Speciation of thorium in phosphate-containing solutions

B. Fourest, N. Baglan, R. Guillaumont, G. Blain and Y. Legoux

Groupe de Radiochimie, Institut de Physique Nucléaire, CNRS/IN$_2$P$_3$, BP 1, F-91406 Orsay Cedex (France)

Abstract

The equilibrium between thorium orthophosphate (Th$_3$(PO$_4$)$_4$), labelled with the radioactive thorium isotope ^{227}Th, and phosphate-containing solutions has been investigated as a function of pH and total concentration of phosphate groups ($5 < [\text{pH}] < 9$; $0 < c_{\text{PO}_4} < 1.5$ mol l^{-1}). Since Th$_3$(PO$_4$)$_4$ is a very insoluble compound, even in relatively concentrated phosphoric media, ^{227}Th has been detected in solutions near neutrality only for $c_{\text{PO}_4} > 0.1$ mol l^{-1}. Under these conditions, the thorium concentration has been measured after ultrafiltration (cutting size of the species at 5 nm) by γ-ray spectroscopy in the range 10^{-9}–10^{-5} mol l^{-1}. The solubility curves, c_{Th} *vs.* pH value at constant c_{PO_4} and O$_2$ *vs.* c_{PO_4} at constant pH, lead to the determination of the prevailing species in the solutions: at a pH of 6–7, [ThO(HPO$_4$)$_3$(H$_2$PO$_4$)]$^{5-}$ and [ThO(HPO$_4$)$_3$(H$_2$PO$_4$)$_2$]$^{6-}$ are the presumed complex forms of thorium for $0.3 < c_{\text{PO}_4} < 0.8$ mol l^{-1} and $0.8 < c_{\text{PO}_4} < 1.5$ mol l^{-1} respectively.

1. Introduction

The speciation of heavy elements in aqueous media near neutrality is particularly difficult, owing to the competition between hydrolysis and complexation, which is at a maximum for the tetravalent state. In non-complexing media, hydrolysed species are often very sorbable and can generate colloid or pseudocolloids, depending upon their concentration. Different species which result from complexation can coexist in the ranges of pH values and concentrations of complexing reagent under investigation. Moreover, at very low metal concentrations, these species depend only on the concentrations of the various complexing anionic species. These in turn depend on the ionic strength and the dissociation constants of the complexing reagent, which are more or less known, as in the case of phosphoric acid. An additional experimental difficulty arises from the necessity to maintain the pH at a predetermined constant value.

When the element is present in solution at a concentration such that conventional methods cannot be used, the only available methods for speciation are transport and partition methods. Transport methods cannot be used easily however [1]. Among the partition methods, solvent extraction from chelates is well modeled but its application is essentially limited to acidic media, in order to avoid the presence of chelates in the aqueous solutions [1]. The distribution between a solid phase and a solution appears to be a possible method to investigate in media of pH around 7, when the solid compound is not very soluble in the solutions

under consideration. This is the case for thorium orthophosphate (Th$_3$(PO$_4$)$_4$), as has been shown in previous work [2]. Consequently, it was interesting to attempt the identification of thorium complexes with some phosphate anions, from solubility measurements of Th$_3$(PO$_4$)$_4$ in phosphoric media.

Very few data on these complexes can be found in the literature [3–5], and the thermodynamical constants collected by Wagman *et al.* [6] are the same as those reported in the second edition of the book of Sillén and Martell [7]. The main reasons for this lack of information are related to the above-mentioned experimental difficulties: a limited number of available methods, and the competition between hydrolysis and complex formation, which is described in a previous paper [2, 8].

2. Experimental details

About 50 mg Th$_3$(PO$_4$)$_4$ were produced from a mixture of thorium nitrate and phosphoric acid (5 mol l^{-1}), leading to the correct stoichiometric proportion of thorium over phosphorus, *i.e.* 3/4. Radioactive ^{227}Th was introduced (in the form of a nitrate) into this liquid mixture and the mixture was rapidly homogenized before it gelled. The thermal treatment detailed in ref. 8 was then applied to obtain the high temperature form (1400 °C) of Th$_3$(PO$_4$)$_4$. Finally, the powder was weighed, counted and washed three times with water, in order to eliminate the finest particles.

^{227}Th ($T_{1/2} = 18.7$ days) was prepared from a stock solution of ^{227}Ac, according to the purification method given in ref. 9. It was used in the present study only as a γ emitter (236 and 256 keV), since the separation from its daughter ^{223}Ra ($T_{1/2} = 11.4$ days, α, γ), involving solvent extraction, prevents the production of α sources. In fact, the above separation, which cannot be avoided [2], is more difficult to achieve in phosphoric media, as a result of the strong complexing power of phosphate groups. We have used the extraction of thorium by di-(2 ethylhexyl)phosphoric acid in benzene, according to the results published by Elyahyaoui et al. [10]. ^{23}Ra, which was extracted with the ^{227}Th, was removed from the organic solution by two successive washes with HNO_3 (1 mol 1^{-1}).

The structure of the solid phase contacted with the solution under investigation (5 ml) was verified from a blank synthesized under the same conditions. The X-ray pattern was the same as that published by Laud and Hummel [11]. After months of immersion in different solutions, the structure conservation was verified by two different methods. First, for the structure of the bulk, no change was detected in the X-ray pattern. Secondly, for the structure at the solid–solution interface, zeta potential measurements, carried out on the finest $Th_3(PO_4)_4$ particles, showed no variation [12].

Batch experiments and counts were carried out as previously described [8]. Equilibrium at room temperature was verified over periods of time as long as several weeks. It was fully reached after 8 h. Special attention was devoted to the separation of the phases. A first centrifugation was followed by ultrafiltration (Millipore PLGC filters of 10 000 Daltons) to detect only soluble species (of size less than 5 nm) in solution. Ultracentrifugation (50 000 rev min^{-1} with a Beckman L5-65 apparatus) gave the same results as ultrafiltration.

3. Results

The compositions of the different solutions used in the present work are given in Table 1. The experiments were carried out in phosphate buffer solutions (appropriate mixtures of KH_2PO_4 and NaOH) to control the pH value (pH value of 6, 7 or 8). As a result of the very low solubility of $Th_3(PO_4)_4$, the total concentration c_{Th} of thorium was measured without ambiguity for a total concentration c_{PO_4} of phosphate groups of at least 0.3 mol 1^{-1}. For less concentrated media, the γ detection limit of ^{227}Th, which corresponds to about 10^{-9} mol 1^{-1} for c_{Th}, is encountered (Fig. 1). In Fig. 1, the experimental values of log c_{Th} are plotted against the pH values. For each c_{PO_4} value, a distinct curve is obtained, which shows a broad maximum around pH 7.

TABLE 1. Characteristics (composition, pH and ionic strength I) of the phosphate buffers used to investigate the solubility ($S = c_M$) of $Th_3(PO_4)_4$ in phosphoric media

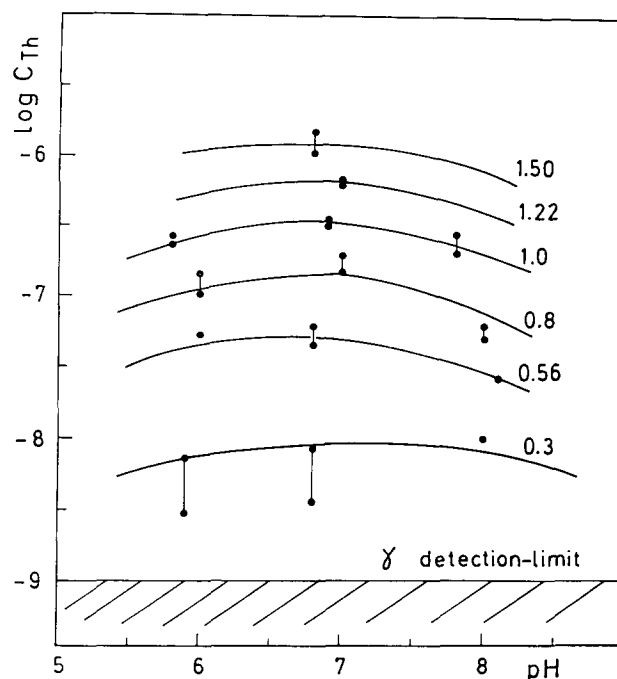| pH	[KH$_2$PO$_4$] (mol 1^{-1})	[NaOH] (mol 1^{-1})	I (mol 1^{-1})	c_{Th} (mol 1^{-1})
5.9	0.30	0.04	0.34	6.8×10^{-9}
6.8	0.30	0.12	0.42	8.5×10^{-9}
8.0	0.30	0.25	0.55	9.9×10^{-9}
6.0	0.56	0.085	0.645	5.0×10^{-8}
6.8	0.56	0.22	0.78	6.0×10^{-8}
8.1	0.56	0.46	1.02	2.7×10^{-8}
6.0	0.80	0.04	0.84	1.4×10^{-7}
7.0	0.80	0.32	1.12	1.9×10^{-7}
8.0	0.80	0.665	1.465	6.1×10^{-8}
5.8	1.00	0.20	1.20	2.7×10^{-7}
6.9	1.00	0.40	1.40	3.4×10^{-7}
7.8	1.00	0.83	1.83	2.7×10^{-7}
7.0	1.22	0.63	1.85	6.8×10^{-7}
6.8	1.50	0.69	2.19	1.5×10^{-6}

Fig. 1. Variation of the total concentration of thorium detected in solution (from the γ-rays of ^{227}Th) vs. the pH value of the solution, for various phosphate anion concentrations.

The accuracy of the data depends on numerous factors: the volumes of the samples ($\Delta v/v < 0.5\%$), the weighed amount of powder ($\Delta m/m \approx 1\%$) and the γ counting, which is the most important (about 6.5%). The resulting error is estimated to be about 10%.

During the experiments, some important points arose concerning the ultrafiltration of the solutions and the formation of colloids and/or aggregates during the establishment of the equilibrium between the two phases. The activity remaining on the filter was observed to

increase somewhat with the time of shaking and with the pH value of the filtered phosphate solution (between 6 and 8). However, under the worst conditions, generating a maximum amount of colloids, a linear response of the filter was verified over the 4 ml of solution to be filtered.

4. Discussion

To interpret these results, we have to consider the various chemical equilibria involved in and between the two-phase system. For this purpose, a symbolic notation is needed [1]. Since, in general, when using trace quantities of an element M, we can only determine the order l and the charge $(n-y)$ of the complex of M present in the solution, these complexes can be formulated as $M(H_pL)_lH_{-y}^{(n-y)+}$, with $H_pL \equiv H_3PO_4$ being the non-dissociated form of the complexing agent, which can dissociate to give $H_{p-1}L^-$, ..., L^{p-}. The formal notation H_{-y} represents yH^+ for $y < 0$ or yOH^- for $y > 0$.
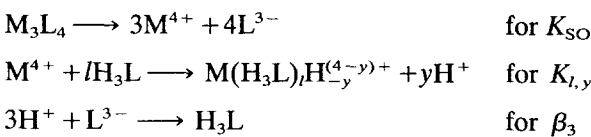
With these conventions, the complexation of the aquo ion $M^{n+} = Th^{4+}$ can be written as

$$M^{n+} + lH_pL \longrightarrow M(H_pL)_lH_{-y}^{(n-y)+} + yH^+$$
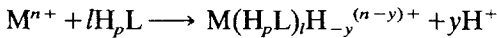
Under our experimental conditions, the first difficulty arises from the high concentration of phosphate groups $(L \equiv PO_4)$, which leads to the possible existence of the dimer $(H_3L)_2$ or H_6L_2, as well as complex anionic forms of this dimer. The equilibrium concentrations of H_3L and H_6L_2 are mutually dependent. Consequently, there can be ambiguity over the complexes formed; they could be $M(H_3L)_lH_{-y}$ or $M(H_6L_2)_{l/2}H_{-y}$. We will return to this point later.

Let us start with the first formulation. In such a case, the experimental data must be analysed as a function of the independent parameters $[H_pL]$ and $[H^+]$, in order to obtain l and y. This is the classical way, which proceeds as follows.

The resulting equilibrium of the various equilibria involving the dissolution of the solid phase and complexation of the aqua ion of thorium, i.e. of

$$M_3L_4 \longrightarrow 3M^{4+} + 4L^{3-} \qquad \text{for } K_{SO}$$

$$M^{4+} + lH_3L \longrightarrow M(H_3L)_lH_{-y}^{(4-y)+} + yH^+ \qquad \text{for } K_{l,y}$$

$$3H^+ + L^{3-} \longrightarrow H_3L \qquad \text{for } \beta_3$$

is given by

$$\frac{1}{3}(M_3L_4)_{\text{solid}} \rightleftharpoons$$

$$M(H_3L)_lH_{-y}^{(4-y)+} + \left(\frac{4}{3} - l\right)H_3L + (y-4)H^+$$

Omitting the charges, the solubility of thorium $(S = c_{Th})$ can be written as

$$S = \sum[M(H_3L)_lH_{-y}]$$

with the summation extending (here and in the following) over l and y. In terms of the independent parameters $[H_3L]$ and $[H^+] = h$, S reads as

$$S = \beta_3 K_{SO} \sum K_{l,y}[H_3L]^{(l-4/3)}h^{(4-y)}$$

and the variations of $\log S$ vs. $\log[H_3L]$ and $\log h$ have respective slopes of

$$\frac{\delta \log S}{\delta \log[H_3L]} = \langle l \rangle - \frac{4}{3}$$

$$\frac{\delta \log S}{\delta \log h} = 4 - \langle y \rangle$$

The derivation gives average values of l and y, which has been proved mathematically [1].

At this stage, a second difficulty arises. This is related to the necessity of knowing simultaneously the values of all the equilibrium constants of the equilibria involving species coming from H_3PO_4, at the ionic strengths under consideration. They are needed to calculate the concentration of free H_3L at equilibrium. To avoid a rigorous choice of these constants, we propose choosing the experimental concentration c_{PO_4} instead of $[H_3PO_4]$ to obtain the order of the thorium complexes with respect to the PO_4 group and their charges. The following treatment leads to the solution.

The dissociation constants of the complexing agent are called K_{1x} $(x = 1, 2, 3)$ for H_3L and K_{2x} $(x = 1, 2, 3, 4)$ for H_6L_2. The dimerization constant of H_3L is K_{20}. It is convenient to introduce the parameters

$$\alpha_{1x} = \frac{\Pi K_{1x}}{h^x}$$

$$\alpha_{2x} = \frac{\Pi K_{2x}}{h^x}$$

For a solution where c_{PO_4} is maintained at a constant value, we have

$$c_{PO_4} = (1 + \alpha_{11} + \alpha_{12} + \alpha_{13})[H_3L] + 2K_{20}$$

$$\times (1 + \alpha_{21} + \alpha_{22} + \alpha_{23} + \alpha_{24})[H_3L]^2$$

which can be written as

$$c_{PO_4} = A[H_3L] + B[H_3L]^2$$

Thus, in phosphate-containing solutions, $[H_3L]$ can be theoretically deduced, as well as $[H_6L_2] = K_{20}[H_3L]^2$, only if the experimental values of c_{PO_4} and the pH are known. This also applies for solutions additionally containing very low concentrations of thorium, as is the present case.

When dimerization can be neglected, we have

$$[H_3L] = \frac{c_{PO_4}}{A}$$

and, in the other cases, we have

$$[H_3L] = \frac{-A + (A^2 + 4Bc_{PO_4})^{1/2}}{2B}$$

Within the former approximation, and taking into account the calculations developed in Appendix A, we have, at constant h

$$\frac{\delta \log S}{\delta \log c_{PO_4}} = p_1 = \langle l \rangle - \frac{4}{3}$$

and, at constant c_{PO_4}, we have

$$\frac{\delta \log S}{\delta \log h} = p_2 = (4 - \langle y \rangle) + \left(\langle l \rangle - \frac{4}{3} \right) \epsilon$$

where ϵ is a corrective factor given by

$$\epsilon = \frac{K_{11}/h + 2K_{11}K_{12}/h^2 + 3K_{11}K_{12}K_{13}/h^3}{1 + K_{11}/h + K_{11}K_{12}/h^2 + K_{11}K_{12}K_{13}/h^3}$$

or, more simply, this can be written as

$$\epsilon = \frac{\delta \log A}{\delta \log h}$$

ϵ has been estimated both graphically and by calculation (Fig. A1, in Appendix A) to vary from 1.25 ($I = 0.3$) to 1.4 ($I \geqslant 1$) at pH 6; from 1.7 ($I = 0.3$) to 1.8 ($I \geqslant 0.8$) at pH 7; and to be around 2 at pH 9. These approximate values are based on K_{1x} values read on the smoothed curves represented in Fig. 2, which are drawn from a compilation of literature data. The uncertainty in these K_{1x} values, particularly at high ionic
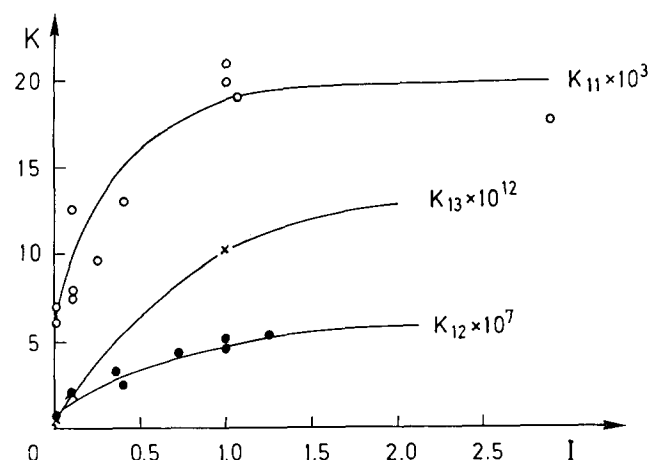

Fig. 2. Variation of the three dissociation constants of phosphoric acid K_{11}, K_{12} and K_{13} vs. the ionic strength I (mol l^{-1}). The data reported on the graph can be found in refs. 7 and 13. The values of K_{2x} are 2×10^{-2} ($x = 1$), 2.5×10^{-3} ($x = 2$), 1.6×10^{-6} ($x = 3$) and 2×10^{-9} ($x = 4$) [14].

strength, does not really affect the ϵ value or, consequently, the p_2 value. The curves in Fig. 1 show that p_2 is not very different from 0, regardless of what c_{PO_4} and the pH value may be (it is slightly negative at pH values of 6.5 or less, and more or less positive at pH values of 7 or more).

Now, if $\log c_M$ is plotted vs. $\log c_{PO_4}$ for the three pH values under consideration, it appears that the value of p_1 depends significantly on c_{PO_4} and is not very sensitive to the pH value of the solution. For $0.3 < c_{PO_4} < 0.8$ mol l^{-1}, $p_1 = 2.8$ and a value of 4 can be attributed to l. For $0.8 < c_{PO_4} < 1.5$ mol l^{-1}, the slope is higher, $p_1 = 3.6$ and the number of phosphoric ligands becomes equal to 5.

In the first case, we have

$$y = p_2 - 4 - \epsilon \left(l - \frac{4}{3} \right) = 9$$

with $\epsilon = 1.8$ (pH 7). The complex formed under these conditions contains four ligands and has a charge equal to $4 - y = -5$. Knowing that both HPO_4^{2-} and $H_2PO_4^{-}$ ions are the dominant anions in the solution, the best empirical formula which accounts for the results appears to be $[ThO(HPO_4)_3(H_2PO_4)]^{5-}$.

In the second case, $y = 10$, which implies a charge of -6 for five ligands, and the corresponding complex is probably $[ThO(HPO_4)_3(H_2PO_4)_2]^{6-}$. According to the more or less known K_{2x} ($x = 0$, 1, 2, 3, 4) values (Fig. 2), at pH 7, the dominant species coming from $H_6P_2O_8$ would be $H_3P_2O_8^{3-}$. Thus, we cannot exclude the existence of the alternative species $[ThO(HPO_4)(H_3P_2O_8)_2]^{6-}$.

If we now take into account a possible dimerization of H_3L to calculate $[H_3L]$ as a function of c_{PO_4}, we obtain (Appendix B)

$$\frac{\delta \log S}{\delta \log c_{PO_4}} = p_1 = \left(\langle l \rangle - \frac{4}{3} \right) \gamma$$

$$\frac{\delta \log S}{\delta \log h} = p_2 = (4 - \langle y \rangle) + \left(\langle l \rangle - \frac{4}{3} \right) \zeta$$

where γ and ζ stand for corrective factors which depend upon $[H_3PO_4]$ and the parameters A and B previously introduced, such that

$$\gamma = \frac{c_{PO_4}}{[H_3PO_4](2B[H_3PO_4] + A)}$$

$$\zeta = \frac{\delta \log[H_3PO_4]}{\delta \log h}$$

Estimations of γ and ζ, unlike the estimation of ϵ, require the K_{2x} values as a function of the ionic strength. Because there is a great uncertainty in the B values, which are K_{2x} dependent, only an attempt to correct

the previous l and y values can be made. At pH 7, in the investigated range of c_{PO_4}, γ is not far from unity and ζ is around 1.8. These corrections cause a slight increase in the l value and a slight decrease in the charge of the complexes. However, these corrections seem to be too speculative to be taken into account and, in waiting for new K_{2x} values, we can keep the previous sets of l and y values.

According to these considerations, in the range of c_{PO_4} and pH investigated, the theoretical expression of the solubility of thorium takes the form

$$S = \beta_3 K_{SO} \left\{ K_{4,9} c_{PO_4}^{(4-4/3)} \frac{h^{(4-9)}}{A^{(4-4/3)}} \right.$$

$$\left. + K_{5,10} c_{PO_4}^{(5-4/3)} \frac{h^{(4-10)}}{A^{(5-4/3)}} \right\}$$

From this, taking for K_{SO} the values previously determined as a function of ionic strength [2], one can estimate the equilibrium constants $K_{l,y}$. The best fit is obtained for log $K_{4,9} = 100.0$ and log $K_{5,10} = 99.3$. The very high values of these formal equilibrium constants are in direct relation to the K_{SO} values, which are very low (log $K_{SO} \approx -100$).

5. Conclusions

We have shown that, at around pH 7, it is possible to identify complexes of thorium in phosphoric media by measuring the true solubility of labelled $(^{227}Th)Th_3(PO_4)_4$. Unfortunately, the solubility of this compound is so low for $c_{PO_4} < 0.3$ mol l^{-1} that we have not achieved our goal of modelling natural aqueous solutions in which the concentrations of phosphate anions, in the forms HPO_4^{2-} or $H_2PO_4^-$, are lower than about 10^{-2} mol l^{-1}. Improvements in speciation of thorium could arise from the use of a method, such as inductively coupled plasma mass spectrometry, which enables thorium concentrations to be determined down to 10^{-12} mol l^{-1}.

For high c_{PO_4} concentrations of 0.3–1.2 mol l^{-1}, the "solubility method" gives strong indications of the presence of mixed hydroxophosphato anionic complexes of orders 4 and 5 with respect to the phosphate ligand, carrying 5 and 6 unit charges respectively. There are several possible empirical formulae, as is usually the case for trace quantities of an element. To obtain such orders and charges, we have derived a special treatment of the direct experimental data to minimize the use of the dissociation constants of H_3PO_4 and its possible dimerized form. Improvements could arise from new data on the acid–base behavior of concentrated aqueous solutions of phosphoric acid.

References

1 J.P. Adlof and R. Guillaumont, *Fundamental of Radiochemistry*, CRC Press, Boca Raton, FL, 1993, p. 221.
2 N. Baglan B. Fourest, R. Guillaumont, G. Blain, J.F. Le-Du and M. Genet, *New J. Chem.*, in press.
3 A.I. Moskvin, L.N. Essen and T.N. Bukhtiyarova, *Russ. J. Inorg. Chem.*, 12 (12) (1967) 1794.
4 J.J. Katz and G.T. Seaborg, *The Chemistry of the Actinide Elements*, Wiley, New York, 1957, p. 108.
5 E.L. Zebrovski, H.W. Alter and F.K. Heuman, *J. Am. Chem. Soc.*, 73 (1951) 5646.
6 D.D. Wagman, R.H. Schumm and V.B. Parker, A computer assisted evaluation of the thermochemical data of compounds of thorium, *Nat. Bur. Standards Dept. Commerce, Internal Rep. NBSIR 77* (1300) (1977) 93.
7 L.G. Sillén and A.E. Martell, *Stability Constants of Metal Ion Complexes*, Vol. 17, The Chemical Society, London, 1964, pp. 184, 187, 273, 275; Vol. 25, 1971, pp. 109–112.
8 N. Baglan, *Thesis 2473*, University Paris XI, Orsay, 1992.
9 J.F. Ledu, *Thesis 1542*, University Paris XI, Orsay, 1991.
10 A. Elhyahyaoui, S. Bouhlassa, S. Hussonnois and L. Brillard, *J. Less Common Met.*, 135 (1987) 147.
11 K.R. Laud and F.A. Hummel, *J. Am. Chem. Soc.*, 296 (1971) 54.
12 B. Fourest, N. Baglan, N. Hakem, Y. Legoux and R. Guillaumont, to be published.
13 R.M. Smith and A.E. Martell, *Critical Stability Constants*, Vol. 6, Plenum, New York, 1989.
14 G. Ferroni, *Thesis 9842*, Université de Provence, Faculté des Sciences, Provence, 1974.

Appendix A

From

$$S = \beta_3 K_{SO} \sum K_{l,y} [H_3L]^{(l-4/3)} h^{(4-y)}$$

$$[H_3L] = \frac{c_{PO_4}}{A}$$

and, with $c = c_{PO_4}$, we can write for a simplified presentation

$$S = a \sum K_{l,y} c^{(l-4/3)}$$

where a is a constant for a fixed value of h. Taking the derivative of S, we proceed as follows:

$$\frac{\delta \log S}{\delta \log c} = \frac{\delta \log \sum K_{l,y} c^{(l-4/3)}}{\delta \sum K_{l,y} c^{(l-4/3)}} \frac{\delta \sum K_{l,y} c^{(l-4/3)}}{\delta c} \frac{\delta c}{\delta \log c}$$

$$\frac{\delta \log S}{\delta \log c} = \frac{1}{\sum K_{l,y}c^{(l-4/3)}}\left\{\sum\left(l-\frac{4}{3}\right)K_{l,y}c^{(l-4/3)-1}\right\}c$$

$$\frac{\delta \log S}{\delta \log c} = \frac{\sum(l-4/3)K_{l,y}c^{(l-4/3)}}{\sum K_{l,y}c^{(l-4/3)}} = \langle l \rangle - \frac{4}{3}$$

Indeed, by definition, we have

$$\langle l \rangle = \frac{c - [PO_4]}{c_M} = \frac{\sum l K_{l,y}c^l}{\sum K_{l,y}c^l}$$

Now, if c is constant, S takes the form

$$S = b\sum K_{l,y}\frac{h^{(4-y)}}{A^{(l-4/3)}} = b\sum K_{l,y}u$$

where b is a constant and

$$\frac{\delta \log S}{\delta \log h} = \frac{\delta \log \sum K_{l,y}u}{\delta \sum K_{l,y}u}\frac{\delta \sum K_{l,y}u}{\delta h}\frac{\delta h}{\delta \log h}$$

The only term which requires further calculation is the second term:

$$\delta\sum K_{l,y}\frac{\delta u}{\delta h} = \sum K_{l,y}\left\{(4-y)h^{(4-y)-1}A^{(4/3-l)}\right.$$

$$\left. + h^{(4-y)}\left(\frac{4}{3}-l\right)A^{(4/3-l)-1}\frac{\delta A}{\delta h}\right\}$$

$$= \sum K_{l,y}h^{(4-y)}A^{(4/3-l)}$$

$$\times\left\{(4-y)h^{-1}+\left(\frac{4}{3}-l\right)A^{-1}\frac{\delta A}{\delta h}\right\}$$

Finally, we have

$$\frac{\delta \log S}{\delta \log h}$$

$$= \frac{\delta \log \sum K_{l,y}u\{(4-y)h^{-1}+(4/3-l)A^{-1}\delta A/\delta h\}}{\delta\sum K_{l,y}u}h$$

$$\frac{\delta \log S}{\delta \log h} = (4-\langle y \rangle) + \left(\frac{4}{3}-\langle l \rangle\right)A^{-1}\frac{\delta A}{\delta h}h$$

The value of

$$\epsilon = A^{-1}\frac{\delta A}{\delta h}h$$

can be calculated from its true expression

$$\epsilon = \left(\frac{K_{11}}{h} + \frac{2K_{11}K_{12}}{h^2} + \frac{3K_{11}K_{12}K_{13}}{h^3}\right)\Bigg/$$

$$\left(1 + \frac{K_{11}}{h} + \frac{K_{11}K_{12}}{h^2} + \frac{K_{11}K_{12}K_{13}}{h^3}\right)$$

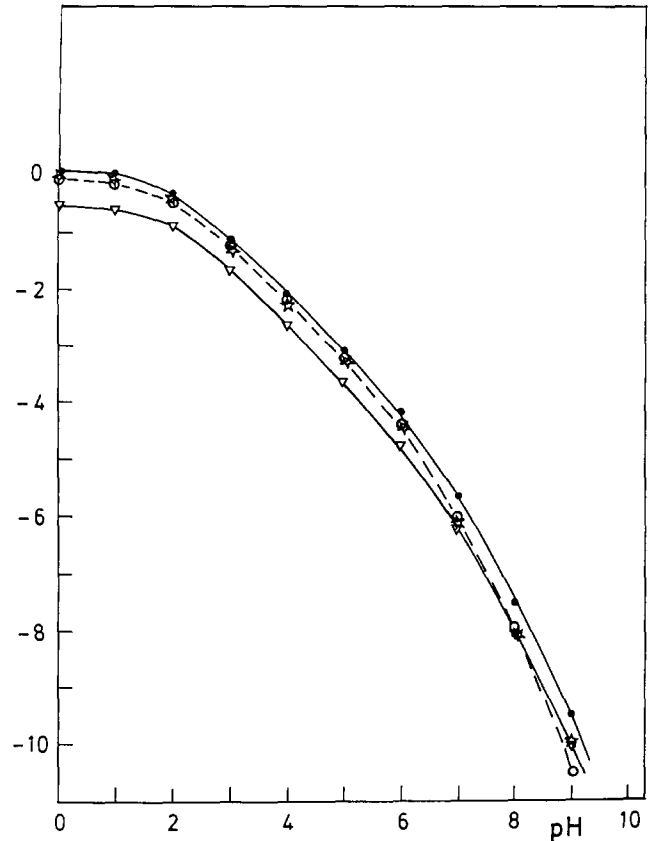or estimated graphically from the variations of $\log A$ vs. $\log h$ (Fig. A1), because it can be deduced from

Fig. A1. Variation of $-\log A$ ($=\log c_{PO_4}-\log[H_3PO_4]$) and of $\log[H_3PO_4]$ ($=\log[-A+(A^2+4Bc)^{1/2}]/2B$; see text) as a function of the pH value of the solution, for two values of c_{PO_4}: $\triangledown$, $-\log A$, $c_{PO_4}=0.3$ mol l^{-1}; $\bigcirc$, $-\log A$, $c_{PO_4}=1.22$ mol l^{-1}; $\bullet$, $\log[H_3PO_4]$, $c_{PO_4}=0.3$ mol l^{-1}; $\star$, $\log[H_3PO_4]$, $c_{PO_4}=1.22$ mol l^{-1}.

$$\frac{\delta A}{\delta h} = \frac{\delta A}{\delta \log A}\frac{\delta \log A}{\delta \log h}\frac{\delta \log h}{\delta h} = A\frac{\delta \log A}{\delta \log h}\frac{1}{h}$$

so that we can write

$$\epsilon = \frac{\delta \log A}{\delta \log h}$$

Appendix B

From

$$S = \beta_3 K_{SO}\sum K_{l,y}[H_3L]^{(l-4/3)}h^{(4-y)}$$

and

$$v = [H_3L] = \frac{-A+(A^2+4Bc)^{1/2}}{2B}$$

we can write

$$S = a\sum K_{l,y}v^{(l-4/3)}$$

where a is a constant for a fixed value of h. However, here, v is h dependent. Therefore, to have the full expression of the derivative of $\log S$ vs. $\log c$, i.e.

$$\frac{\delta \log S}{\delta \log c} = \frac{\delta \log \sum K_{l,y} v^{(l-4/3)}}{\delta \sum K_{l,y} v^{(l-4/3)}}$$
$$\times \frac{\delta \sum K_{l,y} v^{(l-4/3)}}{\delta v} \frac{\delta v}{\delta c} \frac{\delta c}{\delta \log c}$$

we need to calculate $\delta v/\delta c$, all the other terms now being obvious following the previous considerations.

One finds

$$\frac{\delta v}{\delta c} = \frac{1}{2Bv + A}$$

so that

$$\frac{\delta \log S}{\delta \log c} = \frac{\sum K_{l,y}(l-4/3)v^{(l-4/3)}}{\sum K_{l,y} v^{(l-4/3)}} \frac{c}{v(2Bv + A)}$$

and

$$\frac{\delta \log S}{\delta \log c} = \left(\langle l \rangle - \frac{4}{3}\right) \frac{c}{v(2Bv + A)} = \left(\langle l \rangle - \frac{4}{3}\right)\gamma$$

To take the derivative of $\log S$ vs. $\log h$ at constant c values, it is convenient to write

$$S = b\sum K_{l,y} v^{(l-4/3)} h^{(4-y)} = b\sum K_{l,y} f$$

where b is a constant term. It follows that

$$\frac{\delta \log S}{\delta \log h} = \frac{\delta \sum K_{l,y} f}{\delta \sum K_{l,y} f} \frac{\delta \sum K_{l,y} f}{\delta f} \frac{\delta f}{\delta h} \frac{\delta h}{\delta \log h}$$

and, obviously, the term which we have to calculate to go further is $\delta f/\delta h$.

One finds that

$$\frac{\delta f}{\delta h} = h^{(4-y)} v^{(l-4/3)} \left\{\left(l - \frac{4}{3}\right)v^{-1} \frac{\delta v}{\delta h} + (4-y)h^{-1}\right\}$$

Finally, we have

$$\frac{\delta \log S}{\delta \log h}$$
$$= \frac{\sum K_{l,y} h^{(4-y)} v^{(l-4/3)}\{(l-4/3)v^{-1}h\delta v/\delta h + (4-y)\}}{\sum K_{l,y} h^{(4-y)} v^{(l-4/3)}}$$

and

$$\frac{\delta \log S}{\delta \log h} = (4 - \langle y \rangle) + \left(\langle l \rangle - \frac{4}{3}\right)\frac{h}{v}\frac{\delta v}{\delta h}$$

Then, taking into account that

$$\zeta = \frac{h}{v}\frac{\delta v}{\delta h} = \frac{h}{v}\frac{\delta v}{\delta \log v}\frac{\delta \log v}{\delta \log h}\frac{\delta \log h}{\delta h} = \frac{\delta \log[H_3L]}{\delta \log h}$$

these reduce to the expression

$$\frac{\delta \log S}{\delta \log h} = (4 - \langle y \rangle) + \left(\langle l \rangle - \frac{4}{3}\right)\frac{\delta \log[H_3L]}{\delta \log h}$$

ζ can be evaluated graphically from the second curve in Fig. A1, which has been drawn according to the existing data, the poor significance of which has been discussed in the main text.