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HEATS OF PRECIPITATION OF ZINC PHYTATE

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We respectfully dedicate this paper to Professor Eraldo Antonini, Institute of Chemistry, Faculty of Medicine and Surgery, University of Rome, in memory of his outstanding human and scientific qualities which we had the fortune to experience.

ABSTRACT

The heat of precipitation for the reaction of zinc ion with the phytate ion in aqueous solution has been determined. The reaction is endothermic. From the value of the equilibrium constant associated with the reaction, the entropy change has been calculated. The entropy change is large and positive. This is consistent with the view that when zinc reacts with phytate to form solid zinc phytate there is an increase in the number of particles in the system.

INTRODUCTION

The nutritional importance and effect of phytic acid, myo-inositol 1,2,3,5/4,6 hexakis(dihydrogen phosphate), on the bioavailability of various essential metal ions has been the subject of several recent papers [1–3]. The structure of phytic acid proposed by Anderson [4] is apparently the most likely choice [5–7]. As such, only twelve of the total of eighteen hydrogens are titratable [8].

The interaction between phytic acid and mineral ions to form insoluble complexes appears to be the major factor responsible for the adverse nutritional effects observed in high-phytate diets. There is substantial evidence that soluble phytate added to purified diets decreases zinc availability [9–12]. Recent studies indicate that zinc may be necessary for the development of effective disease resistance in higher animals and possibly man [13,14].

In vitro studies indicate that zinc forms the most stable (insoluble) complex with phytic acid [15]. In studies recently completed on the interaction of zinc ion with phytic acid in aqueous solution, analysis of the solid products resulting from this interaction indicated four zinc and three potassium ions combined per phytate when the phosphorus : zinc mole ratio was 6 : 1 in the reaction mixture [16]. In the present work, heats of reaction between zinc ion and the phytate ion, in aqueous solution, have been determined calorimetrically. The reaction has been studied according to eqn. (1)

$$\mathrm{Phy}^{9-}_{(aq)} + 4\ \mathrm{Zn}^{2+}_{(aq)} + 3\ \mathrm{K}^{+}_{(aq)} \rightleftharpoons \mathrm{Zn_4K_3Phy} \cdot x\ \mathrm{H_2O}_{(s)} + y\ \mathrm{H_2O} + 2\ \mathrm{H}^{+} \qquad (1)$$

where Phy^{-9} represents the phytate ion with nine negative charges.

EXPERIMENTAL

Phytic acid was prepared as described elsewhere [8]. All other reagents used were analytical grade. Zinc determinations were made by atomic absorption spectrophotometry whereas phosphorus content was determined by the method of Fiske and Subbarow [17], from which the total phytate concentration was calculated. The calorimetric experiments were carried out in a microcalorimeter, the construction and uses of which have been described previously [18–20].

The experimental procedure involved first forming the phytate anion by the interaction of phytic acid with the appropriate amount of potassium hydroxide and potassium chloride [8]. The resulting solution was 0.001 M in phytate, 0.2 M in KCl and had a pH of 7.58 at 25°C. To 3.955 ml of this solution in the calorimeter was added 0.289 ml of 0.0137 M zinc sulfate solution, 0.2 M in KCl, whereupon the zinc phytate (hydrate) precipitated from solution. The phosphorus : zinc mole ratio on mixing, but before reaction, was 6 : 1. The pH of the solutions from the calorimetric experiments was measured and then the solutions were centrifuged and the supernatants analyzed for their phosphorus and zinc content.

RESULTS AND DISCUSSION

The results of the calorimetric experiments are listed in Table 1. The dilution heat of the zinc solution was compensated by adding 0.289 ml of the zinc solution to approximately 4 ml of 0.2 M KCl in the tare cell of the calorimeter. The dilution heat of the phytate solution was negligible as determined by experiment. It should perhaps be mentioned that pH 6 is the

TABLE 1

Heat of precipitation of zinc phytate at 25°C
Initial pH = 7.58 (3.955 μmole phytic acid reacted with 3.959 μmole $ZnSO_4$)

$[Zn]_{final}$ $(M \times 10^4)$	$[Phy.\ acid]_{final}$ $(M \times 10^4)$	final pH	Q_{exp} (mcal)	$Q_{corr.}$ (mcal)	Mole Zn / Mole phy. acid	ΔH^0 (kcal mole^{-1})
1.40	7.30	5.89	39.5	20.5	3.9	23.9
1.41	7.30	5.86	39.8	20.8	3.9	24.3
1.35	7.30	5.87	39.8	20.8	4.0	24.3
1.38	7.30	5.86	39.7	20.7	3.9	24.2
1.38	7.30	5.86	39.2	20.2	3.9	23.6
1.40	7.30	5.87	38.9	19.9	3.9	23.2
1.43	7.30	5.89	39.4	20.4	3.9	23.8
		5.87 ± 0.01				23.90 ± 0.41

approximate pH of the duodenum where most of the absorption of divalent cations occur [21].

As shown in Table 1, when zinc ion is added to a phytate solution at pH 7.58 there is a substantial drop in pH when the zinc reacts with phytate to form the insoluble zinc phytate complex. This drop in pH is associated with the ionization of hydrogens from the phytate ion when it complexes with zinc. At pH 7.58 there are initially an average of 8.6 hydrogens ionized [8]. Of the remaining unionized hydrogens, approximately 2.4 must have ionized in order for the zinc phytate complex to have formed according to eqn. (1). The heat of ionization of these groups is approximately 2 kcal mole^{-1} [22]. This correction has been applied to the experimental heats in column 4 of Table 1 to yield the corrected experimental values in column 5. The ΔH values are per mole of phytic acid. On the other hand, the average ΔH value per mole of zinc is 6.08 ± 0.10 kcal.

From the data recorded in Table 1, it is possible to calculate a solubility product constant. In order to do so it is necessary to know the concentration of the phytate ion with eleven negative charges. The total phytate concentration is determined analytically and the ratio, (phytate ion with eleven negative charges)/(total phytate concentration), can be calculated by use of the ionization constants of phytic acid. From a consideration of mass balance and the various ionization constants it can be shown that this ratio is given by

$$\frac{[\mathrm{Phy}^{11-}]}{[\mathrm{Phy_T}]} = \frac{K_5 K_6 K_7 \ldots K_{11}\left(1/[H^+]^{11}\right)}{\left(1/[H^+]^4\right) + \left(K_5/[H^+]^5\right) + \left(K_5 K_6/[H^+]^6\right) \ldots + \left(K_5 K_6 \ldots K_{12}/[H^+]^{12}\right)} \quad (2)$$

At the final pH listed in Table 1 the first four ionization constants can be disregarded in the calculation of this ratio [23].

By means of eqn. (2) and the average concentrations shown in Table 1, the following values were obtained for the components in solution of reaction (1): $-\log[\mathrm{Phy}^{11-}] = 12.821$, $-\log[\mathrm{Zn}^{2+}] = 3.857$. The K^+ concentration is essentially the same before and after reaction and was calculated to be $-\log [K^+] = 0.712$. From these quantities and the relation

$$[\mathrm{Zn}^{2+}]^4[\mathrm{K}^+]^3[\mathrm{Phy}^{11-}] = K_s \tag{3}$$

a value of $-\log K_s = 30.4$ is obtained.

As is shown in Table 1, the heat production when zinc ion reacts with the phytate ion is an endothermic process. The ΔG^0 value corresponding to reaction (1) is -41.5 kcal mole^{-1}. From

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{4}$$

ΔS^0 is calculated to be 220 e.u.

Although enthalpy changes have been taken as a measure of metal–ligand bond strength in the formation of chelates in the solvated state, it would seem that the high stability towards dissociation of the solid zinc phytate to aqueous ions is due solely to the favorable entropy increase accompanying the formation of the solid. The entropy increase is probably a consequence of the increase in the number of particles in the system. Both the metal cation and the phytate ion are undoubtedly hydrated in solution. Most of the bound water would be released into the body of the solution when the solid zinc phytate is formed. Interestingly enough, it has recently been shown that the reaction between the Mg^{2+} ion and 2,3-diphosphoglycerate ($\log K = 4.4$) is an endothermic process. There is a sizeable entropy increase, $\Delta S = +36.4$ e.u., which has been attributed to the release of water from the solvation sphere when the complex is formed [24].

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