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THE EFFECT OF BACKGROUND ON THE PROTONATION OF PYRIDINE: A COMPLEX FORMATION MODEL

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ABSTRACT

The protonation constants of pyridine were obtained in aqueous solutions of LiCl, NaCl, $NaClO_4$, $NaNO_3$, NaI, KNO_3, KI, RbCl, CsCl, $MgCl_2$, $CaCl_2$, tetramethylammonium iodide, tetraethylammonium iodide, tetramethylammonium chloride and tetraethylammonium chloride in the ranges $0 \le I \le 1$ mol l^{-1} and $10 \le T \le 45\,^\circ C$. The differences in the protonation thermodynamic parameters of pyridine in the various solutions were interpreted in terms of weak species formation between the components.

INTRODUCTION

In a previous study on this topic [1], we reported the results of a potentiometric investigation on the determination of protonation constants of pyridine (py) in different solutions, at various temperatures and ionic strengths. The values of log K^H obtained for the different salts in the solutions were collected in three different groups: (i) salts of alkali metals; (ii) salts of alkaline earth metals; (iii) salts of tetraalkylammonium cations. The differences were tentatively explained by the formation of weak species between the components present in the solutions, i.e. chloride complexes with the metal cations, chloride–proton–pyridine complexes and pyridine–metal cation–tetraalkylammonium cation complexes. A similar hypothesis was proposed by us to explain the analogous behaviour of log K^H of imidazole [2] and α-alanine [3]. In addition, from an analysis of the literature data on the protonation of amines, we have indicated the differences in log K^H values which can be explained in terms of the formation of weak complexes between the components of the systems under study.

It is now necessary to verify the proposed hypothesis by increasing the number of compounds used. Salts with anions Cl^-, NO_3^-, ClO_4^- and I^- were chosen. In this way differences in log K^H for salts with the same cation but different anions (under the same analytical conditions) can be used to indicate the type of anion and the specific complexing ability.

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EXPERIMENTAL

Reagents

Pyridine (Fluka) was handled and stored according to Perrin et al. [5]; its purity, checked acidimetrically, was found to be $\geq 99.8\%$. Alkali metal chlorides (Fluka) were dried under vacuum and the corresponding stock solutions were prepared by weighing. Tetraalkylammonium salts (Fluka or Merck) were recrystallized from ethanol and/or water–ethanol [6]; the stock solutions were prepared daily. Magnesium and calcium chloride solutions were prepared from purum Fluka products and were standardized using EDTA [7].

Apparatus

Measurements were carried out by potentiometric reading of the hydrogen ion concentrations using a potentiometer Metrohm model 600 and/or a home-made semi-automatic potentiometer. The systems were coupled with glass and saturated calomel electrodes, supplied by Metrohm and/or Ingold. The instrumental resolution was 0.1 mV and the reproducibility was ±0.2 mV for both systems.

Procedure

The solution (50 ml) containing pyridine (5 mmol l^{-1}), HCl (7.5 mmol l^{-1}) and the background salt was titrated with standard KOH (0.1 mol l^{-1}). HCl was added in excess in order to calculate the internal $E^{\ominus}$ value ($E^{\ominus}_{int}$); separate titrations of HCl at the same temperature and ionic strength allowed us to calculate the $E^{\ominus}_{ext}$ value. If $|E^{\ominus}_{int} - E^{\ominus}_{ext}| \geq 1.0$ mV, the titration was rejected.

All the concentrations, ionic strengths and thermodynamic quantities were expressed in the molar scale.

Calculations

The calculations for the determination of protonation constants were carried out using the non-linear least-squares computer program ESAB2M [7], which also refines analytical and instrumental parameters. The parameters for the dependence of log K^{H} on temperature and ionic strength were calculated using the non-linear least-squares computer program REGIS [8]. The formation constants of the weak complexes were calculated using the non-linear least-squares program ES2WC [9].

Other details are reported in ref. 1.

RESULTS AND DISCUSSION

The values of the protonation constants obtained for the various backgrounds, without allowing for any weak interaction which may occur in solution, are reported in Table 1 (alkali metals), Table 2 (tetraalkylammonium cations) and Table 3 (alkaline earth metals). In these tables, the log K^H values are reported at three ionic strengths (smoothed values) and the dependence on temperature is taken into account by calculating the enthalpy $\Delta H^\ominus$ of protonation.

General remarks on log K^H values

(a) At low ionic strength ($I = 0.1$ mol l^{-1}) similar log K^H values are obtained for all the backgrounds considered (log $K^H = 5.23_5 \pm 0.02_5$ (16 values, $T = 25$ °C)) and, at $I = 0$ mol l^{-1} and $T = 25$ °C [1], log $K^H = 5.207 \pm 0.002_3$.

(b) At rather high ionic strength ($I = 1$ mol l^{-1}) the log K^H values obtained for the various backgrounds are very different.

(c) The same ((a) and (b)) holds for the $\Delta H^\ominus$ values.

TABLE 1

Protonation constants of pyridine in alkali metal salts

Salt	T (°C)	log K^{H} [a]			$-\Delta H^\ominus$ (kJ mol^{-1}) [a]	
		$I = 0.1$	$I = 0.5$	$I = 1$	$I = 0.5$	$I = 1$
LiCl	10	–	5.56	5.71		
	25	5.24	5.37	5.51	21.9	23.3
	45	–	5.11	5.23		
NaCl	10	–	5.58	5.74		
	25	5.24	5.38	5.53	20.8	22.3
	45	–	5.15	5.28		
$NaClO_4$	25	5.25	5.43	5.60		
$NaNO_3$	25	5.24	5.38	5.52		
NaI	25	5.25	5.38	5.52		
KCl	10	5.43	5.56	5.70		
	25	5.24	5.36	5.49	20.8	21.8
	45	5.02	5.13	5.25		
KNO_3	25	5.24	5.35	5.45		
KI	25	5.24	5.39	5.54		
RbCl	10	–	5.53	5.65		
	25	5.24	5.34	5.45	20.8	22.8
	45	5.02	5.10	5.18		
CsCl	10	5.43	5.54	5.66		
	25	5.24	5.35	5.47	20.4	21.4
	45	5.02	5.12	5.22		

[a] $3s(\log K^H) = 0.005–0.015$; $3s(\Delta H^\ominus) = 0.5–1$.

TABLE 2

Protonation constants of pyridine in tetraalkylammonium salts

Salt	T (°C)	log K^{H} [a]			$-\Delta H^{\ominus}$ (kJ mol^{-1}) [a]	
		$I=0.1$	$I=0.5$	$I=1$	$I=0.5$	$I=1$
Me_4NCl	10	5.42	5.46	–		
	25	5.22	5.25	5.25	21.3	–
	45	5.00	5.02	5.02		
Me_4NI	25	5.24	5.29	–		
Et_4NCl	25	5.21	5.19	5.11		
Et_4NI	10	5.41	5.41	5.37		
	25	5.22	5.22	5.16	21.4	22.3
	45	4.99	4.97	4.91		

[a] $3s(\log K^{H}) = 0.02–0.05$; $3s(\Delta H^{\ominus}) = 1–3$.

In all cases, the log K^{H} values can be fitted by the equation [10,11]

$$\log K^{H} = \log {}^{T}K^{H} + c_0 I + d_0 I^{3/2} \tag{1}$$

${}^{T}K^{H}$ is the protonation constant at infinite dilution. The values of c_0 and d_0 are reported in Table 4.

The complex formation model

In a solution containing pyridine, a salt MX_p and H^+ we must take into account the following equilibria

$$py^0 + H^+ = [(py)H]^+ \tag{2}$$

$$py^0 + H^+ + X^- = [X(py)H]^0 \tag{3}$$

$$py^0 + M^{z+} = [M(py)]^{z+} \tag{4}$$

$$M^{z+} + X^- = [M(X)]^{[(z^+)-1]} \tag{5}$$

TABLE 3

Protonation constants of pyridine in alkali earth metal chlorides

Salt	T (°C)	log K^{H} [a]			$-\Delta H^{\ominus}$ (kJ mol^{-1}) [a]	
		$I=0.1$	$I=0.5$	$I=1$	$I=0.5$	$I=1$
$MgCl_2$	10	5.41	5.51	5.61		
	25	5.23	5.31	5.40	20.8	21.8
	45	5.01	5.08	5.16		
$CaCl_2$	10	5.41	5.51	5.60		
	25	5.23	5.32	5.40	20.9	21.3
	45	5.00	5.08	5.16		

[a] $3s(\log K^{H}) = 0.01–0.02$; $3s(\Delta H^{\ominus}) = 1–2$.

TABLE 4

Parameters for the effect of background on the protonation of pyridine at 25 ° C (see eqn. (1))

Salt	c_0	$-d_0$
LiCl	0.40_5	0.10
NaCl	0.44	0.11
$NaClO_4$	0.51	0.12
$NaNO_3$	0.47	0.15
NaI	0.50	0.19
KCl	0.41	0.12
RbCl	0.34	0.10
CsCl	0.38	0.12
Et_4NI	0.21_5	0.26
Et_4NCl	0.10	0.19
KI	0.47	0.13_5
KNO_3	0.43	0.18
Me_4NCl	0.22	0.17
Me_4NI	0.58	0.59
$MgCl_2$	0.27	0.07
$CaCl_2$	0.28	0.08

with the relative equilibrium constants (c = equilibrium concentrations)

$$K^{\mathrm{H}} = c_{[(\mathrm{py})\mathrm{H}]} c_{\mathrm{py}}^{-1} c^{-1} \tag{6}$$

$$K^{\mathrm{X}} K^{\mathrm{H}} = c_{[\mathrm{X}(\mathrm{py})\mathrm{H}]} c_{[(\mathrm{py})\mathrm{H}]}^{-1} c_{\mathrm{X}}^{-1} \tag{7}$$

$$K^{\mathrm{Mpy}} = c_{[\mathrm{M}(\mathrm{py})]} c_{\mathrm{M}}^{-1} c_{\mathrm{py}}^{-1} \tag{8}$$

$$K^{\mathrm{MX}} = c_{[\mathrm{M}(\mathrm{X})]} c_{\mathrm{M}}^{-1} c_{\mathrm{X}}^{-1} \tag{9}$$

When neglecting eqns. (3)–(5) (and eqns. (7)–(9)), i.e. by assuming that only $[(\mathrm{py})\mathrm{H}]^+$ forms, the mass balance equations can be written (C = analytical concentrations)

$$C_{\mathrm{py}} = c_{\mathrm{py}} + K^{\mathrm{H}} c_{\mathrm{py}} c_{\mathrm{H}} \tag{10}$$

$$C_{\mathrm{H}} = c_{\mathrm{H}} + K^{\mathrm{H}} c_{\mathrm{py}} c_{\mathrm{H}} - K_{\mathrm{w}} c_{\mathrm{H}}^{-1} \tag{11}$$

When the formation of all the species is taken into account, the mass balance equations are written (c'_{py} = "true" free concentration of pyridine)

$$C_{\mathrm{M}} = c_{\mathrm{M}} + K_{(\mathrm{e})}^{\mathrm{MX}} c_{\mathrm{M}} c_{\mathrm{X}} + K^{\mathrm{Mpy}} c_{\mathrm{M}} c'_{\mathrm{py}} \tag{12}$$

$$C_{\mathrm{py}} = c'_{\mathrm{py}} + K_{(\mathrm{e})}^{\mathrm{H}} c'_{\mathrm{py}} c_{\mathrm{H}} + K^{\mathrm{Mpy}} c_{\mathrm{M}} c'_{\mathrm{py}} + K^{\mathrm{X}} K_{(\mathrm{e})}^{\mathrm{H}} c_{\mathrm{X}} c'_{\mathrm{py}} c_{\mathrm{H}} \tag{13}$$

$$C_{\mathrm{H}} = c_{\mathrm{H}} + K_{(\mathrm{e})}^{\mathrm{H}} c'_{\mathrm{py}} c_{\mathrm{H}} + K^{\mathrm{X}} K_{(\mathrm{e})}^{\mathrm{H}} c_{\mathrm{X}} c'_{\mathrm{py}} c_{\mathrm{H}} - K_{\mathrm{w}} c_{\mathrm{H}}^{-1} \tag{14}$$

$$C_{\mathrm{X}} = c_{\mathrm{X}} + K_{(\mathrm{e})}^{\mathrm{HX}} c_{\mathrm{M}} c_{\mathrm{X}} + K^{\mathrm{X}} K_{(\mathrm{e})}^{\mathrm{H}} c_{\mathrm{X}} c'_{\mathrm{py}} c_{\mathrm{H}} \tag{15}$$

The subscript (e) indicates "effective" quantities, such as log $K_{(\mathrm{e})}^{\mathrm{H}}$ and $I_{(\mathrm{e})}$, i.e. quantities calculated by taking into account all the interactions occurring in solution.

By equating eqns. (11) and (14) and substituting c'_{py} and c_{py} from eqns. (10) and (13), we obtain

$$K^{H} = K^{H}_{(e)} \frac{1 + K^{X} c_{X}}{1 + K^{MPy} c_{M}} \tag{16}$$

Equation (16) shows that the formation of $[X(py)H]^0$ increases the conditional protonation constant and, conversely, the formation of $[M(py)]^{z+}$ decreases $K^{H}_{(e)}$. In general, we can write

$$\log K^{H} = \log K^{H}_{(e)} + \sum \log(1 + \chi c_{S})(-1)^{k} \tag{17}$$

where χ is the formation constant for the reaction

$$S^{z\pm} + [(py)H_{k}]^{k} = [S(py)H_{k}] \tag{18}$$

The dependence of the formation constants on the ionic strength can be expressed by the equation [10–12]

$$\log K(I) = \log K(I=0) - z^{*} I^{1/2}_{(e)} / \left(2 + 3 I^{1/2}_{(e)}\right) + CI + DI^{3/2} \tag{19}$$

with

$$C = c_0 p^{*} + c_1 z^{*} \tag{20}$$

$$D = d_0 p^{*} + d_1 z^{*} \tag{21}$$

$$z^{*} = \sum (\text{charges})^2_{\text{reactants}} - \sum (\text{charges})^2_{\text{products}} \tag{22}$$

$$p^{*} = \sum (\text{reactants}) - \sum (\text{products}) \tag{23}$$

For the parameters of eqns. (19)–(21) we found [12]

$$\begin{aligned} c_0 &= 0.10 \\ c_1 &= 0.23 \\ d_0 &= 0.0 \\ d_1 &= -0.10 \end{aligned} \tag{24}$$

According to this model we performed some calculations in order to evaluate the different contributions of various factors to the effect of background on the protonation constant of pyridine.

Alkali metal salts

Mean values for log K^{H} determined in all alkali metal salts are (at 25 °C):

$\log K^{H}(I=0.1) = 5.24 \quad (s = 0.01, 2\%)$

$\log K^{H}(I=0.5) = 5.37 \quad (s = 0.03, 7\%)$

$\log K^{H}(I=1) = 5.51 \quad (s = 0.05, 12\%)$

TABLE 5

Protonation constants in NaCl and KCl

T(°C)	I	log K^{H}		log K^{H}[a]		log K^{H}[b]
		NaCl	KCl	NaCl	KCl	NaCl + KCl
10	0.05	5.395	5.411	5.394	5.412	5.409
	0.15	5.443	5.448	5.446	5.451	5.451
	0.25	5.486	5.483	5.495	5.490	5.492
	0.5	5.582	5.562	5.609	5.587	5.596
	0.75	5.663	5.632	5.711	5.685	5.699
	1	5.732	5.695	5.804	5.785	5.803
25	0.05	5.215	5.222	5.214	5.223	5.223
	0.15	5.258	5.256	5.261	5.258	5.261
	0.25	5.298	5.289	5.305	5.294	5.299
	0.5	5.387	5.363	5.408	5.385	5.395
	0.75	5.464	5.430	5.503	5.478	5.492
	1	5.531	5.491	5.592	5.572	5.589
45	0.05	4.994	5.001	4.996	5.002	5.000
	0.15	5.031	5.032	5.034	5.034	5.034
	0.25	5.066	5.061	5.072	5.066	5.068
	0.5	5.146	5.129	5.161	5.148	5.154
	0.75	5.217	5.192	5.247	5.233	5.241
	1	5.282	5.250	5.331	5.320	5.329

[a] These values were calculated by assuming real values for the concentrations of NaCl and KCl, i.e. by taking into account the formation of $[\mathrm{Na(Cl)}]^0$ and $[\mathrm{K(Cl)}]^0$ ion pairs (see ref. 8).

[b] These values were calculated in the same way by averaging the protonation constants in NaCl and KCl.

The standard deviation increases linearly with ionic strength and can be expressed as $s(\%) \approx 12I$. The variability of the protonation constants of pyridine in the various alkali backgrounds can be explained by considering four factors: (a) the different purity of the various salts; (b) experimental errors; (c) the different degree of association of the various salts; (d) specific effects. Factor (a) is difficult to take into account. Nevertheless, some calculations of the error propagation which account for the possible effects of purity of less than 100% of the background showed that $3s(\%) < 4I$ for $[100 - \text{purity}(\%)] \geq 99.5\%$. Factor (b) accounts for $\leq 5\%$. To illustrate the effect of factor (c), the protonation constants obtained in NaCl and KCl backgrounds with and without correction for $[\mathrm{M(Cl)}]^0$ ($\mathrm{M} = \mathrm{K}^+$, Na^+) ion pair formation are reported in Table 5. When taking into account the formation of $[\mathrm{M(Cl)}]^0$ ion pairs, the difference between log K^{H} determined in NaCl and KCl reduces from 9.2% to 4.6% (25 °C, $I = 1$). Factor (d) can be deduced as the difference. Some results illustrating the separation into the four effects of variability of log K^{H} in alkali metal salts are reported in Table 6.

TABLE 6

Variability of log K^H values due to different factors (see text)

I	ϵ% (tot) [a]	α% (a)	ϵ% (b)	ϵ% (c)	ϵ% (d)
0.1	7	0.57 (7) [b]	5 (71)	1 (14)	0.5 (7)
0.5	22	2 (9)	5 (23)	7 (32)	8 (36)
1	37	4 (11)	5 (13)	18 (49)	10 (27)

[a] ϵ% = variability (percentage) ≈ 3 standard deviations. [b] The contribution of the factor (referred to 100) is given in parentheses.

As reported in previous papers, the dependence of the protonation constants of amines on ionic strength which is different from that expected, can be explained by assuming the formation of $[X(py)H]^0$ species (X = monocharged anion). Calculations performed with the ES2WC program gave the following results

$$\log K^X = -0.11 \pm 0.15 \qquad (T = 25\,°C,\ I = 0) \tag{25}$$

using log K^H obtained in NaCl solutions without considering the formation of $[Na(Cl)]^0$. Using KCl and NaCl data corrected for the formation of $[M(Cl)]^0$ ion pairs (third column of Table 5), we obtained

$$\log K^X_{(e)} = 0.0 \pm 0.2 \qquad (T = 25\,°C,\ I = 0) \tag{26}$$

From the dependence on temperature of log K^X we calculated

$\Delta H^\ominus = -7 \pm 1.5$ kJ mol^{-1}

for the reaction $[(py)H]^+ + X^- = [X(py)H]^0$.

Alkaline earth metal salts

Log K^H values obtained in $CaCl_2$ and $MgCl_2$ solutions are lower than those in NaCl and KCl solutions. The difference is significant if it is considered that, at the same ionic strength, the concentration of alkaline earth cation is one-third of that of the alkaline cation; this indicates complex formation. We performed some calculations with the ES2WC computer program assuming: (a) no complex formation between Na^+ and K^+ with pyridine (therefore, the protonation constants determined in NaCl and KCl were used as reference); (b) complex formation between Ca^{2+} and Mg^{2+} and pyridine, and between $[(py)H]^+$ and Cl^-; (c) complex formation between Ca^{2+} and Mg^{2+} and pyridine (for these complexes the formation constant values of ref. 8 were used). These calculations gave, at $T = 25\,°C$,

$$\log K^{Mg} = -0.37(\pm 0.04) + 0.085 I_{(e)} \tag{27}$$

$$\log K^{Ca} = -0.48(\pm 0.05) + 0.081 I_{(e)} \tag{28}$$

$$\log K^{Cl} = -0.03(\pm 0.15) - 2 I_{(e)}^{1/2}\left(2 + 3 I_{(e)}^{1/2}\right) + 0.4 I_{(e)} \tag{29}$$

$I_{(e)}$ is the effective ionic strength, i.e. the ionic strength calculated by also considering metal–chloride complexes. From the dependence of the formation constants on temperature, we calculated (at $I_{(e)} = 0.5$ and 25 °C)

$$\Delta H^{Mg} = -10.5 \pm 1.5 \text{ kJ mol}^{-1} \tag{30}$$

$$\Delta H^{Ca} = -11 \pm 3 \text{ kJ mol}^{-1} \tag{31}$$

$$\Delta H^{Cl} = -9 \pm 2 \text{ kJ mol}^{-1} \tag{32}$$

Tetraalkylammonium salts

The protonation constants determined in tetraalkylammonium salt solutions are significantly lower than those obtained in alkali metal solutions. This was interpreted, using the program ES2WC, as being due to the formation of $[X(py)H]^0$ ($X = I^-, Cl^-$) and $[A_4N(py)]^+$ ($A_4N^+ = Me_4N^+, Et_4N^+$) complexes, with the formation constants

$$\log K^X = -0.05(\pm 0.15) - 2I_{(e)}^{1/2}\left(2 + 3I_{(e)}^{1/2}\right) + 0.6I_{(e)} \tag{33}$$

$$\log K^{Me_4N} = -0.11(\pm 0.1) + 0.06I_{(e)} \tag{34}$$

$$\log K^{Et_4N} = 0.07(\pm 0.1) + 0.08I_{(e)} \tag{35}$$

The dependence on temperature enabled a calculation of the enthalpy changes to be made (at $I = 1$ mol l^{-1}, $T = 25$ °C)

$$\Delta H^{Me_4N} = 17 \text{ kJ mol}^{-1}$$

$$\Delta H^{Et_4N} = 11 \text{ kJ mol}^{-1}$$

These values must be regarded as indicative.

Relevance of weak species

In Table 7 we report some formation percentages for weak species. Of the weak species, $[A_4N(py)]^+$ and $[H(py)Cl]^0$, are the most significant. Calcium (and magnesium) species account for a few per cent; nevertheless, their formation, in the light of errors associated with formation percentages, must be taken into account for a rigorous speciation of the system. As regards literature comparisons there are few data available for all the interactions studied here.

CONCLUSIONS

The main conclusion of this work is that the proposed model is effective in explaining experimental data; in particular, the self-consistency of the model should be noted; no result contradicts its formulation. The depen-

TABLE 7

Formation percentages of pyridine complexes at 25 ° C and $I \approx 1$ mol l^{-1} [a]

pH	$[Et_4N(py)]^+$ (%)	$[Ca(py)]^{2+}$ (%)	$[H(py)Cl]^0$ (%)
3	–	–	49 ±6
4	0.7±0.2 [b]	–	48 ±6
4.5	2.0±0.3	–	45 ±5
5	5.2±0.8	0.7±0.1	37 ±5
5.5	10.3±1.4	1.5±0.2	25 ±4
6	15 ±2	2.2±0.3	12.0±2.5
6.5	18 ±2	2.6±0.3	4.6±1.0

[a] $C_{Na} = 0.4$, $C_{Et_4N} = C_{Ca} = 0.2$, $C_{Cl} = 1$, $C_{py} = 0.1$ mol l^{-1}; percentages are calculated with respect to pyridine. [b] ± standard deviation.

dence on ionic strength predicted by eqn. (19) is obtained in practice fairly independently in eqns. (25), (28), (29) and (33)–(35). It is important to note that when dealing with background in the determination of equilibria constants, it is necessary to consider the formation of all the weak species between all the components present in the solution. Further studies on amines are in progress to confirm the general model.

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REFERENCES

1 S. Capone, A. Casale, A. Currò, A. De Robertis, C. De Stefano, S. Sammartano and R. Scarcella, Ann. Chim. (Rome), 76 (1986) 441.
2 P.G. Daniele, A. De Robertis, C. De Stefano and S. Sammartano, J. Solution Chem., in press.
3 A. Casale, A. De Robertis, C. De Stefano and A. Gianguzza, Thermochim. Acta, in press.
4 A. Casale, P.G. Daniele, C. De Stefano and S. Sammartano, Talanta, submitted.
5 D.D. Perrin, W.L.F. Armorego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1966.
6 H.A. Flaschka, EDTA Titrations, Pergamon, London, 1959.
7 C. De Stefano, P. Princi, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 77 (1987) 643.
8 A. De Robertis, C. Rigano, S. Sammartano and O. Zerbinati, Thermochim. Acta, 115 (1987) 241.
9 A. De Robertis, C. De Stefano, C. Rigano and S. Sammartano, Talanta, 34 (1987) 933.
10 P. G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, J. Chem. Soc., Dalton Trans., (1985) 2353.
11 A. Casale, P.G. Daniele, A. De Robertis and S. Sammartano, Ann. Chim. (Rome), 78 (1988) 253.
12 P.G. Daniele, C. Rigano and S. Sammartano, Anal. Chem., 57 (1985) 2956.