



On the interaction of phytate with proton and monocharged inorganic cations in different ionic media, and modeling of acid-base properties at low ionic strength



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ABSTRACT

In this paper, new data are reported on the protonation of phytate at $T = 298.15$ K in different ionic media and ionic strengths, namely $\text{NH}_4\text{Cl}_{(\text{aq})}$ ($0.1 \leq I/\text{mol} \cdot \text{kg}^{-1} \leq 1.9$) and $\text{NaNO}_3_{(\text{aq})}$ ($0.1 \leq I/\text{mol} \cdot \text{kg}^{-1} \leq 5.4$). A complete set of phytate protonation constants, with general formula H_iPhy (with $1 \leq i \leq 7$) was proposed. The data were modeled by a logarithmic empiric equation, as well as an Extended Debye–Hückel (EDH) and specific ion interaction theory (SIT) models. A strong similarity was found between protonation data in $\text{NH}_4\text{Cl}_{(\text{aq})}$, $\text{NaNO}_3_{(\text{aq})}$ and those previously reported in $\text{NaCl}_{(\text{aq})}$, $\text{KCl}_{(\text{aq})}$ and $\text{KNO}_3_{(\text{aq})}$, so that a unique set of thermodynamic protonation data has been proposed for phytate protonation at $I \leq 0.15 \text{ mol} \cdot \text{kg}^{-1}$. Thermodynamic parameters obtained in these conditions can be useful to model the behavior of phytate in real aqueous systems at low ionic strengths. An empirical relationship has also been proposed for all the protonation data at $0 < I/\text{mol} \cdot \text{kg}^{-1} \leq 0.15$: $T\Delta S (\pm 1.5) = 11.7 - 0.72 \cdot \Delta G$. Using literature data for the phytate protonation in $(\text{C}_2\text{H}_5)_4\text{NI}_{(\text{aq})}$, the weak complexes between Na^+ or NH_4^+ and phytic acid have been calculated by the ΔpK method (i.e., by the comparison of the protonation constants determined in an interacting medium, such as $\text{NH}_4\text{Cl}_{(\text{aq})}$, and those obtained in a non-interacting supporting electrolytes, like tetraalkylammonium salts). In terms of weak complex formation constants, the results are similar for $\text{NaNO}_3_{(\text{aq})}$ and $\text{NH}_4\text{Cl}_{(\text{aq})}$, and twelve $\text{H}_i\text{M}_j\text{Phy}$ species are reported together with their stability. For example, for the formation of the M_6Phy species, it is: $\log \beta = 25.9$ and $25.6 (\pm 0.2)$ for $\text{M} = \text{Na}^+$ and NH_4^+ , respectively, at $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$. This paper represents an advance in the understanding of the acid-base behavior of phytic acid in a wide number of ionic media at different ionic strengths.

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1. Introduction

In order to fully understand the behavior of many substances involved in physiological, industrial and environmentally relevant processes, the knowledge and the modeling of their aqueous solution properties is fundamental to comprehend their activity and their network of interactions in a given system. These properties are regulated, for many molecules, by their acid-base properties that are, in turn, dependent on the chemical (e.g., composition, ionic strength) and physical (e.g., temperature, pressure) conditions of the system itself. That is why the determination and the modeling of the protonation constants of various ligands in different conditions is very important. While this does usually not represent a particular problem, many difficulties arise when

dealing with high charged molecules, owing to high errors generally associated to the experimental determination of their protonation constants.

Phytic acid takes place in many physiological reactions, and its use in many fields is continuously growing, mainly thanks to its binding ability towards many metal and organo-metal cations, as well as other ligands [1–6]. These properties, together with many other possible use of phytate (e.g., in electrochemistry), are well described in many books and papers (e.g., [7–18] and references therein). This research group has studied the acid-base and the binding properties of phytic acid in many experimental conditions [12,19–27]. Recently, in Bretti *et al.* [27] (and references therein), the protonation of phytate in weakly interacting media, such as the tetraalkylammonium salts, has been analyzed together with the most reliable literature data. As regards interacting ionic media, such as Na^+ or K^+ containing salts, in table 1 the most reliable protonation data in Na^+ and K^+ media are reported

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TABLE 1
Protonation constants of phytate reported in the literature at $T = 298.15 \text{ K}$,^a $p = 0.1 \text{ MPa}$ and at $I = 0.1 \text{ mol} \cdot \text{dm}^{-3} \sim 0.1 \text{ mol} \cdot \text{kg}^{-1}$ in Na^+ and K^+ 1:1 supporting electrolytes.

References	Medium	HPhy	H ₂ Phy	H ₃ Phy	H ₄ Phy	H ₅ Phy	H ₆ Phy	H ₇ Phy
Hoff-Jorgensen [28]	$\text{NaCl}_{(\text{aq})}$	10.21	9.94	9.09	8.18	6.55	5.26	3.29
Perrin [29]	$\text{NaCl}_{(\text{aq})}$	9.97	9.69	9.54	8.13	6.29	5.00	3.00
Evans et al. [30]	$\text{KCl}_{(\text{aq})}$	9.91	9.86	9.46	8.20	6.41	5.31	3.21
Li et al. [31]	$\text{NaClO}_{4(\text{aq})}$	8.81	10.72	9.18	7.94	6.22	4.94	2.52
Brigandoet al. [32]	$\text{Na}^+_{(\text{aq})}$	10.23	9.45	8.90	7.43	5.58	4.46	2.19
De Stefano et al. [19]	$\text{NaCl}_{(\text{aq})}$	9.58	9.84	9.50	8.14	6.50	5.25	2.88
De Stefano et al. [20]	$\text{KCl}_{(\text{aq})}$	10.24	9.50	9.93	8.37	6.62	5.35	2.93
Torres et al. [33]	$\text{NaClO}_{4(\text{aq})}$	9.56	9.45	9.34	8.44	7.15	5.99	5.13
De Carli et al. [34]	$\text{KCl}_{(\text{aq})}$	10.97	10.04	9.88	9.15	7.57	6.08	3.86
Crea et al. [35]	$\text{NaNO}_{3(\text{aq})}$	9.48	9.98	9.53	8.20	6.49	5.17	3.02
Bretti et al. [26]	$\text{KNO}_{3(\text{aq})}$	10.28	9.75	9.80	8.31	6.44	5.20	2.99
Average ^b		9.93 ± 0.33^c	9.84 ± 0.21	9.47 ± 0.19	8.23 ± 0.24	6.53 ± 0.30	5.27 ± 0.27	3.18 ± 0.46

^a Standard uncertainties u are $u(T) = 0.1 \text{ K}$, $u(p) = 1 \text{ kPa}$, $u(I) = 0.0001 \text{ mol} \cdot \text{dm}^{-3} = 0.0001 \text{ mol} \cdot \text{kg}^{-1}$.

^b Calculated considering only literature data.

^c $\pm 95\%$ confidence interval (C.I.).

[19,20,26,28–35]. Note that in the table the data are reported in the molar concentration scale because it is more correct when comparing results obtained in different ionic media [36], however, dealing with the electrolytes used in this work at low ionic strength ($I \leq 0.15 \text{ mol} \cdot \text{dm}^{-3}$), molar and molal concentration scales are practically equivalent.

As can be noted, some authors reported the protonation constants of all the twelve steps whereas some others reported data for seven or eight protonation constants. In our opinion, the determination of more than eight protonated species of phytate is affected by a large uncertainty.

In order to improve the knowledge of the phytate protonation constants in the most important 1:1 electrolytes, data in $\text{NH}_4\text{Cl}_{(\text{aq})}$ and in $\text{NaNO}_{3(\text{aq})}$ are also desired. In this light, new experiments have been performed in this work in $\text{NH}_4\text{Cl}_{(\text{aq})}$ at $0.101 \leq I/\text{mol} \cdot \text{kg}^{-1} \leq 1.933$ ($0.100 \leq I/\text{mol} \cdot \text{dm}^{-3} \leq 1.796$), and in $\text{NaNO}_{3(\text{aq})}$ at $0.118 \leq I/\text{mol} \cdot \text{kg}^{-1} \leq 5.440$ ($0.117 \leq I/\text{mol} \cdot \text{dm}^{-3} \leq 4.603$) (some data in NaNO_3 at $I \leq 1.0 \text{ mol} \cdot \text{kg}^{-1}$ were already reported in Crea et al. [35]). The ionic strength dependence has been studied considering different models. The stability constants of NH_4^+/Phy species have also been determined at different ionic strengths. Moreover, some suggested thermodynamic data are given for low ionic strength conditions ($I \leq 0.15 \text{ mol} \cdot \text{dm}^{-3} \sim 0.15 \text{ mol} \cdot \text{kg}^{-1}$), valid for all NH_4^+ , Na^+ and K^+ containing ionic media, since these conditions are particularly important for many natural fluids.

2. Experimental section

2.1. Chemicals

Aqueous solutions of fully protonated phytic acid (H_{12}Phy) were prepared by weighing the dipotassium salt ($\text{K}_2\text{H}_{10}\text{Phy}$), and passing it over a strong cationic exchange resin (Dowex 50 WX8) in H^+ form. The concentration of H_{12}Phy was checked potentiometrically by alkalimetric titrations and the potassium residual concentration was evaluated by flame emissions spectrometry, resulting always below the L.O.Q. Hydrochloric acid, nitric acid and carbonate free sodium hydroxide solutions were prepared by diluting concentrated ampoules and were standardized against sodium carbonate and potassium hydrogen phthalate, respectively, previously dried in an oven at $T = 383.15 \text{ K}$. $\text{NH}_4\text{Cl}_{(\text{aq})}$ and $\text{NaNO}_{3(\text{aq})}$ solutions were prepared by weighing the pure salt dried in an oven at $T = 383.15 \text{ K}$. All solutions were prepared with analytical grade water ($R = 18 \text{ M}\Omega \cdot \text{cm}$) and using grade A glassware. All chemicals were purchased from Sigma–Aldrich (Italy) and its brands, see table 2.

TABLE 2
Materials used for this paper, purchased from Sigma–Aldrich.

Chemical name	Purity (mass/mass)
$\text{K}_2\text{H}_{10}\text{Phy}^a$	$\geq 95\%$
HCl	$\geq 99\%$
HNO_3	70% water solution
Na_2CO_3	$\geq 99\%$
NaOH	$\geq 99\%$
KHphthalate	99%
NH_4Cl	$\geq 99.5\%$
NaNO_3	$\geq 99\%$

^a Passed over strong cationic exchange resin to obtain the H_{12}Phy ; final purity equal to that of the $\text{K}_2\text{H}_{10}\text{Phy}$.

2.2. Apparatus and procedure

Potentiometric measurements were carried out (at $T = 298.15 \pm 0.1 \text{ K}$ and $p = 0.1 \pm 0.001 \text{ MPa}$) using two different apparatuses, detailed in reference [37]. Estimated precision for both systems was $\pm 0.15 \text{ mV}$ and $\pm 0.003 \text{ cm}^3$ for e.m.f. and titrant volume readings, respectively. Titrations were carried out on 25 or 50 cm^3 of titrand solution, containing phytate ($0.001 \leq c_{\text{Phy}}/\text{mol} \cdot \text{kg}^{-1} \leq 0.010$), strong acid (HCl, HNO_3 , $0.001 \leq c_{\text{H}}/\text{mol} \cdot \text{kg}^{-1} \leq 0.010$) and the ionic medium ($\text{NH}_4\text{Cl}_{(\text{aq})}$ or $\text{NaNO}_{3(\text{aq})}$) in order to obtain the established total ionic strength. As regards measurements performed at low ionic strengths, the contribution of the ligand has to be considered. Under the most critical conditions (i.e., $I \sim 0.10 \text{ mol} \cdot \text{kg}^{-1}$), this contribution is about (7 to 8)%, which introduces a relatively small error into the calculation. However, this error was taken into account by giving appropriate weights during data analysis. The titrand solutions were titrated with standard $\text{NaOH}_{(\text{aq})}$ up to $\text{pH} \sim 8.5$ for the measurements in $\text{NH}_4\text{Cl}_{(\text{aq})}$ (to avoid the formation of $\text{NH}_3(\text{g})$) and to $\text{pH} \sim 11.0$ for those in $\text{NaNO}_{3(\text{aq})}$, bubbling pre-saturated $\text{N}_2(\text{g})$. For each experiment, independent titrations of strong acid solutions with a standard base were carried out under the same medium and ionic strength conditions of the systems to be investigated, to determine the standard electrode potential (E^0), the acidic junction potential ($E_j = j_a [\text{H}^+]$). The reliability of the titrations in the alkaline range was verified determining the ionic product of water ($\text{p}K_w$). The equilibrium state during titrations was checked adopting some usual precautions [38]. These included checking the time required to reach equilibrium and performing back-titrations.

2.3. Calculations

The non-linear least squares computer program ESAB2M was used for the refinement of all the parameters of the acid-base

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