (a) $c_0 = 0.10$, (b) K$^+$ does not form a complex species with 2,2′-bipyridyl, (c) the bipyridinium ion does form a complex species with Cl$^-$ and (d) the general equation (eqn. (9)) for the dependence on ionic strength is valid for all the protonation and complex species,

$$\log K = \log {}^{T}K - z'\sqrt{I}/(2 + 3\sqrt{I}) + (c_0 p^* + c_1 z^*)I + d_1 z^* I^{3/2} \qquad (9)$$

where $z^* = \sum (\text{charges})^2_{\text{reactants}} - \sum (\text{charges})^2_{\text{products}}$ and $p^* = \sum (\text{moles})_{\text{reactants}} - \sum (\text{moles})_{\text{products}}$, the calculations (performed by ES2WC) give the following results (±std. dev.).

$$\log K^{\mathrm{H}} = 4.3548 \pm 0.0005\ (25°\mathrm{C});\ \partial \log K^{\mathrm{H}}/\partial T$$
$$= -(9.043 \pm 0.026) \times 10^{-3};\ \partial^2 \log K^{\mathrm{H}}/\partial T^2 = (6.11 \pm 0.13) \times 10^{-5}$$

$$\log \beta^{\mathrm{Cl}} = 4.414 \pm 0.005\ (25°\mathrm{C});\ \partial \log K^{\mathrm{Cl}}/\partial T$$
$$= -(5.3 \pm 0.7) \times 10^{-3};\ \partial^2 \log K^{\mathrm{Cl}}/\partial T^2 = (6.8 \pm 0.5) \times 10^{-5}$$

$c_0 = -d_1 = 0.10$; $\partial c_0/\partial T = -(2.6 \pm 0.5) \times 10^{-3}$; $\partial d_0/\partial T = -(5.7 \pm 0.8) \times 10^{-3}$

$c_1 = 0.225 \pm 0.003$; $\partial c_1/\partial T = (2.2 \pm 1.0) \times 10^{-3}$

The fit is excellent, being $s(\bar{p}) = 7 \times 10^{-4}$ and $\varepsilon(\log K'^{H}) = 8.4 \times 10^{-4}$ (ε = mean dev.; $\bar{p}$ = number of protons bound to the ligand). In Tables 6 and 7 smoothed log K^{H} and log β^{Cl} values at different temperatures and ionic strengths are reported, together with thermodynamic parameters.

Protonation constants in the other media follow the trends $KCl \approx NaCl \approx LiCl > Me_4NCl > Et_4NI$; $KCl > BaCl_2 > SrCl_2 > CaCl_2 > MgCl_2$.

These differences were interpreted as being caused by formation of some complex species. In performing calculations relative to these systems one must handle the data with considerable care, because the results are strictly dependent on the assumption upon which they are based. In particular, we must stress that when dealing with the formation of very weak species it is important to also take into account the association of the background salt. In a recent literature data analysis on the association of Cl^- with Na^+, K^+, Mg^{2+} and Ca^{2+}, approximate (for Na^+ and K^+) and quite reliable (for Mg^{2+} and Ca^{2+}) values of formation constants were reported [13]. These values are used in this work to calculate effective concentrations of various cations and to give effective ionic strengths. LiCl was considered as completely dissociated, as is generally accepted in the literature. Tetraalkylammonium salts were also assumed to be completely dissociated. For $SrCl_2$ and $BaCl_2$ there is insufficient data in the literature and we assumed the association of these salts to be equal to that of $CaCl_2$. The errors arising from these assumptions and from the use of not very accurate formation constants for Na^+ and K^+ chloride complexes are quite small, i.e. <5% in I_e (effective ionic strength), and <2% for alkaline earth metal cations.

TABLE 8

Formation constants of weak complexes of 2,2'-bipyridyl with Me_4N^+ and Et_4N^+

Reaction	I^a	Log K
$Me_4N^+ + bipy^0 = Me_4N(bipy)^+$	0	0.02 ± 0.12^b
	0.1	0.02
	0.25	0.04
	0.5	0.07
	1	0.12
$Et_4N^+ + bipy^0 = Et_4N(bipy)^+$	0	0.23 ± 0.09^b
	0.1	0.24
	0.25	0.26
	0.5	0.28
	1	0.33

[a] Ionic strength in mol l^{-1}. [b] $\pm 3s$ (std. dev.).

Protonation data in tetraalkylammonium and alkaline earth metal salts were also explained by assuming the formation of 1:1 cation–2,2′bipyridyl complexes. The relative formation constants are reported in Tables 8 and 9. The stability of these species is quite low, as expected for amino compounds, and fits the behaviour of similar systems [8, 12].

Furthermore, it is necessary to check the validity of the model of the ionic strength dependence of the formation constant, because the parameters of eqn. (9) drastically influence the value of the formation constants. Calculations performed by also refining the parameter c_1 gave

TABLE 9

Thermodynamic parameters for the formation of alkaline-earth–2,2′-bipyridyl metal complexes

I_c [a]	T (°C)	log K	$\Delta G^{\ominus}$ [b]	$\Delta H'$ [c]	$\Delta S^{\ominus}$ [d]
Mg(bipy) complex species					
0.20	5	0.38	−2.0	7	32
0.20	15	0.43	−2.3	7	34
0.20	25	0.47	−2.7	8	36
0.20	35	0.52	−3.1	9	38
0.20	45	0.57	−3.5	9	39
0.50	5	0.32	−1.7	13	54
0.50	15	0.41	−2.3	14	57
0.50	25	0.50	−2.9	15	61
0.50	35	0.59	−3.5	16	64
0.50	45	0.68	−4.2	17	68
0.75	5	0.28	−1.5	18	72
0.75	15	0.40	−2.2	20	77
0.75	25	0.53	−3.0	21	81
0.75	35	0.65	−3.8	23	86
0.75	45	0.78	−4.7	24	91
Ca(bipy) complex species					
0.20	5	−0.25	1.3	18	61
0.20	15	−0.13	0.7	20	66
0.20	25	0.00	0.0	21	71
0.20	35	0.12	−0.7	23	76
0.20	45	0.25	−1.5	24	80
0.50	5	−0.31	1.6	25	83
0.50	15	−0.14	0.8	27	89
0.50	25	0.03	−0.2	28	96
0.50	35	0.19	−1.1	30	102
0.50	45	0.36	−2.2	32	108
0.75	5	−0.35	1.9	30	101
0.75	15	−0.15	0.8	32	109
0.75	25	0.05	−0.3	34	116
0.75	35	0.25	−1.5	37	124
0.75	45	0.46	−2.8	39	132

TABLE 9 (continued)

I_c [a]	T (°C)	log K	$\Delta G^{\ominus}$ [b]	$\Delta H'$ [c]	$\Delta S^{\ominus}$ [d]
Sr(bipy) complex species					
0.20	5	−0.45	2.4	15	46
0.20	15	−0.35	1.9	16	50
0.20	25	−0.25	1.4	18	54
0.20	35	−0.14	0.8	19	58
0.20	45	−0.04	0.2	20	62
0.50	5	−0.47	2.5	18	57
0.50	15	−0.34	1.9	20	62
0.50	25	−0.22	1.2	21	67
0.50	35	−0.09	0.5	23	72
0.50	45	0.03	−0.2	24	76
0.75	5	−0.48	2.5	21	67
0.75	15	−0.33	1.8	23	72
0.75	25	−0.19	1.1	24	77
0.75	35	−0.05	0.3	26	83
0.75	45	0.09	−0.6	28	88
Ba(bipy) complex species					
0.20	5	−0.61	3.2	20	62
0.20	15	−0.47	2.6	22	67
0.20	25	−0.33	1.9	23	72
0.20	35	−0.19	1.1	25	78
0.20	45	−0.05	0.3	27	83
0.50	5	−0.62	3.3	24	73
0.50	15	−0.46	2.5	25	79
0.50	25	−0.30	1.7	27	85
0.50	35	−0.14	0.8	29	91
0.50	45	0.02	−0.1	31	97
0.75	5	−0.63	3.3	26	82
0.75	15	−0.45	2.5	28	89
0.75	25	−0.27	1.6	30	95
0.75	35	−0.10	0.6	32	102
0.75	45	0.08	−0.5	34	109

[a] Effective ionic strength in mol l^{-1}. [b] kJ mol^{-1}. [c] kJ mol^{-1}. [d] J K^{-1} mol^{-1}.

(on average), a value of $c_1 = 0.23 \pm 0.02$, which is in good agreement with previous results [10].

In Tables 6, 7 and 9 we report the thermodynamic values $\Delta H'$ and $\Delta C_p'$ (molar scale); these values must be corrected to the molal scale, as reported in Appendix.

ACKNOWLEDGEMENTS

We thank CNR and MURST for partial financial support.

REFERENCES

1 W.A.E. McBryde, A critical review of equilibrium data for proton and metal complexes of 1,10-phenanthroline and 2,2'-bipyridyl and related compounds, IUPAC Chemical Data Series, No. 17, Pergamon, Oxford, 1979.
2 G. Anderegg, Helv. Chim. Acta, 46 (1963) 2397.
K. Some P. Krumholtz and H. Stammrich, J. Am. Chem. Soc., 77 (1955) 777.
3 R. Näsänen, Suom. Kemistil. B, 28 (1955) 161.
4 S. Capone, A. De Robertis, C. De Stefano and R. Scarcella, Talanta, 32 (1985) 675.
5 H.A. Flaschka, EDTA Titrations, Pergamon, London, 1959.
6 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1966.
7 S. Capone, A. Casale, A. Curro, A. De Robertis, C. De Stefano, S. Sammartano and R. Scarcella, Ann. Chim. (Rome), 76 (1986) 441.
8 P.G. Daniele, A. De Robertis, C. De Stefano and S. Sammartano, J. Solution Chem., 18 (1989) 23.
9 A. Casale, P.G. Daniele, C. De Stefano and S. Sammartano, Talanta, 36 (1989) 903.
10 P.G. Daniele, A. De Robertis, C. De Stefano and S. Sammartano, in S. Alegret et al. (Eds.), Miscellany of Scientific Papers Offered to Enric Casassas, Barcelona, 1991.
11 A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, J. Solution Chem., 19 (1990) 569.
12 A. Casale, A. De Robertis, F. Licastro and C. Rigano, J. Chem. Res., (S) (1990) 204; (M) (1990) 1601–1620.
13 A. De Robertis, C. Rigano, S. Sammartano and O. Zerbinati, Thermochim. Acta, 115 (1987) 241.
14 L.G. Hepler, Thermochim. Acta, 50 (1981) 69.

APPENDIX

As pointed out by Hepler [14], the correct value of $\Delta H^{\ominus}$ and $\Delta C_p^{\ominus}$ can be obtained from the temperature dependence of formation constants only by using the molal scale. If the measurements are performed in the molal scale, corrections can be obtained from the equations

$$\log K_m = \log K_c + p^* \log (c/m) = \log K_c + p^*\delta(\log K)$$

$$\Delta G_m^{\ominus} = -RT \ln K_m = \Delta G_c^{\ominus} - p^*RT \ln (c/m) = \Delta G_c^{\ominus} + p^*\delta(\Delta G)$$

$$\Delta H^{\ominus} = RT^2(\partial \ln K_m/\partial T) + p^*RT^2[\partial \ln (c/m)/\partial T] = \Delta H' + p^*\delta(\Delta H)$$

$$\begin{aligned}\Delta C_p^{\ominus} &= R[2T(\partial \ln K/\partial T) + T^2(\partial^2 \ln K/\partial T^2)] \\ &\quad - p^*R\{2T[\partial \ln (c/m)/\partial T] + T^2[\partial^2 \ln (c/m)/\partial T^2]\} = \Delta C_p' + p^*\delta(\Delta C_p)\end{aligned}$$

From literature data on densities of KCl, $MgCl_2$ and $CaCl_2$ aqueous solutions we calculated $\delta(X)$ corrections ($X = \log K$, ΔG, ΔH and ΔC_p) as reported in Table A1. Corrections for $SrCl_2$ and $BaCl_2$ solutions can be estimated using δ(X) for $CaCl_2$, with negligible error. Note that when formation constants are determined with accuracy of ±0.02–±0.05 (as happens in most cases reported in the literature) these conditions are of little significance.

TABLE A1

δX corrections

I	T	$\delta(\log K)$	$\delta(\Delta G^{\ominus})$	$\delta(\Delta H^{\ominus})$	$\delta(\Delta S^{\ominus})$	$\delta(\Delta C_p^{\ominus})$
For KCl						
0.0	5	0.0000	0.000	−0.04	−0.1	−6
0.0	15	−0.0004	0.002	−0.10	−0.4	−7
0.0	25	−0.0013	0.007	−0.18	−0.6	−8
0.0	35	−0.0025	0.015	−0.26	−0.9	−9
0.0	45	−0.0042	0.026	−0.36	−1.2	−10
0.0	55	−0.0063	0.039	−0.47	−1.5	−11
0.1	5	−0.0011	0.006	−0.04	−0.2	−6
0.1	15	−0.0015	0.008	−0.11	−0.4	−7
0.1	25	−0.0024	0.014	−0.19	−0.7	−8
0.1	35	−0.0037	0.022	−0.27	−1.0	−9
0.1	45	−0.0054	0.033	−0.37	−1.3	−10
0.1	55	−0.0075	0.047	−0.47	−1.6	−11
0.5	5	−0.0059	0.031	−0.06	−0.3	−6
0.5	15	−0.0065	0.036	−0.13	−0.6	−7
0.5	25	−0.0075	0.043	−0.21	−0.8	−8
0.5	35	−0.0090	0.053	−0.30	−1.1	−9
0.5	45	−0.0108	0.066	−0.40	−1.5	−10
0.5	55	−0.0131	0.082	−0.50	−1.8	−11
1.0	5	−0.0126	0.067	−0.09	−0.6	−6
1.0	15	−0.0134	0.074	−0.16	−0.8	−7
1.0	25	−0.0146	0.083	−0.24	−1.1	−8
1.0	35	−0.0162	0.095	−0.33	−1.4	−9
1.0	45	−0.0182	0.111	−0.43	−1.7	−10
1.0	55	−0.0206	0.129	−0.54	−2.0	−11
For $CaCl_2$						
0.1	5	−0.0033	0.018	−0.04	−0.2	−6
0.1	15	−0.0038	0.021	−0.11	−0.4	−7
0.1	25	−0.0047	0.027	−0.18	−0.7	−8
0.1	35	−0.0060	0.035	−0.27	−1.0	−9
0.1	45	−0.0077	0.047	−0.37	−1.3	−10
0.1	55	−0.0097	0.061	−0.47	−1.6	−11
0.5	5	−0.0176	0.093	−0.06	−0.5	−6
0.5	15	−0.0182	0.100	−0.13	−0.8	−7
0.5	25	−0.0192	0.109	−0.20	−1.1	−8
0.5	35	−0.0206	0.121	−0.29	−1.3	−9
0.5	45	−0.0224	0.136	−0.39	−1.7	−10
0.5	55	−0.0246	0.154	−0.50	−2.0	−11
1.0	5	−0.0364	0.194	−0.08	−1.0	−6
1.0	15	−0.0372	0.205	−0.15	−1.2	−7
1.0	25	−0.0383	0.219	−0.23	−1.5	−8
1.0	35	−0.0399	0.235	−0.32	−1.8	−9
1.0	45	−0.0418	0.255	−0.42	−2.1	−10
1.0	55	−0.0442	0.278	−0.53	−2.5	−11

TABLE A1 (continued)

I	T	$\delta(\log K)$	$\delta(\Delta G^{\ominus})$	$\delta(\Delta H^{\ominus})$	$\delta(\Delta S^{\ominus})$	$\delta(\Delta C_p^{\ominus})$
For $MgCl_2$						
0.1	5	−0.0029	0.016	−0.04	−0.2	−6
0.1	15	−0.0034	0.019	−0.11	−0.4	−7
0.1	25	−0.0043	0.024	−0.18	−0.7	−8
0.1	35	−0.0055	0.033	−0.27	−1.0	−9
0.1	45	−0.0072	0.044	−0.36	−1.3	−10
0.1	55	−0.0093	0.058	−0.47	−1.6	−11
0.5	5	−0.0151	0.081	−0.05	−0.5	−6
0.5	15	−0.0157	0.087	−0.12	−0.7	−7
0.5	25	−0.0167	0.095	−0.20	−1.0	−8
0.5	35	−0.0180	0.106	−0.29	−1.3	−9
0.5	45	−0.0198	0.121	−0.38	−1.6	−10
0.5	55	−0.0220	0.138	−0.49	−1.9	−11
1.0	5	−0.0311	0.165	−0.07	−0.9	−6
1.0	15	−0.0318	0.175	−0.14	−1.1	−7
1.0	25	−0.0329	0.188	−0.22	−1.4	−8
1.0	35	−0.0343	0.203	−0.31	−1.7	−9
1.0	45	−0.0362	0.221	−0.41	−2.0	−10
1.0	55	−0.0385	0.242	−0.52	−2.3	−11