

# The effect of the tetraalkylammonium salts on the protonation thermodynamics of the phytate anion



Clemente Bretti, Rosalia Maria Cigala, Concetta De Stefano, Gabriele Lando, Silvio Sammartano\*

Dipartimento di Scienze Chimiche, Università di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy

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## ABSTRACT

In this paper new potentiometric titrations were performed on the protonation of phytate at different temperatures  $278.15\text{ K} \leq T/\text{K} \leq 323.15$ , ionic strengths and in different ionic media, namely  $(\text{CH}_3)_4\text{NCl}$  ( $0.1 \leq I/\text{mol dm}^{-3} \leq 3.0$ ) and  $(\text{C}_2\text{H}_5)_4\text{NI}$  ( $0.1 \leq I/\text{mol dm}^{-3} \leq 1.2$ ). A complete set of phytate protonation constants, with general formula  $\text{H}_i\text{Phy}$  (with  $1 \leq i \leq 8$ ), was proposed.

The dependence of protonation constants on ionic strength was calculated by using three different approaches: (i) Debye–Hückel (DH) type equation, (ii) SIT (specific ion interaction theory) approach and (iii) the formation of weak complexes. It is important to underline that the whole study was done using  $\text{K}_2\text{H}_{10}\text{Phy}$  as phytate source, because the presence of an interacting cation, such as  $\text{K}^+$ , affects significantly the values of the apparent protonation constants. Different  $\text{K}^+$  concentrations in the considered range ( $0.001 \leq c_{\text{K}}/\text{mol dm}^{-3} \leq 0.01$ ) cause a difference of  $\pm 0.05$  in the protonation data.

Furthermore, the weak complexes between phytate and  $(\text{CH}_3)_4\text{N}^+$  cation were determined at different ionic strengths, and different protonated species, having general formula  $\text{H}_i\text{M}_j\text{Phy}$  [ $0 \leq i \leq 6$  and  $1 \leq j \leq 5$ ] were reported.

This paper represents an improvement in the understanding of the solution behavior of phytic acid in a wide range of ionic strengths and in different ionic media.

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## 1. Introduction

Dealing with important molecules, especially the natural ones, involved in many physiological, industrial and environmentally relevant processes, the knowledge and the modeling of the acid–base properties are fundamental to understand the activity and the interaction of this molecule in a multi component system. In fact, almost all the solution properties of a molecule are dependent on its acid–base behavior; for example, the binding ability of a ligand towards a metal cation is strongly dependent on the protonation of the ligand and on the hydrolytic process of the metal cation. Phytic acid is a relatively simple molecule (see Fig. 1) widely distributed in nature, particularly in cereals and has an important role in several biological processes. It has six phosphate groups in its structure and, potentially, twelve negative charges, for which it appears to be a strong sequestering agent for (virtually all) inorganic and organic cations (e.g., polyammonium cations [1]).

In the last twelve years, this research group performed several investigations on phytate coordination properties (last contributions in Refs. [2–5]). Recently, a review on the sequestering ability

of this ligand in aqueous solutions, with particular reference to natural waters and biological fluids [6], has also been reported. Some applications of phytic acid regard its use in the remediation field for the removal of toxic metal and organo-metal cations [7–10], in electrochemistry as sensor [11] and many others described in recent reviews [6,12–16].

Although in the literature phytate protonation constant data have been widely reported by many authors, a comprehensive study about the nature of the proton binding is still missing and the agreement among the findings is not satisfactory. The speciation model, the protonation constant values and the dependence on temperature and ionic strength are not homogeneous and often the data are given at a single ionic strength. The most reliable protonation constants reported in the literature at different ionic strengths are listed in Table 1.

Generally, the phytate protonation constants were reported in different interacting media, such as NaCl,  $\text{NaNO}_3$ ,  $\text{NaClO}_4$ , KCl,  $\text{KNO}_3$ , whereas few authors reported data in weakly interacting media, for example  $(\text{C}_3\text{H}_7)_4\text{NBr}$  or  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ . The influence of the ions of the supporting electrolyte has not been deeply analyzed in the past. This research group published the phytate protonation constants in different media, considering also the protonation in self medium and the formation of binuclear protonated species at  $c_{\text{phy}} > 12 \text{ mmol dm}^{-3}$  [23–29]. Usually, tetraalkylammonium salts

\* Corresponding author. Tel.: +39 90 393659; fax: +39 90 392827.

E-mail address: [ssammartano@unime.it](mailto:ssammartano@unime.it) (S. Sammartano).

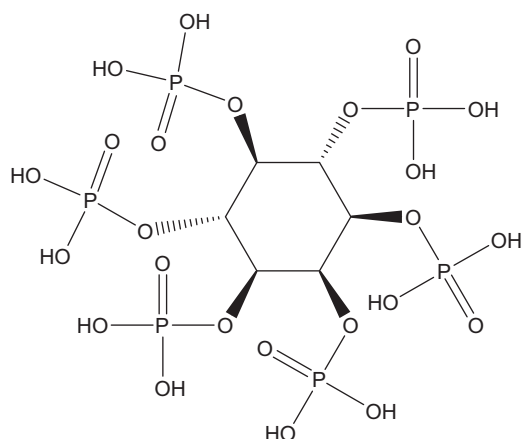
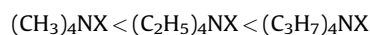


Fig. 1. Structural formula of phytic acid.

have been widely used as supporting electrolytes in the studies of acid–base properties and ligand–metal complexation. In particular, they were used in the case of the presence in solution of ligands with many binding sites as polycarboxylates [30–34], complexones [35–43], resorcinols [44], amines [45,46], amino acids [47,48], sulfates [49–51], phosphates [38], nucleotides [52]. The importance of the use of the tetraalkylammonium salts is highlighted by the fact that 15% of all the data collected (~24,000 references) in the IUPAC stability constants database [53] refers to equilibrium constants in these media.

The protonation constant values of charged O-donor ligands determined in tetraalkylammonium salts follow the trend:



The protonation constants of uncharged N-donor ligands have an opposite trend, due to the formation of weak complexes between the deprotonated nitrogen atom and the tetraalkylammonium cation [54], due to probably hydrophobic interaction.

These salts show very different characteristics than the supporting electrolyte ones generally used in the study of protonation and metal complex formation in solutions, namely alkali metal chlorides, nitrates and perchlorates. This is mainly due to two factors: the size of the cation and hydrophobic characteristic

of alkyl group. Moreover, their activity coefficients are much higher than those of alkali metal salts [55–59].

Usually, tetraalkylammonium salts are used as baseline electrolytes for the determination of weak complexes between alkali metal cations and a ligand. Some paradigmatic examples are reported in De Stefano et al. [24], where phytate protonation was studied in LiCl, NaCl, KCl and CsCl and the weak complexes between phytate and  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$  were determined from the difference between the values of the protonation constants in alkali metal salts and tetraethylammonium iodide. It was found that the stability constant of a species decreases from  $\text{Li}^+$  to  $\text{Cs}^+$ , therefore the  $\text{Li}^+/\text{Phy}^{12-}$  species are stronger than the  $\text{Na}^+/\text{Phy}^{12-}$  and the order of magnitude of the species is  $\log K = 23.0, 20.4$  and  $19.2$  for the  $\text{Li}_7\text{Phy}^{3-}$ ,  $\text{Na}_7\text{Phy}^{5-}$  and  $\text{K}_7\text{Phy}^{5-}$ , respectively at  $I = 0.5 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ . It is easy to understand that with these kind of stability constants the concentration of alkali metal cations is fundamental and that even the phytate protonation constants determined in a not interacting ionic medium (e.g.,  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ ) are conditional if the  $\text{Na}^+$  or  $\text{K}^+$  concentration is millimolar. On the light of these considerations the selection of an appropriate model for the ionic strength dependence of protonation constants is very hard and many experimental data with adequate accuracy, a strong expertise in the field of the solution thermodynamics and computer programs which can deal with the ionic strength variation during a titration, are required.

For these reasons, in this work, the influence of the tetraalkylammonium cations on the acid base properties of phytate has been evaluated studying its protonation constants in different conditions. In particular potentiometric measurements have been performed in  $(\text{CH}_3)_4\text{NCl}$  ( $0.096 \leq I/\text{mol dm}^{-3} \leq 2.984$ ) and  $(\text{C}_2\text{H}_5)_4\text{NI}$  ( $0.118 \leq I/\text{mol dm}^{-3} \leq 1.182$ ) aqueous solutions. In the case of the  $(\text{C}_2\text{H}_5)_4\text{NI}$ , some measurements have been performed in the temperature range  $278.15 \text{ K} \leq T/\text{K} \leq 323.15$  to determine the protonation enthalpy changes in different conditions.

Data collected were analyzed by different models, namely the Debye–Hückel type equation and the SIT (specific ion interaction theory) approach. In addition the weak complexes of the phytate anion with  $(\text{CH}_3)_4\text{N}^+$  cation were also determined at different ionic strengths. A critical analysis of the literature data has been performed and selected values are proposed for the ionic media studied in this work.

Table 1

Literature protonation constants at  $T = 298.15 \pm 0.1 \text{ K}$  in tetraalkylammonium background electrolytes.

Species	$I = 0.1^a$ <sup>b</sup> ( $\text{C}_2\text{H}_5$ ) <sub>4</sub> NClO <sub>4</sub>	$I = 0.1^a$ <sup>b</sup> ( $\text{C}_4\text{H}_9$ ) <sub>4</sub> NBr	$I = 0.1^a$ <sup>c</sup> ( $\text{C}_4\text{H}_9$ ) <sub>4</sub> NBr	$I = 0^a$ <sup>d</sup>	$I = 0.17^a$ <sup>e</sup> ( $\text{C}_2\text{H}_5$ ) <sub>4</sub> NClO <sub>4</sub>	$I = 0.1^a$ <sup>f</sup> NaOH	$I = 0.15^a$ <sup>g</sup> ( $\text{CH}_3$ ) <sub>4</sub> NCl	$I = 0.1^a$ <sup>h</sup> ( $\text{C}_2\text{H}_5$ ) <sub>4</sub> NI	$I = 0.1^a$ <sup>i</sup> ( $\text{CH}_3$ ) <sub>4</sub> NCl	$I = 0.1^a$ <sup>i</sup> ( $\text{C}_2\text{H}_5$ ) <sub>4</sub> NI
HPhy	>12	>12	12.0	11.76	>13	11.2	10.8		11.86	
H <sub>2</sub> Phy	>12	>12	10.0	10.98	>13	10.2	10.5		11.76	11.72
H <sub>3</sub> Phy	>12	>12	10.0	10.43	12.3	10.6	10.33	12.21	11.50	11.52
H <sub>4</sub> Phy	11.47	11.50	7.60	8.96	9.92	9.42	8.79	9.92	10.08	10.09
H <sub>5</sub> Phy	8.12	7.97	6.85	7.11	7.42	7.45	6.90	7.53	7.64	7.69
H <sub>6</sub> Phy	6.51	6.41	5.70	5.99	6.13	6.14	5.72	6.11	6.05	6.12
H <sub>7</sub> Phy	4.00	3.93	2.10	3.72	3.59	3.70	3.10	3.53	3.55	3.60
H <sub>8</sub> Phy	2.68	2.73	2.10	2.61	2.0	2.35	1.9			2.64
H <sub>9</sub> Phy	1.80	2.00	1.70	1.84	2.4	1.85	1.9			
H <sub>10</sub> Phy	<1.50	<1.50	1.50	(0.85)	1.0	0.04				
H <sub>11</sub> Phy	<1.50	<1.50	1.50	(0.41)	<1.0	0.02				
H <sub>12</sub> Phy	<1.50	<1.50	1.10	(−0.15)	<1.0	−0.15				

<sup>a</sup>In  $\text{mol dm}^{-3}$ ,  $u(I) = 0.0001 \text{ mol dm}^{-3}$ .

<sup>b</sup> Bieth et al. [17].

<sup>c</sup> Costello et al. [18] at  $T = 301.15 \text{ K}$ .

<sup>d</sup> Brigando et al. [19], values in parenthesis are not experimentally determined.

<sup>e</sup> Bebot-Brigaud et al. [20] at  $T = 293.15 \text{ K}$ .

<sup>f</sup> Sala et al. [21] at  $T = 293.15 \text{ K}$ .

<sup>g</sup> Torres et al. [22] at  $T = 310.15 \text{ K}$ .

<sup>h</sup> De Stefano et al. [23].

<sup>i</sup> This work.

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