

Equilibrium studies on interactions of rare earth ions with phytic acid

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The interaction between phytic acid and trivalent rare earth metal ions, viz., Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} and HO^{3+} has been investigated potentiometrically at 25°C. The proton-ligand stability constants (pK_Y^H) of phytic acid and the stability constants ($\log K$) of metal complexes formed in aqueous medium ($\mu = 0.1 \text{ M NaClO}_4$) have been evaluated. The results indicate that eight protons of phytic acid are highly acidic, two are weakly acidic and two very weakly acidic, titrable in the pH ranges 1.2-4.9, 5.0-8.15 and 8.3-11.0 respectively. The stability of each phytic acid-lanthanide ion complex decreases with an increase in pH and follows the usual trend through the series.

Though interaction of phytic acid with transition metal ions has been investigated in the recent past^{1,8-10}, no effort seems to have been made to study its dissociation in aqueous NaClO_4 medium and stability constants of lanthanide chelates with phytic acid. Here we report the proton ligand stability constants for phytic acid, its metal ligand stability constants with trivalent rare earth ions and its conformation.

Experimental

A digital pH-meter (Elico, Model L1-120) in combination with a glass electrode was used. It was standardized with standard buffer solutions. Perchloric acid (Riedel), sodium perchlorate (Trizma), sodium hydroxide and oxalic acid (BDH) solutions were prepared in CO_2 -free doubly distilled water. The reagent grade metal chlorides were used as obtained. Their solutions were made in 0.15 M HClO_4 in order to prevent hydrolysis. Sodium phytate solution was converted into acid by ion-exchange using an Amberlite IRN77 (H) resin. Three

successive passages were made in order to minimise the sodium ion concentration in the solution. The concentration of phytic acid was determined titrimetrically.

Procedure

The strength of stock solution of HClO_4 was determined by titration against standard NaOH , and suitably diluted to 0.15 M . The concentration of the metal ions was determined titrimetrically^{2,3}. The "Calvin-Bjerrum" titration technique as modified by "Irving and Rossotti"⁴ was followed. The following solutions containing (i) 0.15 M HClO_4 , (ii) $0.15 \text{ M HClO}_4 + 0.005 \text{ M}$ phytic acid and (iii) HClO_4 containing metal ions (0.005 M) + 0.005 M phytic acid were titrated against standard sodium hydroxide solution (0.192 M). The volume in each set was kept at 50 ml by suitable dilutions and ionic strength was maintained at 0.1 M using 1 M NaClO_4 solution. The approximate values of proton-ligand stability constants, pK_Y^H were obtained by pointwise calculations at respective pH and $\bar{n}_A$ values, the proton-ligand formation number.

The hydrolysis of metal ions was prevented by working with solutions in low pH range. From the titration curves, the metal-ligand formation number $\bar{n}$, the free ligand exponent, pL and finally the metal-ligand stability constants, the $\log K$ values were calculated.

Results and discussion

Since a change in temperature does not affect the dissociation and stability constant of phytic acid

Table 1—Proton-ligand stability constants for phytic acid
(Temp : $25^\circ \pm 1^\circ \text{C}$; $\mu = 0.1 \text{ M NaClO}_4$)

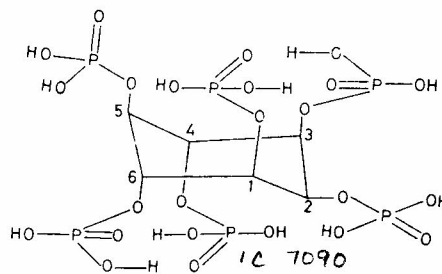
Y	pK_Y^H	pH range
2	1.20	1.1-1.8
3	2.48	2.0-2.4
4	2.82	2.5-2.9
5	3.43	3.0-3.4
6	3.89	3.5-3.9
7	4.36	4.0-4.4
8	4.88	4.5-4.9
9	6.03	5.0-6.65
10	8.03	6.8-8.15
11	8.40	8.3-9.75
12	10.60	10.0-11.0

Table 2—Stability constant ($\log K$) values of lanthanide complexes with phytic acid
(Temp : $25 \pm 1^\circ\text{C}$; $\mu = 0.1\text{ M NaClO}_4$)

Metal ion	pH									
	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
Ce ³⁺	7.06	5.90	5.41	4.97	4.51	4.01	3.53	2.9	2.45	1.92
Pr ³⁺	—	6.08	5.64	5.28	4.87	4.41	3.94	3.31	2.80	2.28
Nd ³⁺	7.85	6.29	5.73	5.26	4.75	4.26	3.77	3.14	2.65	2.14
Sm ³⁺	7.48	6.40	5.93	5.45	4.99	4.50	4.00	3.37	2.88	2.36
Gd ³⁺	8.82	6.22	5.73	5.34	4.90	4.41	3.94	3.32	2.84	2.33
Tb ³⁺	8.27	6.43	5.88	5.44	4.96	4.46	4.00	3.36	2.86	2.35
Dy ³⁺	8.61	6.40	5.88	5.47	5.00	4.51	4.01	3.39	2.88	2.36
Ho ³⁺	8.82	6.40	5.94	5.47	5.17	4.51	4.02	3.39	2.90	2.39

significantly, all experiments were carried out at 25°C . Phytic acid acts as a quasi-diprotic acid when titrated with standard sodium hydroxide. It is due to the presence of two dissociable protons on each phosphate group that behaves as individual entity. The charges developed on various species in solution lie on the concerning phosphate groups because phytate ion as a whole is too big to be regarded as a point charge.

The conflicting results on the ionization of phytic acid have been reported. Barre⁵ deduced that six protons were very acidic (pK_a 1.4-1.8), two protons were weakly acidic (pK_a 6.3) and rest of the four protons very weakly acidic (pK_a 9.7). On the other hand, Costello⁶ reported six protons as very strongly acidic, three weakly acidic and three very weakly acidic. Their results were based on the inflection points in the pH Vs δ (^{31}P) curves for different phosphate groups. We represent pK_a as pK_Y^H which shows the extent of binding of protons to phytic acid where Y is the total number of protons dissociated. It was found that lesser the value for pK_Y^H , the greater is the dissociation of proton (or the lesser the proton-phytic acid stability), while higher value for pK_Y^H shows firm proton-phytic acid association. Surprisingly, a large variation is seen in these values reported by other workers¹¹. It is observed from our results (Table 1) that two protons are very highly acidic which are released at pH 1.5 ± 0.3 (pK_2^H 1.2). The other six protons dissociate in the pH range 2.0-4.8 (pK_3^H 2.48- pK_8^H 4.88), two protons in the pH range 5.0-8.0 (pK_9^H 6.03- pK_{10}^H 8.03) and last two protons being very weakly acidic are released between pH 8.3-11.0 (pK_{11}^H 8.4- pK_{12}^H 10.6). On the basis of these findings, structure (I) of phytic acid has been suggested which is in accordance with the observation made by Emsley and Niazi⁷. This conformation exists in the pH range 5.0-11.0.



It has been reported^{8,9} that in the complexation reaction of phytic acid with Ca(II), Zn(II) and Cu(II) ions as a function of pH, the metal to phytic acid ratio is 5:1, 4:1 and 6:1 respectively. The Ni(II) and Co(II) metal ions bind in the ratio 6:1. It has also been reported¹⁰ that Cu(II) binds more readily than Zn(II). However, our investigations show that there is weak complexation in 1:1 ratio between phytic acid and lanthanide³⁺ ions as reflected from $\bar{n}$ values. The stability of these complexes decreased with an increase in pH (Table 2). The results indicate the interference of increasing sodium ion concentration in the complexation of phytic acid with rare earth ions. The phytate ion containing 18 active donor oxygen atoms¹¹, is a hard base and preferably complexes with sodium ions, reduce the availability of phytic acid for complexation with the lanthanide ions. The calculated stability constants as well as the thermodynamic parameters (ΔG) show that stability of complexes follows the series, $\text{Ho}^{3+} > \text{Dy}^{3+} > \text{Tb}^{3+} > \text{Sm}^{3+} > \text{Gd}^{3+} > \text{Nd}^{3+} > \text{Pr}^{3+} > \text{Ce}^{3+}$.

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