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Speciation of phytate ion in aqueous solution. Dimethyltin(IV) interactions in $NaCl_{aq}$ at different ionic strengths[☆]

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Abstract

As the introduction of a systematic study on the sequestering ability of phytate (Phy) towards heavy metal and organometal cations, this paper describes the results of an investigation (at $t=25$ °C by potentiometry, ISE-H^+ glass electrode) of its interactions with dimethyltin(IV) cation [$(CH_3)_2Sn^{2+}$, DMT] in NaCl aqueous solutions at different ionic strengths ($0.1 \leq I$ (mol L^{-1}) ≤ 1), in the pH range $2.5 \leq pH \leq 8.5$ and considering metal to ligand ratios $1:1 \leq DMT:Phy \leq 4:1$. We observed the formation of 18 $DMT_iH_jPhy^{(12-2i-j)-}$ species: with $i=1$ and $0 \leq j \leq 7$; $i=2$ and $0 \leq j \leq 5$; $i=3$ and $0 \leq j \leq 3$. Their complex formation constant values are fairly dependent on ionic strength and this dependence was modeled by a Debye-Hückel type equation. The speciation of phytic acid and dimethyltin(IV) is also dependent on the metal to ligand ratio; the dependence of the stability of phytate-dimethyltin(IV) species on both the phytate protonation step and the number of cations bound to the ligand has been modeled and an empirical predictive relationship is also proposed. From the results obtained it emerged that phytate has very good sequestering ability towards $(CH_3)_2Sn^{2+}$. Comparisons are made with other ligands, such as ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA) and phosphate.

Keywords: Phytate; Alkyltin(IV); Complex formation constants; Dependence on ionic strength; Predictive relationships

1. Introduction

In our previous contributions to this series of papers on the speciation of 1,2,3,4,5,6 hexakis (di-hydrogen phosphate) *myo*-inositol, better known as phytic acid, we have repeatedly underlined the importance of this compound, due to its widespread presence in natural environments and liberal use in industrial applications [1–5]. One of the most important characteristics of this ligand is that it strongly interacts with many (alkaline, alkaline earth, heavy) metal and organometal cations and with a wide number of ligands and compounds of environmental and biological interest (proteins, sugars, starch, biogenic amines, etc.). It is also well known that, in many cases, phytate complexes are scarcely soluble or so stable that their bioavailability and, therefore, their chemical and biological activity, are lowered ([1–8] and references therein).

In order to understand the speciation of phytic acid in aqueous solution, in previous papers we determined (in various aqueous media and at different ionic strengths): (i) its protonation constants [1,2]; (ii) its complex formation constants with alkali metal cations [2]; (iii) its binding ability towards other ligands of biological or environmental interest such as biogenic amines [3]; (iv) the solubility of some calcium complexes [4]; (v) its protonation enthalpies and entropies [5]. In these studies, several equations for the dependence of thermodynamic parameters on ionic medium and/or ionic strength and numerous predictive relationships were proposed. Comparisons of phytic acid and other ligands were also made.

[☆] Previous contributions to this series: [1–5].

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We began our systematic study of the sequestering ability of phytate towards heavy metal and organometal cations of great environmental and biological interest with an investigation (at $t = 25$ °C by potentiometry, ISE-H^+ glass electrode) on its interactions with dimethyltin(IV) cation [$(CH_3)_2Sn^{2+}$, DMT] in NaCl aqueous solutions at different ionic strengths ($0.1 \leq I$ (mol L^{-1}) ≤ 1). We chose sodium chloride as ionic medium because it is the main dissolved inorganic salt in natural waters and biological fluids.

We opted to investigate an organometal as first cation because, despite the many existing papers dealing with phytate–metal cation interactions (with particular emphasis given to the bioavailability of metals in the presence of the ligand), to our knowledge at the present time no articles have been published on interactions between this ligand and organometal cations. More specifically, we chose an organotin(IV) compound because, since their biocidal activity was first demonstrated in the 1950s, these have become the most widely used organometal compounds and, owing to their widespread use in industrial applications (e.g., as fungicides and acaricides in agriculture, wood and stone preservatives, stabilizers and catalysts in PVC and in foam production) they are now widely distributed in the environment [9–12]. The main reason for the increasing interest in organotin compounds lies in the fact that they are highly toxic towards living organisms, as demonstrated by a number of articles published in recent decades [13–15]. Recently, interactions among organotin(IV) compounds and DNA have also been investigated [14]. Their environmental impact depends strongly on their ability to enter biological systems and, therefore, on the chemical form in which they are present in solution (hydroxo-species, complexes), i.e., on their speciation. During the past few years, we have also undertaken a systematic investigation of the aqueous chemistry of soluble alkyltin(IV) cations, studying both their hydrolytic behavior in different ionic media and ionic strengths, and their complexation by several organic and inorganic ligands of environmental and biological interest [15–17]. Here we have studied dimethyltin(IV) cation as the main representative of diorganotin(IV) compounds. These are less toxic than triorganotin(IV) derivatives and their toxicity is expressed by their inhibition of the oxidation of α-chetoacids due, probably, to their binding to the thiol groups of some enzymes and/or coenzymes. Interestingly, however, more recent research on diorganotin(IV) compounds suggests them to possess anticarcinogenic activity, in contrast with the suspected carcinogenicity of other organotin(IV) compounds (tri-derivatives first) [14,18].

On the basis of the above considerations on both phytic acid and dimethyltin(IV) cation, it can be evinced the importance of the present study from an environmental and biological point of view. In fact, a study of the sequestering ability of phytate towards dimethyltin(IV) (together with the fact that this ligand is non-toxic and naturally biosynthesized in large amounts in some vegetal species) could help to determine how this ligand might modify the availability of the organometal cation in biological systems.

2. Experimental section

2.1. Chemicals

Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Riedel-deHaën) and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. NaCl solutions were prepared by weighing pure salt (Fluka) dried in an oven at 110 °C. Phytic acid solutions were prepared by weighing Aldrich dipotassium salt $K_2H_{10}Phy$, and passing it over a strong cationic exchange resin (Dowex 50 $W \times 8$). Concentration was checked potentiometrically by alcalimetric titrations, and the absence of potassium was demonstrated by flame emission spectrometry. Dimethyltin(IV) dichloride (Alfa-Aesar) was used without further purification. The concentration of dimethyltin(IV) solutions was checked potentiometrically by alcalimetric titrations and its purity was always $\geq$ 99.5%. All solutions were prepared with analytical grade water ($R = 18$ MΩ cm^{-1}) using grade A glassware.

2.2. Apparatus and procedure

Potentiometric titrations were carried out (at 25.0 ± 0.1 °C) using apparatus consisting of a Model 713 Metrohm potentiometer, equipped with a half cell glass electrode (Ross type 8101, from Orion), a double junction reference electrode (type 900200, from Orion) and a Model 765 Metrohm motorized burette. Estimated accuracy was ± 0.15 mV and ± 0.003 mL for e.m.f. and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery, data acquisition and to check for e.m.f. stability. All titrations were carried out under magnetic stirring and bubbling purified presaturated N_2 through the solution in order to exclude O_2 and CO_2 inside. The titrand solution consisted of different amounts of phytic acid (0.8–1 mmol L^{-1}), dimethyltin(IV) dichloride (1–4 mmol L^{-1}), an excess of hydrochloric acid (1 mmol L^{-1}), and the background salt in order to obtain pre-established ionic strength values ($0.1 \leq I$ (mol L^{-1}) ≤ 1.0). Potentiometric measurements were carried out by titrating 25 mL of the titrand solution with standard NaOH solutions up to pH = 8.5. In some titrations we reached pH values as high as pH = 10.5. 80–100 points were collected for each titration and the equilibrium state during titrations was checked using usual precautions. These include monitoring the time necessary to reach equilibrium and perform back titrations. For each experiment, independent titrations of strong acid solution with a standard base were carried out under the same medium and ionic strength conditions as present in the systems to be investigated, with the aim of determining electrode potential (E^0) and acidic junction potential ($E_j = j_a$ [H$^+$]). For measurements performed at low ionic strengths, the contribution of the ligand has to be considered: in the most critical conditions (i.e., $I = 0.1$ mol L^{-1}) its contribution to ionic strength is about 7–8%, which introduces a not dramatic error in the calculations. However, this error was taken into account by giving appropriate weights to the results at low ionic strengths when fitting different functions.

2.3. Calculations

The BSTAC [19] and STACO [20] computer programs were used in the refinement of all the parameters of an acid–base titration (E^0, pK_w, coefficient of junction potential j_a, analytical concentration of reagents) and in the calculation of complex formation constants. The ES4ECI [21] program was used to draw speciation diagrams and to calculate species formation percentages. The LIANA [22] program was used to test the dependence of log K on ionic strength using different equations.

Dependence on ionic strength was taken into account by a Debye-Hückel type equation already proposed by our research group [23]:

$$\log K = \log {}^{\mathrm{T}}K - z^{*}0.51 I^{1/2}\left(1 + 1.5 I^{1/2}\right)^{-1} + CI \tag{1}$$

with

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

where K is the formation constant and $^{\mathrm{T}}K$ is the formation constant at infinite dilution and where C parameter is dependent on I, according to the relationship:

$$C = c^{\infty} + \left(c^0 - c^{\infty}\right)F(I) \tag{3}$$

with

$$F(I) = (I + 1)^{-1}. \tag{4}$$

Note that, in this approach, when $c^{\infty} = c^0$, and I and K are expressed in the molal concentration scale (m, mol kg [H$_2$O]$^{-1}$), Eq. (1) becomes the classical and widely used SIT (Specific Interaction Theory) equation [24].

Complex formation constants are given according to the equilibrium

$$i\mathrm{DMT} + j\mathrm{H}^+ + \mathrm{Phy}^{12-} = \mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-} \qquad \beta_{ij} \tag{5}$$

or

$$i\mathrm{DMT} + \mathrm{H}_j\mathrm{Phy}^{(12-j)-} = \mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-} \qquad K_{ij} \tag{6}$$

Formation constants, concentrations and ionic strengths are expressed in the molar (mol L^{-1}) concentration scale.

3. Results and discussion

3.1. Stability of proton-dimethyltin(IV)-phytate species

In order to make appropriate calculations from the potentiometric data obtained for the system investigated, we needed a preliminary knowledge of acid–base behavior of both phytate and the dimethyltin(IV) cation. For phytate we considered the protonation constants previously determined in NaCl$_{aq}$ [1,2], and for DMT hydrolysis constants we did the same [16]. As an example, Table 1 shows dimethyltin(IV) hydrolysis constants values and phytate protonation constants determined in NaCl$_{aq}$ at $I = 0.1$ mol L^{-1} ionic strength (values taken from these previous papers) [1,2,16]. The use in calculations of conditional protonation and hydrolysis constants determined in sodium chloride aqueous solutions is very important for phytate, because the sodium ions of background salt and titrant solution strongly interact with this ligand. It is well documented that, owing to its 12 displaceable protons, a single molecule of phytic acid (its totally and partially protonated species) forms several ion pairs with one or more sodium cations [2] and these species are so stable that, for example, conditional protonation constants determined in ionic media containing sodium ions (e.g., NaClO$_4$, NaCl) are ~3 orders of magnitude (in logarithmic scale) lower than corresponding ones obtained in background salts which scarcely interact with phytate ligand (e.g., tetraalkylammonium salts) [1]. Therefore, such large discrepancies in protonation constants could result in the determination of "unreliable" complex formation constants for proton-dimethyltin(IV)-phytate species. Accurate hydrolysis constant values are necessary for dimethyltin(IV) due to the fact that hydrolysis processes dominate the chemistry of this cation in aqueous solution, and the use of inappropriate values could again give unreliable results.

With the above premise in mind, analysis of experimental data in the pH range $2.5 \leq \mathrm{pH} \leq 8.5$ by both STACO and BSTAC computer programs provided evidence on the formation of 18 phytate-proton-dimethyltin(IV) species: DMTPhy^{10-}, DMTHPhy^{9-}, DMTH$_2$Phy^{8-}, DMTH$_3$Phy^{7-}, DMTH$_4$Phy^{6-}, DMTH$_5$Phy^{5-}, DMTH$_6$Phy^{4-}, DMTH$_7$

Table 1
Phytate protonation constants[a] and dimethyltin(IV) hydrolysis constants[b] in NaCl aqueous solution at $I = 0.1$ mol L^{-1} ionic strength and at $t = 25$ °C

Phytate

log K_1^{H}	log K_2^{H}	log K_3^{H}	log K_4^{H}	log K_5^{H}	log K_6^{H}	log K_7^{H}
9.58	9.84	9.50	8.14	6.50	5.25	2.88

Dimethyltin(IV)

log β_{11}	log β_{12}	log β_{13}	log β_{22}	log β_{23}
−3.12	−8.45	−19.48	−5.26	−9.61

[a] [1,2], K_j^{H} refer to the equilibrium: $\mathrm{H}^+ + \mathrm{H}_{j-1}\mathrm{Phy}^{(12-j+1)} = \mathrm{H}_j\mathrm{Phy}^{(12-j)-}$.

[b] [16], β_{pq} refer to the equilibrium: $p(\mathrm{CH_3})_2\mathrm{Sn}^{2+} = [(\mathrm{CH_3})_2\mathrm{Sn(OH)_q}]^{(2-q)} + q\mathrm{H}^+$.

Table 2
Complex formation constants for phytate-dimethyltin(IV) mononuclear species in $NaCl_{aq}$ at different ionic strengths and $t=25$ °C

I (mol L^{-1})	log β_{ij}[a] (log K_{ij})[b]							
	$DMTPhy^{10-}$	$DMTHPhy^{9-}$	$DMTH_2Phy^{8-}$	$DMTH_3Phy^{7-}$	$DMTH_4Phy^{6-}$	$DMTH_5Phy^{5-}$	$DMTH_6Phy^{4-}$	$DMTH_7Phy^{3-}$
0.10	14.87 ± 0.06[c] (14.87)	23.76 ± 0.12[c] (14.18)	31.78 ± 0.06[c] (12.36)	39.45 ± 0.06[c] (10.53)	45.70 ± 0.06[c] (8.64)	50.08 ± 0.09[c] (6.52)	53.11 ± 0.03[c] (4.30)	54.49 ± 0.06[c] (2.80)
0.15	14.44 ± 0.06 (14.44)	23.08 ± 0.09 (13.67)	31.11 ± 0.03 (12.03)	38.54 ± 0.03 (10.13)	44.68 ± 0.03 (8.30)	49.00 ± 0.06 (6.27)	51.88 ± 0.03 (4.05)	53.24 ± 0.06 (2.66)
0.25	13.91 ± 0.06 (13.91)	22.45 ± 0.06 (13.25)	30.28 ± 0.03 (11.62)	37.52 ± 0.03 (9.75)	43.45 ± 0.06 (7.92)	47.57 ± 0.06 (5.89)	50.41 ± 0.03 (3.83)	51.51 ± 0.06 (2.34)
0.50	13.60 ± 0.09 (13.60)	21.81 ± 0.09 (12.88)	29.36 ± 0.06 (11.24)	36.31 ± 0.06 (9.36)	42.09 ± 0.09 (7.66)	46.04 ± 0.06 (5.73)	48.49 ± 0.03 (3.53)	49.44 ± 0.09 (2.11)
0.75	13.48 ± 0.06 (13.48)	21.65 ± 0.09 (12.87)	29.07 ± 0.06 (11.25)	35.83 ± 0.06 (9.34)	41.46 ± 0.09 (7.65)	45.21 ± 0.06 (5.66)	47.42 ± 0.03 (3.36)	48.37 ± 0.06 (2.04)
1.00	13.36 ± 0.09 (13.36)	21.39 ± 0.12 (12.70)	28.75 ± 0.09 (11.11)	35.47 ± 0.09 (9.27)	40.81 ± 0.15 (7.40)	44.57 ± 0.12 (5.51)	46.74 ± 0.06 (3.26)	47.55 ± 0.09 (1.85)

[a] β_{ij} refer to reaction: $i\mathrm{DMT}+j\mathrm{H}^{+}+\mathrm{Phy}^{12-}=\mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-}$.

[b] K_{ij} refer to reaction: $i\mathrm{DMT}+\mathrm{H}_j\mathrm{Phy}^{(12-j)-}=\mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-}$.

[c] ± 3 standard deviation.

Phy^{3-}, $(DMT)_2Phy^{8-}$, $(DMT)_2HPhy^{7-}$, $(DMT)_2H_2Phy^{6-}$, $(DMT)_2H_3Phy^{5-}$, $(DMT)_2H_4Phy^{4-}$, $(DMT)_2H_5Phy^{3-}$, $(DMT)_3Phy^{6-}$, $(DMT)_3HPhy^{5-}$, $(DMT)_3H_2Phy^{4-}$, $(DMT)_3H_3Phy^{3-}$. In particular, there are eight mononuclear (with $0 \le j \le 7$), six dinuclear (with $0 \le j \le 5$) and four trinuclear (with $0 \le j \le 3$) species. Their complex formation constants values at different ionic strengths are reported in Tables 2–4, respectively for mononuclear, dinuclear and trinuclear species. The stoichiometry of these species is formally correct, but we must consider the possibility that mixed protonated hydrolytic species may be formed. For example, the formation equilibrium for the species $DMTPhy^{10-}$ could be written

$$\mathrm{DMT} + \mathrm{Phy}^{12-} = \mathrm{DMTPhy}^{10-}$$

or

$$\left[\mathrm{DMT(OH)}_q\right]^{(2-q)} + \mathrm{H}_j\mathrm{Phy}^{(12-j)-} = \left[\mathrm{DMT(OH)}_q\right]\left(\mathrm{H}_j\mathrm{Phy}\right)^{(12-j+q)-}.$$

During calculations, both to determine formation constants and to draw speciation profiles, it is unimportant how the equilibrium is expressed. Nevertheless, it is important to determine the effective nature of the species. Although potentiometric data alone do not permit inferences to be made about effective equilibrium, the pH range in which the species is formed is a reasonably accurate indicator of the involvement of protonated phytate and hydrolyzed DMT. Similar observations can also be made on the other $DMT_iH_jPhy^{(12-2i-j)-}$ species.

The importance of these species can be estimated looking at the speciation diagrams in Figs. 1 and 2 for the phytate/dimethyltin(IV) system, where the formation percentages of phytate species are reported as function of pH. These diagrams were calculated in NaCl medium at $I=0.15$ (Fig. 1) and $I=1$ mol L^{-1} (Fig. 2) and considering different DMT/Phy ratios [DMT/Phy = 1/1 for Figs. 1a and 2a; DMT/Phy = 4/1 for Figs. 1b and 2b]. It is also evident that different conditions (i.e., ionic strength and metal to ligand ratios) affect dimethyltin(IV) and phytate speciation, demonstrating the need for accurate models for interpreting and predicting their chemico-physical behavior in different contexts, such as natural fluids. For example, if we look at the diagrams obtained for different metal to ligand ratios ("a" and "b" in the same figures) we can see that the lower this ratio is (i.e., DMT/Phy = 1/1 in Figs. 1a and 2a), the more complex phytate speciation is and in the same pH range we can

Table 3
Complex formation constants for phytate-dimethyltin(IV) dinuclear species in $NaCl_{aq}$ at different ionic strengths and $t=25$ °C

I (mol L^{-1})	log β_{ij}[a] (log K_{ij})[b]					
	$(DMT)_2Phy^{8-}$	$(DMT)_2HPhy^{7-}$	$(DMT)_2H_2Phy^{6-}$	$(DMT)_2H_3Phy^{5-}$	$(DMT)_2H_4Phy^{4-}$	$(DMT)_2H_5Phy^{3-}$
0.10	25.61 ± 0.12[c] (25.61)	33.39 ± 0.09[c] (23.81)	40.91 ± 0.12[c] (21.49)	47.05 ± 0.06[c] (18.13)	51.37 ± 0.09[c] (14.31)	54.04 ± 0.09[c] (10.48)
0.15	24.66 ± 0.09 (24.66)	32.53 ± 0.06 (23.12)	39.80 ± 0.09 (20.72)	45.90 ± 0.06 (17.49)	50.05 ± 0.06 (13.67)	52.66 ± 0.06 (9.93)
0.25	23.92 ± 0.06 (23.92)	31.46 ± 0.06 (22.26)	38.63 ± 0.06 (19.97)	44.57 ± 0.06 (16.80)	48.66 ± 0.03 (13.13)	51.10 ± 0.03 (9.42)
0.50	23.15 ± 0.09 (23.15)	30.40 ± 0.09 (21.47)	37.47 ± 0.09 (19.35)	43.19 ± 0.06 (16.24)	46.97 ± 0.03 (12.54)	49.15 ± 0.06 (8.84)
0.75	23.01 ± 0.06 (23.01)	30.20 ± 0.09 (21.42)	36.90 ± 0.06 (19.08)	42.50 ± 0.06 (16.01)	46.11 ± 0.03 (12.30)	48.16 ± 0.06 (8.61)
1.00	22.85 ± 0.09 (22.85)	29.86 ± 0.12 (21.17)	36.53 ± 0.09 (18.89)	41.99 ± 0.09 (15.79)	45.52 ± 0.06 (12.11)	47.43 ± 0.09 (8.37)

[a] β_{ij} refer to reaction: $i\mathrm{DMT}+j\mathrm{H}^{+}+\mathrm{Phy}^{12-}=\mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-}$.

[b] K_{ij} refer to reaction: $i\mathrm{DMT}+\mathrm{H}_j\mathrm{Phy}^{(12-j)-}=\mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-}$.

[c] ± 3 standard deviation.

Table 4
Complex formation constants for phytate-dimethyltin(IV) trinuclear species in $NaCl_{aq}$ at different ionic strengths and $t=25$ °C

I (mol L^{-1})	log β_{ij}[a] (log K_{ij})[b]			
	$(DMT)_3Phy^{6-}$	$(DMT)_3HPhy^{5-}$	$(DMT)_3H_2Phy^{4-}$	$(DMT)_3H_3Phy^{3-}$
0.10	35.00 ± 0.15[c] (35.00)	41.17 ± 0.06[c] (31.59)	48.63 ± 0.09[c] (29.21)	52.65 ± 0.15[c] (23.73)
0.15	33.78 ± 0.12 (33.78)	39.94 ± 0.03 (30.53)	47.32 ± 0.06 (28.24)	51.26 ± 0.12 (22.85)
0.25	32.56 ± 0.09 (32.56)	38.57 ± 0.09 (29.37)	45.84 ± 0.09 (27.18)	49.72 ± 0.09 (21.95)
0.50	31.61 ± 0.06 (31.61)	37.39 ± 0.15 (28.46)	44.45 ± 0.15 (26.33)	48.04 ± 0.12 (21.09)
0.75	31.37 ± 0.09 (31.37)	37.05 ± 0.15 (28.27)	43.98 ± 0.15 (26.16)	47.30 ± 0.12 (20.81)
1.00	31.07 ± 0.18 (31.07)	36.53 ± 0.24 (27.84)	43.36 ± 0.24 (25.72)	46.61 ± 0.18 (20.41)

[a] β_{ij} refer to reaction: $i\mathrm{DMT}+j\mathrm{H}^{+}+\mathrm{Phy}^{12-}=\mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-}$.

[b] K_{ij} refer to reaction: $i\mathrm{DMT}+\mathrm{H}_j\mathrm{Phy}^{(12-j)-}=\mathrm{DMT}_i\mathrm{H}_j\mathrm{Phy}^{(12-2i-j)-}$.

[c] ± 3 standard deviation.

observe the simultaneous presence of a wide number of species reaching formation percentages of 30–40%. When the metal to ligand ratio is higher (i.e., DMT/Phy = 4/1 in Figs. 1b and 2b), however, species containing more than one dimethyltin(IV) cation have significantly higher formation percentages than mononuclear or simple protonated phytate species, as is the case, for example, with $DMT_3H_2Phy^{4-}$ and $DMT_3H_3Phy^{3-}$ species, which reach formation percentages of about 90% and 60–70%, respectively.

3.2. Dependence of complex formation constants on ionic strength

Figs. 1 and 2 also show that variations in ionic strength conditions affect phytate speciation, modifying the stability of $DMT_iH_jPhy^{(12-2i-j)-}$ species. The complex formation constant values reported in Tables 2–4 clearly show that this stability is fairly dependent on ionic strength, as best evidenced in Fig. 3 where, as an example, values of log K_{ij} (Eq. (6)) are reported vs. the square root of ionic strength (in mmol L^{-1}), respectively for $DMTH_2Phy^{8-}$, $DMT_2H_2Phy^{6-}$ and $DMT_3H_2Phy^{4-}$ species. The curves shown in the same figure represent the fits of Eq. (1) obtained using the LIANA computer program for the three sets of constants. In fact, Eq. (1) enabled us to model the dependence on ionic strength of the whole data set of constants and, moreover, to calculate the "infinite dilution" values for the stability of $DMT_iH_jPhy^{(12-2i-j)-}$ species. These values are reported in Table 5, while the values of empirical

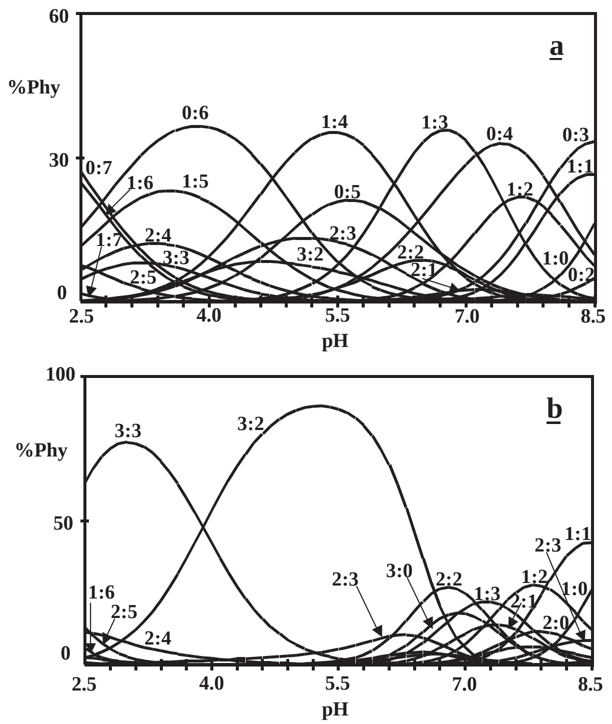

Fig. 1. Speciation diagrams of phytate vs. pH in Phy/DMT system at $I=0.15$ mol L^{-1} in NaCl and at $t=25$ °C. ij indexes in figures are referred to $DMT_iH_jPhy^{(12-2i-j)-}$ species. Experimental conditions: $C_{Phy}=0.001$ mol L^{-1}; $C_{DMT}=0.001$ (a) or 0.004 mol L^{-1} (b).

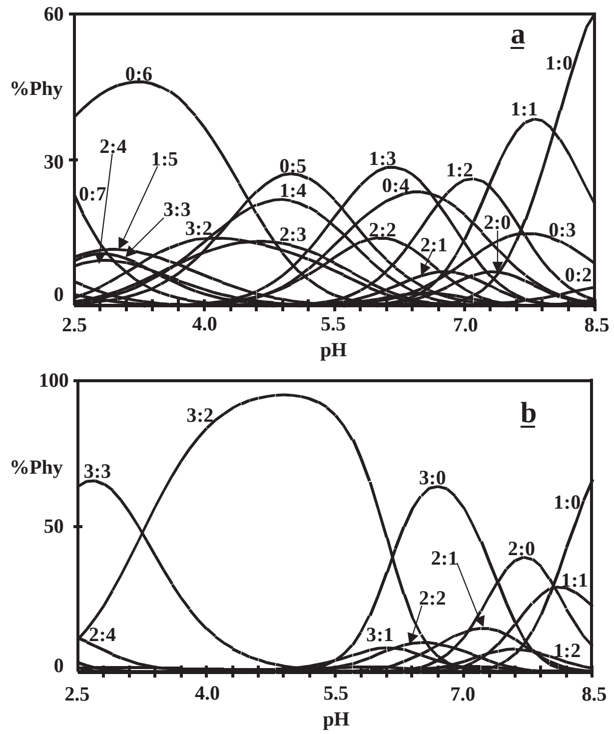

Fig. 2. Speciation diagrams of phytate vs. pH in Phy/DMT system at $I=1$ mol L^{-1} in NaCl and at $t=25$ °C. ij indexes in figures are referred to $DMT_iH_jPhy^{(12-2i-j)-}$ species. Experimental conditions: $C_{Phy}=0.001$ mol L^{-1}; $C_{DMT}=0.001$ (a) or 0.004 mol L^{-1} (b).

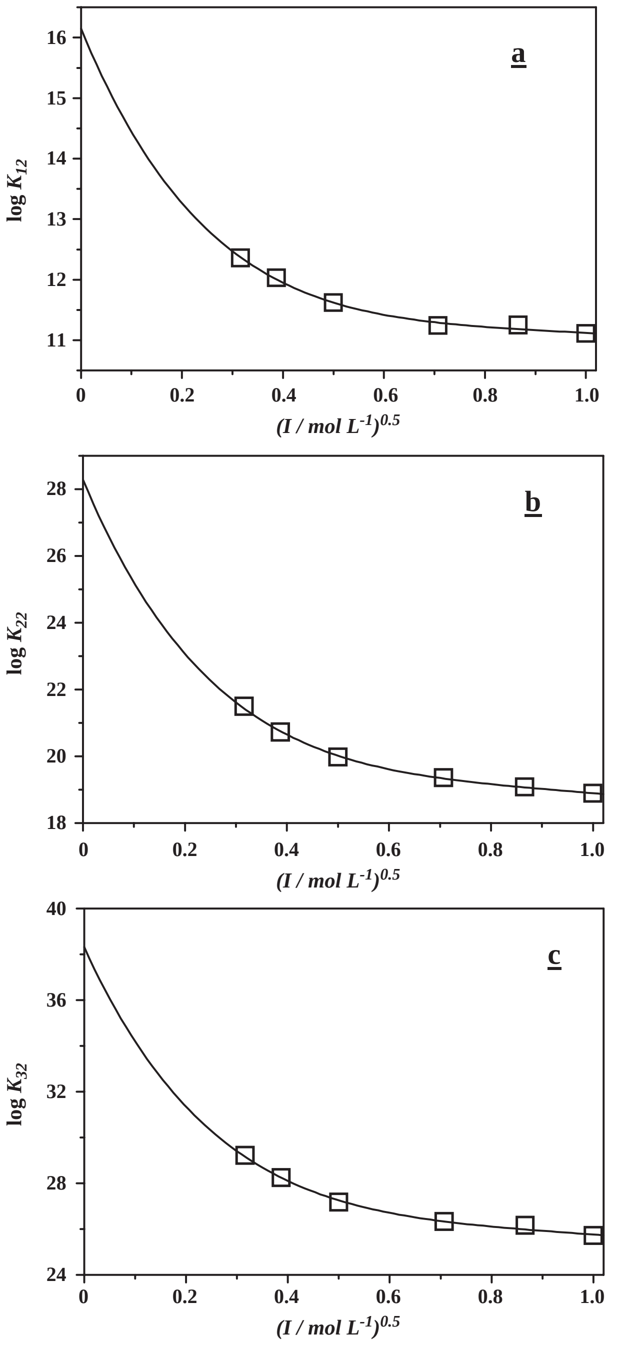

Fig. 3. Complex formation constants (Eq. (6)) for $DMTH_2Phy^{8-}$ (a), $DMT_2H_2Phy^{6-}$ (b), and $DMT_3H_2Phy^{4-}$ (c) species vs. the square root of ionic strength (in mol L^{-1}), in NaCl and at $t = 25$ °C.

parameters c^0 and c^∞ in Eq. (3) used to fit log K_{ij} of $DMT_iH_jPhy^{(12-2i-j)-}$ species to Eq. (1) are reported in Table 6. During refinements, reasonably good fits for the three sets of equations relative to mononuclear, dinuclear and trinuclear species were obtained. Standard deviations for these were $\sigma = 0.05$, $\sigma = 0.05$ and $\sigma = 0.09$, respectively, and these values are within the range of experimental error for the determination of stability constants. The goodness of the fits can also be appreciated from Fig. 4, where experimental vs. calculated (by Eq. (1) using parameters reported in Tables 5 and 6) log K_{ij} values are plotted.

Trends shown in Table 6 for c^0 and c^∞ parameters also suggest that these values can easily be expressed by regular functions. As an example, c^∞ parameter could be represented as a function of z^* (Eq. (2)):

$$c^\infty = \left(c_i^\infty + c_{iz}^\infty z^*\right) \qquad (7)$$

where c_i^∞ and c_{iz}^∞ are empirical parameters. For the fitting of the three sets of constants reported in Tables 2–4 to Eq. (1), these parameters show the same value for all constants in each set (one for each group of species with a specific number of DMT cations bound). In particular, after refinements we obtained: $c_i^\infty = -0.74$ and $c_{iz}^\infty = 0.011$ for the mononuclear species, $c_i^\infty = -1.00$ and $c_{iz}^\infty = 0.006$ for the dinuclear, and $c_i^\infty = -1.53$ and $c_{iz}^\infty = 0.006$ for the trinuclear. Standard deviations for the three new fits are comparable with the corresponding ones performed using Eq. (3). Although this new procedure did not sensibly improve the total goodness of fits, it shows the advantage of reducing the number of refined parameters for each set.

3.3. Dependence of complex formation constants on phytate protonation step

Our previous studies on phytic acid yielded some useful relationships for modeling its thermodynamic behavior in aqueous solution [1–5]. The wide number of species formed by phytate and dimethyltin(IV) suggested we might find some regularities in the stability of these ion pairs. For example, by plotting the values of log $^TK_{ij}$ of $DMT_iH_jPhy^{(12-2i-j)-}$ species vs. the ligand protonation step (j) (see Fig. 5) we observed that this stability is dependent on both the number of protons and the number of cations bound to phytate. The same trend can be observed for the sets of complex formation constants determined at each ionic strength value

Table 5
Complex formation constants for phytate-dimethyltin(IV) species at $I = 0$ mol L^{-1} and $t = 25$ °C

j	log β_{ij}[a] (log K_{ij})[b]		
	$i = 1$	$i = 2$	$i = 3$
0	19.38 ± 0.12[c] (19.38)	33.91 ± 0.24[c] (33.91)	46.29 ± 0.27[c] (46.29)
1	36.48 ± 0.21 (18.31)	49.62 ± 0.18 (31.45)	59.98 ± 0.21 (41.81)
2	49.64 ± 0.15 (16.15)	61.77 ± 0.18 (28.28)	71.80 ± 0.24 (38.31)
3	60.26 ± 0.15 (14.01)	70.43 ± 0.12 (24.18)	77.97 ± 0.27 (31.72)
4	67.94 ± 0.15 (11.64)	75.94 ± 0.15 (19.64)	–
5	73.05 ± 0.15 (9.16)	78.98 ± 0.15 (15.09)	–
6	76.61 ± 0.06 (6.59)	–	–
7	78.27 ± 0.15 (4.73)	–	–

[a] β_{ij} refer to reaction: iDMT + jH$^+$ + Phy^{12-} = $DMT_iH_jPhy^{(12-2i-j)-}$.

[b] K_{ij} refer to reaction: iDMT + $H_jPhy^{(12-j)-}$ = $DMT_iH_jPhy^{(12-2i-j)-}$.

[c] ± 3 standard deviation.

Table 6
c^0 and c^∞ empirical parameters of Eq. (3) for the modeling of the dependence of log K_{ij} for phytate-dimethyltin(IV) species on ionic strength by Eq. (1)

	Species							
	$DMTPhy^{10-}$	$DMTHPhy^{9-}$	$DMTH_2Phy^{8-}$	$DMTH_3Phy^{7-}$	$DMTH_4Phy^{6-}$	$DMTH_5Phy^{5-}$	$DMTH_6Phy^{4-}$	$DMTH_7Phy^{3-}$
c^0	8.14	6.87	6.58	4.80	5.08	4.68	3.70	2.91
c^∞	−0.58	−0.09	−0.32	0.42	−0.45	−0.52	−0.58	−0.49
	$(DMT)_2Phy^{8-}$	$(DMT)_2HPhy^{7-}$	$(DMT)_2H_2Phy^{6-}$	$(DMT)_2H_3Phy^{5-}$	$(DMT)_2H_4Phy^{4-}$	$(DMT)_2H_5Phy^{3-}$		
c^0	14.15	12.44	11.30	10.20	8.43	6.77		
c^∞	−0.38	−0.32	−0.70	−0.84	−0.63	−0.61		
	$(DMT)_3Phy^{6-}$	$(DMT)_3HPhy^{5-}$	$(DMT)_3H_2Phy^{4-}$	$(DMT)_3H_3Phy^{3-}$				
c^0	19.33	17.13	14.86	12.73				
c^∞	−0.76	−0.91	−0.79	−1.03				

investigated and may be represented for each set by the relationship:

$$\log K_{ij} = a_i + b_i j + c_i j^2 \tag{8}$$

where

$$a_i = \Big(p_1 + p_2 i^{1/2}\Big) \tag{9}$$

$$b_i = \Big(p_3 + p_4 i^{1/2}\Big) \tag{10}$$

$$c_i = \Big(p_5 + p_6 i^{1/2}\Big) \tag{11}$$

and p_1–p_6 are empirical parameters. Refined parameter values at each ionic strength investigated are reported in Table 7. Parameters a_i have a clear significance: they represent the values of log K_{10}, log K_{20} and log K_{30}, respectively when $i=1$, 2 and 3. According to this relationship, it should be possible to predict the stability of other $DMT_iH_jPhy^{(12-2i-j)-}$ species than those determined in our experimental conditions. For example, one species that might theoretically be formed in the presence of metal to ligand ratios higher than DMT:Phy = 4:1 is the tetranuclear DMT_4Phy^{4-}, with an estimated stability constant value at infinite dilution of log $^TK_{40} = 55.7 \pm 0.5$ (standard deviation).

3.4. Phytate concentration limits for dimethyltin(IV) complexation

In order to apply all results obtained in this work to real systems, such as biological fluids and natural waters, it is very important to know the lowest ligand concentration limits at which "significant" binding ability towards a given cation [dimethyltin(IV) in our case] can be observed. Such information is very important for those ligands, such as phytate, that are employed as sequestering agents for the removal of traces of heavy metal and organometal cations of environmental and biological interest from aqueous matrices. The suitability of phytate for these purposes is evident from the diagram in Fig. 6, which shows the formation percentage of dimethyltin(IV) species as a function of the free concentration of phytate at $I = 0.75$ mol L^{-1} in NaCl, at pH = 8.2 and at a total dimethyltin(IV) concentration of $C_{DMT} = 1$ mmol L^{-1}. At pPhy ~6.5, ~50% of dimethyltin(IV) is still complexed by the ligand. This constitutes further evidence how, for example, in the presence of a strong excess of another ligand such as chloride ion in seawater ($S = 35$, I

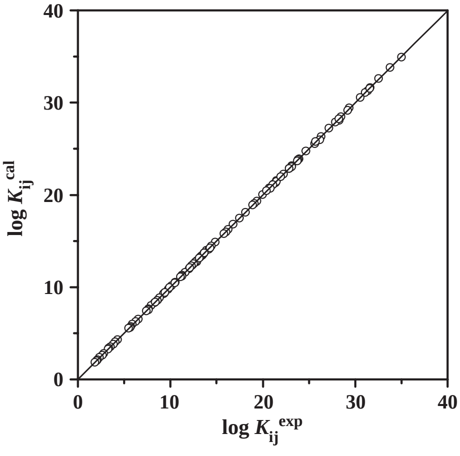

Fig. 4. Differences between experimental log K_{ij} and values calculated by Eq. (1).

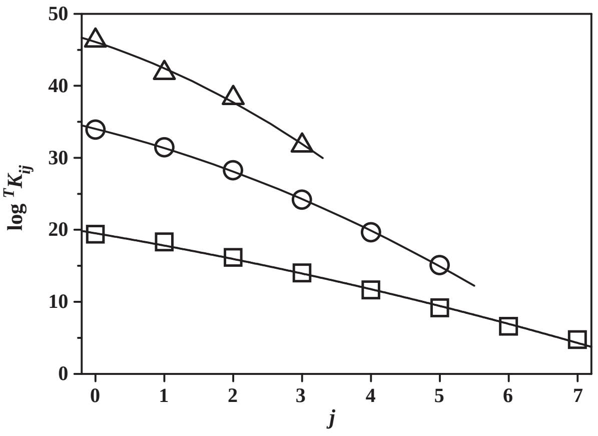

Fig. 5. Complex formation constants (Eq. (6)) at $I = 0$ mol L^{-1} and $t = 25$ °C for $DMT_iH_jPhy^{(12-2i-j)-}$ species vs. phytate protonation step (j). (□) $i = 1$; (○) $i = 2$; (△) $i = 3$.

Table 7
Empirical p_1–p_6 parameters of Eqs. (9)–(11) for the dependence of complex formation constants on both the number of protons and the number of DMT cations bound to phytate (Eq. (8))

I (mol L^{-1})	p_1	p_2	p_3	p_4	p_5	p_6	σ[a]
0	−16.65	1.01	0.31	36.17	−2.64	−0.38	0.42
0.10	−11.87	0.29	0.34	26.88	−1.57	−0.41	0.41
0.15	−11.27	0.06	0.38	25.84	−1.33	−0.45	0.41
0.25	−10.78	0.10	0.35	24.87	−1.33	−0.42	0.39
0.50	−10.29	−0.12	0.39	23.99	−1.12	−0.46	0.40
0.75	−10.25	0.04	0.38	23.87	−1.24	−0.45	0.42
1.00	−10.05	0.15	0.35	23.57	−1.34	−0.42	0.40

[a] Standard deviation of the fit.

~0.7 mol L^{-1}, pH ~8.2, the diagram is obtained at I=0.75 mol L^{-1} in NaCl), low concentrations of phytate are still sufficient to bind satisfactory amounts of dimethyltin(IV) and modify its bioavailability.

3.5. Literature comparisons between phytate and other ligands towards dimethyltin(IV) complexation

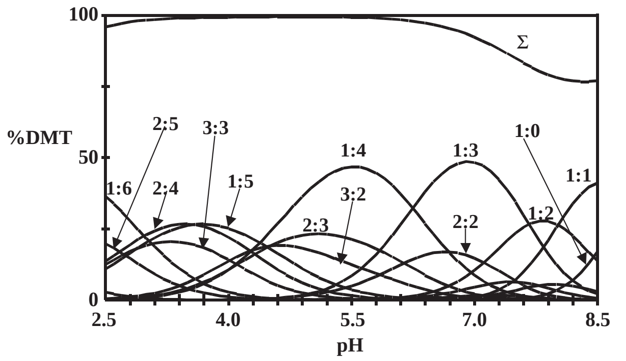

Fig. 7. Speciation diagram of dimethyltin(IV) vs. pH at t=25 °C in Phy/DMT system at I=0.1 mol L^{-1} in NaCl at t=25 °C. ij indexes in figure are referred to $DMT_iH_jPhy^{(12-2i-j)-}$ species, Σ=total percentage of dimethyltin(IV) complexed by phytate. Experimental conditions: C_{Phy}=0.004012 mol L^{-1}; C_{DMT}=0.00304 mol L^{-1}.

Many papers dealing with phytate–metal cation interactions (with particular emphasis given to the bioavailability of metals in the presence of the ligand, see references in [1–8]) can be found in literature, but, to our knowledge, no articles have yet been published on the interactions between this ligand and organometal cations. Therefore, the system investigated is completely new, and the results of our study must be considered as original. The classical sequestering agent for the removal of heavy metal and organometal cations from aqueous matrices is ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA) and, for this reason, it would be interesting to compare phytate with this and other ligands more frequently used for this purpose. An interesting paper of Aizawa et al. deals with both the crystal structures and the complexation equilibria of some amino- (or imino-) carboxylic ligands [25] with $(CH_3)_2Sn^{2+}$. The authors report data concerning the stability of some EDTA/DMT complexes determined in $NaNO_3$ aqueous solution at I=0.1 mol L^{-1}. As expected, analysis of these data shows EDTA to be a very good complexing agent towards dimethyltin(IV) cation. However, as can be seen from a distribution diagram of DMT species in the presence of EDTA, reported by the authors, this ligand is not able to bind the whole amount of DMT present in solution. In fact, although the formation percentage of some EDTA/DMT species is higher than 70–75%, in all the pH range shown by the authors ($2 \leq pH \leq 10$), a significant amount of non-paired, free or hydrolyzed cation is present (~10% at least). On the other hand, as can be noted from the speciation diagram of dimethyltin(IV) in presence of phytate (Fig. 7), obtained in the same experimental conditions used by Aizawa et al., DMT is fully complexed by this ligand in most of investigated pH range ($2.5 \leq pH \leq 8.5$). Only above pH ~7 does the percentage of cation complexed by phytate decrease to ~80% owing to the formation of free hydrolytic $[(CH_3)_2Sn(OH)_2]^0$ species. Due to the presence of chloride ion in the experimental conditions adopted for the drawing of distribution diagram in Fig. 7, some minor differences may be observed in the speciation scheme of dimethyltin(IV)

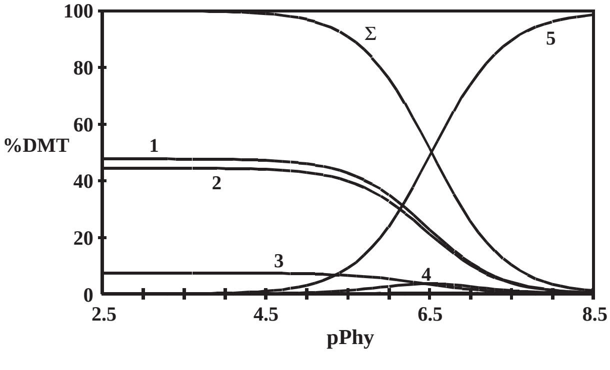

Fig. 6. Speciation diagram of dimethyltin(IV) vs. pPhy at t=25 °C. Species: (Σ) total percentage of dimethyltin(IV) complexed by phytate; (1) DMTPhy; (2) DMTHPhy; (3) $DMTH_2Phy$; (4) DMT_2Phy; (5) $DMT(OH)_2$; [charges omitted for simplicity]. Experimental conditions: pH=8.2, I=0.75 mol L^{-1} in NaCl, C_{DMT}=0.001 mol L^{-1}.

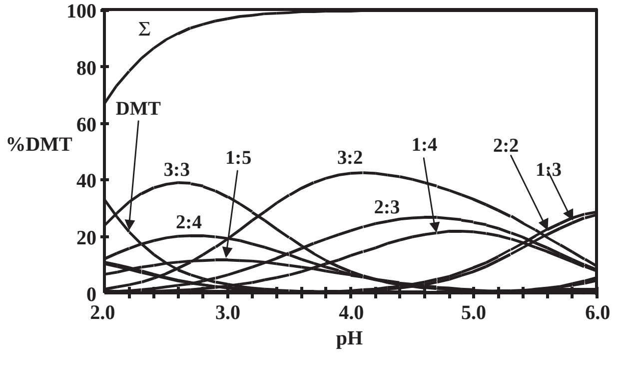

Fig. 8. Speciation diagram of dimethyltin(IV) vs. pH at t=25 °C in Phy/DMT system at I=1 mol L^{-1} in NaCl at t=25 °C. ij indexes in figures are referred to $DMT_iH_jPhy^{(12-2i-j)-}$ species, Σ=total percentage of dimethyltin(IV) complexed by phytate. Experimental conditions: C_{Phy}=C_{DMT}=0.003 mol L^{-1}.

in the presence of phytic acid in nitrate solutions, but, as already pointed out in previous paragraphs, the chloride ion does not significantly affect this scheme, not even when present in large amounts. To conclude the discussion on the binding ability of phytic acid and EDTA towards dimethyltin(IV), there is another reason why the former ligand should be preferred to the latter (or other complexones) for the removal of this organometal cation from aqueous matrices: phytic acid is commonly present in the environment and naturally synthesized in significant amounts by several vegetal species ([6–8] and refs. therein) and, therefore, the environmental impact of its massive use is lower than that of EDTA.

It would also be interesting to compare the binding ability of phytate towards dimethyltin(IV) with that of other phosphoric ligands. Although organotin(IV) interactions have been studied for a wide number of biological molecules containing phosphoric groups (e.g., nucleotides, nucleic acids) [14], to our knowledge just one recent paper deals with interactions between the dimethyltin(IV) cation and the simple phosphate ligand [26]. In this paper, the authors report formation constants values for complex species determined in KNO_3 aqueous solution at $t=25$ °C and $I=1.0$ mol L^{-1} ionic strength. Even if the experimental conditions (i.e., the ionic medium and the metal to ligand ratios) are different, some rough comparisons can be made. For example, analysis of the speciation diagrams shown in the paper of Yuchi et al. reveals that, in those conditions, the phosphate ligand is able to complex no more than ~80% of DMT in the pH range $2 \leq pH \leq 6$, while in the same experimental conditions phytic acid binds the whole amount of this cation starting from pH ~3, while in the more acidic pH range dimethyltin(IV) is still complexed for ~70% (see Fig. 8).

4. Final remarks

The main conclusions regarding phytate/dimethyltin(IV) interactions in $NaCl_{aq}$ at different ionic strengths can be summarized as follows:

a. results for the speciation of the phytate/dimethyltin(IV) system in $NaCl_{aq}$ have been reported here for the first time;
b. in the pH range $2.5 \leq pH \leq 8.5$ the formation of 18 phytate-proton-dimethyltin(IV) species has been hypothesized; these include eight mononuclear (with $0 \leq j \leq 7$), six dinuclear (with $0 \leq j \leq 5$) and four trinuclear (with $0 \leq j \leq 3$) species;
c. complex formation constants for phytate/dimethyltin(IV) species are fairly dependent on ionic strength and this dependence has been modeled;
d. phytic acid and dimethyltin(IV) speciation is dependent both on ionic strength and on metal to ligand ratio;
e. the stability of phytate-dimethyltin(IV) species has been shown to be dependent on both the phytate protonation step and the number of cations bound to ligand and this dependence has been modeled; an empirical predictive relationship has been proposed;
f. the phytate ligand has been shown to be a very good sequestering agent towards $(CH_3)_2Sn^{2+}$, even when compared with other widely used ligands such as EDTA and phosphate.

Acknowledgements

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