

A thermodynamic study of struvite + water system

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Abstract

Equilibrium analysis of the system with $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite) is taken as an interesting example of two-phase system where a change in solid phase composition (conversion) is affected by hydrolytic phenomena. The problem is presented in a comprehensive manner, based on results obtained from calculations made according to iterative computer program. The complex nature of phenomena occurred, with side effects resulting from presence of carbonate species, is explained. The analytical and physicochemical aspects of the matter are considered. © 2005 Published by Elsevier B.V.

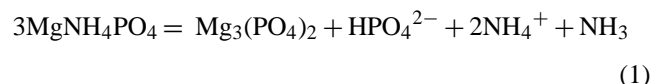
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1. Introduction

Magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is among the most important phosphates involved in urinary stone disease [1–3]. It precipitates from human urine as a result of metabolic disorders [4–6], affected e.g. by (ubiquitous) bacteria producing urease [7–9]. It was found first by Wollaston [10] in the kidney stones. Later on, Ulex discovered it in guano and called struvite, on behalf of his friend, von Struve [11,12]. Struvite also encrusts as a hard crystalline deposit during wastewater (sludge) flowing through pipes, aerators, pumps, etc. [13–15]. The earliest description of infection stones (struvite) was found in a grave mound in Hungary from the late Bronze Age [16].

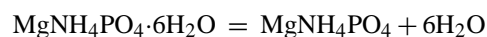
Long before now, it was stated [17] that pure (washed) struvite when introduced into pure water is not a stable solid phase and ammonia is evolved from the solution at room and (more intensely) at elevated temperatures. This fact should be taken into account when washing this precipitate for gravimetric analysis purposes. As will be proven below, pure preparation of struvite when introduced into pure water or into water containing dissolved CO_2 , undergoes the

transformation into $\text{Mg}_3(\text{PO}_4)_2$, according to the reaction notation:



where predominating (at pH ca. 9–9.5) species are involved.

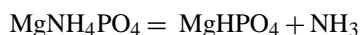
The precipitation of an analyte for quantitative (gravimetric) analysis purposes is always performed with an excess of precipitating reagent(s). Particularly, the struvite precipitation from magnesium salt solution may proceed by addition of an excess of NH_4Cl solution followed by addition of an excess of K_2HPO_4 solution. Adding the reagents in reverse sequence may cause local formation of ‘inappropriate’ precipitate, i.e., $\text{Mg}_3(\text{PO}_4)_2$, that contaminates the desired (from analytical viewpoint) struvite precipitate – even if the final pH of the solution lies within pH – interval related to struvite as the equilibrium solid phase; namely dissolution of the non-equilibrium precipitates, formed in earlier steps, proceeds slowly and incompletely, as a rule. If the resulting precipitate does not consist of pure struvite then, when roasted, it does not form the preparation of pure pyrophosphate salt, as suggested [18,19] by the successive reactions occurred at growing temperatures:



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Nomenclature

K_{sp1}	solubility product for pr1 (Eq. (2))
K_{sp2}	solubility product for pr2
[pr1]	concentration of pr1 = $MgNH_4PO_4$
[pr2]	concentration of pr2 = $Mg_3(PO_4)_2$



owing to the fact that the molar ratio Mg:P, equal to 3:2 in $Mg_3(PO_4)_2$, is different from 2:2 = 1:1 due to $Mg_2P_2O_7$, formed after roasting of the pure struvite (Mg:P = 1:1) at 600 °C [19].

The struvite has been studied from different viewpoints and its chemical and physical properties were described. Amongst others, pH and the solution composition were measured during the struvite precipitation and dissolution, also in recent years [20–24]. In the present paper, the instability of pure struvite in pure water and in presence of carbon dioxide dissolved in water is examined thoroughly. To provide a detailed description of this system, with all attainable physicochemical data involved, the calculating procedure [25], based on the iterative computer program,¹ written in DELPHI language, is applied. Some erroneous approaches to the matter in question are indicated and discussed.

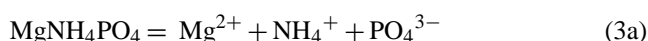
2. Physicochemical data

According to literature data [20–22,26], four possible magnesium phosphate species can crystallize from solutions containing magnesium, ammonia and phosphate species: magnesium ammonium phosphate hexahydrate (struvite, $MgNH_4PO_4 \cdot 6H_2O$), magnesium hydrogen phosphate trihydrate (newberyite, $MgHPO_4 \cdot 3H_2O$) and trimagnesium phosphate in two states of hydration: $Mg_3(PO_4)_2 \cdot 22H_2O$ and $Mg_3(PO_4)_2 \cdot 8H_2O$ (bobierrite) [22].

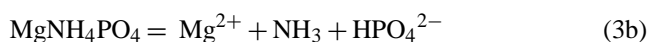
The principal physicochemical data, involved with the solubility of struvite in waters, is the solubility product (K_{sp1}):

$$[Mg^{2+}][NH_4^+][PO_4^{3-}] = K_{sp1} \quad (2)$$

referred to reaction



although, e.g. an alternate reaction notation:



represented by solubility product $K_{sp1'} = [Mg^{2+}][NH_3][HPO_4^{2-}]$ may also be considered, $K_{sp1'} = K_{sp1} k_{1N}/k_3$, where $k_{1N} = [H^+][NH_3]/[NH_4^+]$, $k_3 = [H^+][PO_4^{3-}]/[HPO_4^{2-}]$. As will be stated later, the K_{sp1} (or $K_{sp1'}$) is applicable in such systems only under assumption that some additional requirements are fulfilled.

There is a diversity in $pK_{sp1} = -\log K_{sp1}$ values reported in literature, ranging from 12.36 to 13.26 [14]; the most frequently cited value is $pK_{sp1} = 12.60$ [23]. Similar diversities refer also some other physicochemical data [22,23,27] involved in the set of 20 algebraic relationships collected in Eq. (4):

$$\begin{aligned} [HPO_4^{2-}] &= 10^{12.36}[H^+][PO_4^{3-}] \\ [H_2PO_4^-] &= 10^{19.56}[H^+]^2[PO_4^{3-}] \\ [H_3PO_4] &= 10^{21.6}[H^+]^3[PO_4^{3-}] \\ [HCO_3^-] &= 10^{10.33}[H^+][CO_3^{2-}] \\ [H_2CO_3] &= 10^{16.71}[H^+]^2[CO_3^{2-}] \\ [NH_4^+] &= 10^{9.24}[H^+][NH_3] \\ [MgOH^+] &= 10^{2.57}[Mg^{2+}][OH^-] \\ [MgH_2PO_4^+] &= 10^{0.45}[Mg^{2+}][H_2PO_4^-] \\ [MgHPO_4] &= 10^{2.91}[Mg^{2+}][HPO_4^{2-}] \\ [MgPO_4^-] &= 10^{4.8}[Mg^{2+}][PO_4^{3-}] \\ [MgNH_3^{2+}] &= 10^{0.24}[Mg^{2+}][NH_3] \\ [Mg(NH_3)_2^{2+}] &= 10^{0.2}[Mg^{2+}][NH_3]^2 \\ [Mg(NH_3)_3^{2+}] &= 10^{-0.3}[Mg^{2+}][NH_3]^3 \\ [MgCO_3] &= 10^{3.4}[Mg^{2+}][CO_3^{2-}] \\ [MgHCO_3^+] &= 10^{1.16}[Mg^{2+}][HCO_3^-] \\ K_{sp1} &= [Mg^{2+}][NH_4^+][PO_4^{3-}] = 10^{-12.6} \\ K_{sp2} &= [Mg^{2+}]^3[PO_4^{3-}]^2 = 10^{-24.38} \\ K_{sp3} &= [Mg^{2+}][OH^-]^2 = 10^{-10.74} \\ K_{sp4} &= [Mg^{2+}][CO_3^{2-}] = 10^{-5.17} \\ K_{sp5} &= [Mg^{2+}][HPO_4^{2-}] = 10^{-5.5} \\ [H^+][OH^-] &= 10^{-14.0} \end{aligned} \quad (4)$$

and applied in calculations made in further parts of the paper. At pH < 4, where H_2CO_3 predominates distinctly over other carbonate species in aqueous solution, one can apply the relation:

$$[H_2CO_3] = 10^{-1.43}p(CO_2) \quad (5)$$

where $p(CO_2)$ is the CO_2 pressure (atm). In this case, one can be assumed that aqueous solutions are open to atmospheric carbon dioxide, with partial pressure $p(CO_2) = 10^{-3.5}$ (atm) [28]. However, the contents of CO_2 dissolved in alka-

¹ Attainable on request.

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