

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.

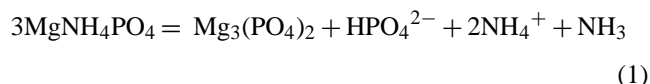
Keywords: Analytical chemistry; Equilibrium analysis; Phase equilibria; Magnesium phosphates

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].

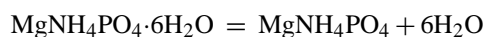
Long before now, it was stated [17] that pure (washed) struvite when introduced into pure water is not a stable solid phase and ammonia is evolved from the solution at room and (more intensely) at elevated temperatures. This fact should be taken into account when washing this precipitate for gravimetric 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.

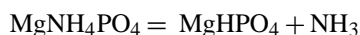
The precipitation of an analyte for quantitative (gravimetric) analysis purposes is always performed with an excess of precipitating reagent(s). Particularly, the struvite precipitation from magnesium salt solution may proceed by addition of an excess of NH_4Cl solution followed by addition of an excess 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.

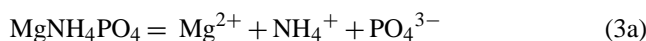
2. Physicochemical data

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].

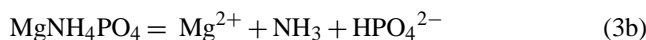
The principal physicochemical data, involved with the solubility of struvite in waters, is the solubility product (K_{sp1}):

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

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.

line (e.g. at pH 9–9.5) media (mainly as HCO_3^- and CO_3^{2-}) exceeds the value $10^{-1.43} \times 10^{-3.5} \approx 10^{-5}$ mol/l calculated from (5). On the other hand, the solubilities of NaHCO_3 and Na_2CO_3 in water exceed 1 mol/l at 20 °C [29]. The pH-values for 1 mol/l NaHCO_3 and Na_2CO_3 are ca. $16.71/2 \approx 8.4$ and $(14 + 10.33)/2 \approx 12.2$, respectively. Any alkaline solution, e.g. NaOH , is gradually ‘enriched’ by carbonates in open systems where total concentration of carbonates may significantly (ca. 10^5 times) exceed the value resulting from partial pressure of CO_2 and Eq. (5).

3. Optimising procedure

The optimising procedure is based on the set of equations consisting the charge and concentration balances (6)–(10) specified below and interrelations (Eq. (4)) between different species expressed by formulae for the corresponding equilibrium constants. All attainable physicochemical knowledge is involved in there and none approximating assumptions are needed.

We refer first to a closed system, with condensed phases (solution or solution + solid phase) bordered by diathermal walls (isothermal processes are assumed). The balances related to the system obtained after introducing $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ into water with CO_2 (C_{CO_2} mol/l) dissolved in it, one can write as follows:

$$\begin{aligned} f1 = & [\text{pr}1] + 3[\text{pr}2] + [\text{Mg}^{2+}] + [\text{MgOH}^+] \\ & + [\text{MgH}_2\text{PO}_4^+] + [\text{MgHPO}_4] + [\text{MgPO}_4^-] \\ & + [\text{MgNH}_3^{2+}] + [\text{Mg}(\text{NH}_3)_2^{2+}] + [\text{Mg}(\text{NH}_3)_3^{2+}] \\ & + [\text{MgHCO}_3^+] + [\text{MgCO}_3] - C_0 = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} f2 = & [\text{pr}1] + [\text{NH}_4^+] + [\text{NH}_3] + [\text{MgNH}_3^{2+}] \\ & + 2[\text{Mg}(\text{NH}_3)_2^{2+}] + 3[\text{Mg}(\text{NH}_3)_3^{2+}] - C_0 = 0 \end{aligned} \quad (7)$$

$$\begin{aligned} f3 = & [\text{pr}1] + 2[\text{pr}2] + [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] \\ & + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] + [\text{MgH}_2\text{PO}_4^+] \\ & + [\text{MgHPO}_4] + [\text{MgPO}_4^-] - C_0 = 0 \end{aligned} \quad (8)$$

$$\begin{aligned} f4 = & [\text{H}^+] - [\text{OH}^-] + [\text{NH}_4^+] + 2[\text{Mg}^{2+}] \\ & + [\text{MgOH}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] \\ & + [\text{MgH}_2\text{PO}_4^+] - [\text{MgPO}_4^-] + [\text{MgHCO}_3^+] \\ & + 2[\text{MgNH}_3^{2+}] + 2[\text{Mg}(\text{NH}_3)_2^{2+}] + 2[\text{Mg}(\text{NH}_3)_3^{2+}] \\ & - [\text{H}_2\text{PO}_4^-] - 2[\text{HPO}_4^{2-}] - 3[\text{PO}_4^{3-}] = 0 \end{aligned} \quad (9)$$

$$\begin{aligned} f5 = & [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{MgHCO}_3^+] \\ & + [\text{MgCO}_3] - C_{\text{CO}_2} = 0 \end{aligned} \quad (10)$$

where C_0 (mol/l) is the total concentration of struvite (pr1) introduced (at $t=0$) into the system, [pr1] is the concentration of pr1 at time t , [pr2] is the concentration of $\text{Mg}_3(\text{PO}_4)_2$, denoted later as pr2, for brevity. In order to simplify the mechanism of phenomena occurred, i.e., to omit diffusion processes, the system is (virtually) mixed thoroughly.

In the optimisation procedure, a choice of a set of independent (fundamental) variables x_i is needed. It is generally advised to choose $x_i = \text{p}X_i = -\log [X_i]$ values for molar concentrations $[X_i]$ of the species X_i involved; it provides higher standard of optimisation efficiency. This results from the fact that the concentration $[X_i] = 10^{-x_i}$ cannot assume negative (i.e., unreal) values for concentrations at any step of optimisation procedure, i.e., $[X_i] > 0$ at any (real) value of the variable x_i considered, i.e., $y = 10^{-x} > 0$ at any real x -value ($x \in \mathfrak{R}$). None further limitations are needed in this case. The optimising procedures are of general nature, after all; they are not designed only for resolution of chemical systems, where the assumption $[X_i] \geq 0$ put on concentrations is an evident limitation. In this paper, the optimising procedure, made according to Marquardt–Levenberg procedure [30,31] has been applied.

The number of independent variables x_i equals to the number of balances involved. Particularly, for the system described by five balances expressed by Eqs. (6)–(10), five independent variables: $x_1 = \text{pMg}$, $x_2 = \text{pNH}_4$, $x_3 = \text{pHPO}_4$, $x_4 = \text{pH}$ and $x_5 = \text{pHCO}_3$ were applied at the start of struvite (pr1) dissolution, i.e., at the starting point for the optimisation procedure based on the iterative computer program.

It is generally advised to choose pH and $\text{p}X_i$ for the predominating species X_i , at the start for optimisation procedure. The main reason of it results from practical purposes; simply, it is easier to suggest starting values for such variables in the optimising procedure.

The systems where $C_{\text{CO}_2} = 0$ (i.e., $\text{p}C_{\text{CO}_2} = \infty$) were also considered, for comparison. In absence of carbonates, the set of modified balances (6)–(9) was taken into account, i.e., Eq. (10) and all the species involving carbonates were omitted in balances (6) and (9). In such a case, the set of four variables $x_1 = \text{pMg}$, $x_2 = \text{pNH}_4$, $x_3 = \text{pHPO}_4$, $x_4 = \text{pH}$ has been chosen at the starting point for optimisation procedure.

In both instances (i.e., $C_{\text{CO}_2} > 0$ and $C_{\text{CO}_2} = 0$), the variables $\text{ppr}2 = -\log [\text{pr}2]$ or $\text{ppr}1 = -\log [\text{pr}1]$, related to the current concentration of pr2 or pr1 in the system, have been taken as the steering variables. This results from the fact that pr1, as the dissolving species, affects the solution composition.

The criterion for optimisation at $C_{\text{CO}_2} > 0$ has been expressed by the sum of squares $\text{SS} = \sum_{i=1}^5 (fi)^2$, where fi ($i = 1, \dots, 5$) were expressed by Eqs. (6)–(10). At $C_{\text{CO}_2} = 0$, the sum of squares $\text{SS} = \sum_{i=1}^4 (fi)^2$ has been taken as the function optimised, applied for the modified balances (6)–(9).

At any stage of the dissolution process, the concentrations of all the species involved in the balances (speciation) and

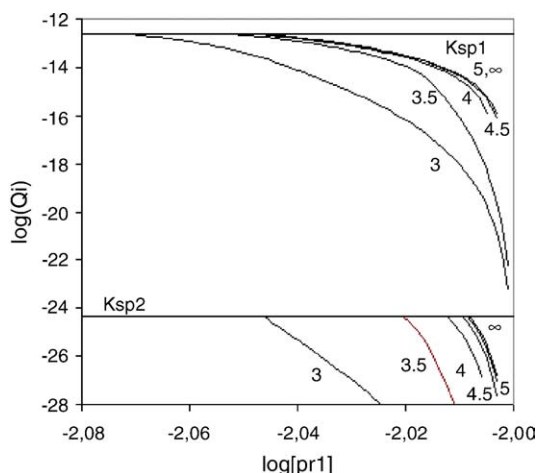


Fig. 1. The plots of $\log Q_1$ and $\log Q_2$ vs. $\log [\text{pr}1]$ relationships and the levels corresponding to $\log K_{\text{sp}1} = -12.6$ and $\log K_{\text{sp}2} = -24.38$ at different $\text{p}C_{\text{CO}_2} = -\log C_{\text{CO}_2}$ values indicated at the lines.

the solubility:

$$s = [\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{MgH}_2\text{PO}_4^+] + [\text{MgHPO}_4] + [\text{MgPO}_4^-] + [\text{MgNH}_3^{2+}] + [\text{Mg}(\text{NH}_3)_2^{2+}] + [\text{Mg}(\text{NH}_3)_3^{2+}] + [\text{MgHCO}_3^+] + [\text{MgCO}_3] \quad (11a)$$

$$s = [\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{MgH}_2\text{PO}_4^+] + [\text{MgHPO}_4] + [\text{MgPO}_4^-] + [\text{MgNH}_3^{2+}] + [\text{Mg}(\text{NH}_3)_2^{2+}] + [\text{Mg}(\text{NH}_3)_3^{2+}] \quad (11b)$$

can be calculated on the basis of the optimised variables x_i considered; Eq. (11a) refers to $C_{\text{CO}_2} > 0$ whereas (11b) refers to $C_{\text{CO}_2} = 0$.

In the optimisation procedure, the possibility of formation of $\text{Mg}(\text{OH})_2$, MgCO_3 (in solutions containing carbonate species) and MgHPO_4 precipitates has also been taken into account. For this purpose, the values for $Q_1 = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}]$ and $Q_2 = [\text{Mg}^{2+}]^3[\text{PO}_4^{3-}]^2$ were 'peered' (Fig. 1) and the values for $Q_3 = [\text{Mg}^{2+}][\text{OH}^-]^2$, $Q_4 = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$ and $Q_5 = [\text{Mg}^{2+}][\text{HPO}_4^{2-}]$ were 'peered', too to confirm that such solid species are not formed in the system. In all instances it was stated that $Q_3 < K_{\text{sp}3}$, $Q_4 < K_{\text{sp}4}$, and $Q_5 < K_{\text{sp}5}$. At $\text{p}C_0 = 3$ and $\text{p}C_{\text{CO}_2} \geq 2$, or at $\text{p}C_0 = 2$ and $\text{p}C_{\text{CO}_2} > 2.012$, the $K_{\text{sp}5}$ value for pr5 (i.e. MeHPO_4 precipitate) is not attained, $Q_5 < K_{\text{sp}5}$. At $\text{p}C_{\text{CO}_2} < 2.012$, pr5 precipitates. At $\text{p}C_0 = 2$, $\text{p}C_{\text{CO}_2} = 2$, pr5 precipitates at $\text{ppr}1 \in < 2.376, 2.506 >$. At $\text{p}C_0 = 2$ and $\text{p}C_{\text{CO}_2} = 1.5$, pr1 transforms totally into pr5, $\text{pr}1 = \text{pr}5 + \text{NH}_3$; the transformation occurs at $\text{ppr}1 > 2.888$.

At the start for dissolution, the value $[\text{pr}2] = 0$ has been assumed in Eqs. (6) and (8) and $\text{ppr}1 = -\log [\text{pr}1]$ has been taken as the steering variable. Later on, when the solubility product for pr2 has been attained, $Q_2 = K_{\text{sp}2}$, $x_1 = \text{ppr}2 = -\log [\text{pr}2]$ has been taken as the

new variable put instead of $x_1 = \text{pMg}$ and the relation $[\text{Mg}^{2+}] = (10^{-24.38}/[\text{PO}_4^{3-}]^2)^{1/3}$ was launched.

For $C_0 = 10^{-3}$ and $C_{\text{CO}_2} = 10^{-4}$, the calculation procedure has been terminated at the point of total pr1 depletion. At $C_{\text{O}_2} = 10^{-2}$ and $C_{\text{CO}_2} = 10^{-4}$, the dissolution of pr1 has been stopped at the point where the solubility product for pr1 has been crossed, $Q_1 = K_{\text{sp}1}$.

The changes in speciation and in the solubility s of struvite (Eqs. (11a) and (11b)) during pr1 dissolution were registered at different C_0 and C_{CO_2} values. Moreover, a decrease in concentration of pr1 involved with a growth in concentration of pr2, expressed by the formula:

$$\vartheta = -\frac{d[\text{pr}1]}{d[\text{pr}2]} \quad (12)$$

was also evidenced as a function of $\log [\text{pr}2]$.

4. Struvite properties in aqueous systems

The dissolution of struvite is an interesting example of a dynamic process similar – from formal viewpoint – to the generation of a reagent in coulometry. In this case, the dissolution can be realised at (practically) constant volume of the two-phase system. Note that the volume of struvite ($M = 227.3 \text{ g/mol}$, $d = 1.7 \text{ g/cm}^3$ [32]) equals ca. 1.3 cm^3 at the concentration $C_0 = 10^{-2} \text{ mol/l}$ assumed, i.e., the change in volume of the system resulted from pr1 dissolution is ca. 0.1%. At $C_0 = 10^{-3} \text{ mol/l}$, the volume change of the system equals ca. 0.01%. It justifies the assumption that the phase transformation proceeds practically at constant volume of the system. This assumption is important in light of the fact that concentrations of solid phases (pr1 and pr2) are calculated against the volume of the system whereas concentrations of soluble species are calculated against the solution volume.

The data obtained from calculations based on iterative computer program can be summarised as follows.

- The solubility product for pr2 is crossed first (Fig. 1), i.e., $Q_2 = K_{\text{sp}2}$ refers to the greater value for $[\text{pr}1]$ whereas $Q_1 = K_{\text{sp}1}$ is attained at a lower $[\text{pr}1]$ value, i.e., at a more advanced step of pr1 dissolution.
- Fig. 2 indicates that, at $C_0 = C_{\text{CO}_2} = 10^{-2}$, i.e., $(\text{p}C_0, \text{p}C_{\text{CO}_2}) = (2, 2)$, we have $Q_1 < K_{\text{sp}1}$, i.e., the solubility product for pr1 is not crossed. At $C_0 = 10^{-2}$ and $C_{\text{CO}_2} < 10^{-3}$ (particularly at $C_0 = 10^{-2}$ and $C_{\text{CO}_2} = 0$), $K_{\text{sp}1}$ value is crossed after partial dissolution of pr1 at $\text{ppr}2 = -\log [\text{pr}2] = 2.743$ (with accuracy to the third decimal point). This means that at $C_0 = 10^{-2}$ and $C_{\text{CO}_2} < 10^{-3}$, the precipitation of pr2 has been stopped at the point where a part of pr1 remained undissolved. At this point, the equalities for the solubility products (i.e., $K_{\text{sp}1}$ and $K_{\text{sp}2}$) are fulfilled simultaneously, $Q_1 = K_{\text{sp}1}$ and $Q_2 = K_{\text{sp}2}$. At $C_0 = 10^{-3}$, pr1 is transformed into pr2 and $K_{\text{sp}1}$ is not crossed, i.e., $Q_1 < K_{\text{sp}1}$. This means that the processes occurred in the system (e.g. the phase

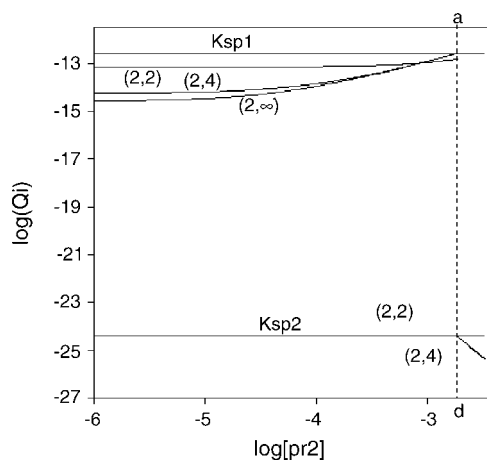
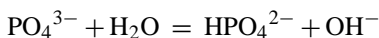


Fig. 2. The plots of $\log Q_1$ vs. $\log [\text{pr}2]$ (upper family of curves) and $\log Q_2$ (lower curve) vs. $\log [\text{pr}2]$ relationships referred to $C_0 = 10^{-2}$ (i.e., $pC_0 = 2$) and indicated pC_{CO_2} values: 2, 4 and ∞ (i.e., $C_{\text{CO}_2} = 0$). The points related to $Q_i > K_{\text{sp}i}$ ($i = 1, 2$) are omitted. The curves for $\log Q_2$ vs. $\log [\text{pr}2]$ relationship referred $pC_{\text{CO}_2} = 2, 4$ and ∞ practically overlap. The line ad corresponds to the line ad in Fig. 3.

composition) depend, to some degree, on C_0 and C_{CO_2} values.

- At $C_0 = 10^{-2}$ and $C_{\text{CO}_2} = 0$, on the first stage of pr1 dissolution, i.e., at $[\text{pr}2] = 0$, concentrations of ions emitted into the solution in the reaction (3a) grow gradually; a part of them reacts with water forming new species, e.g.



or mutually, e.g. $\text{Mg}^{2+} + \text{PO}_4^{3-} = \text{MgPO}_4^-$. Before the solution becomes saturated towards pr1 (i.e., before the solubility product $K_{\text{sp}1}$ for pr1 is attained), the solubility product for pr2 is crossed and precipitation of pr2 starts, $[\text{pr}2] > 0$. Gradual precipitation of pr2 occurs from the solution saturated towards pr2. Simultaneously, this solution is still undersaturated towards pr1 that dissolves gradually, satiating the solution towards pr2; it enables further amounts of pr2 to be formed. Then concentrations of the species HPO_4^{2-} and NH_4^+ , liberated in reaction (1),

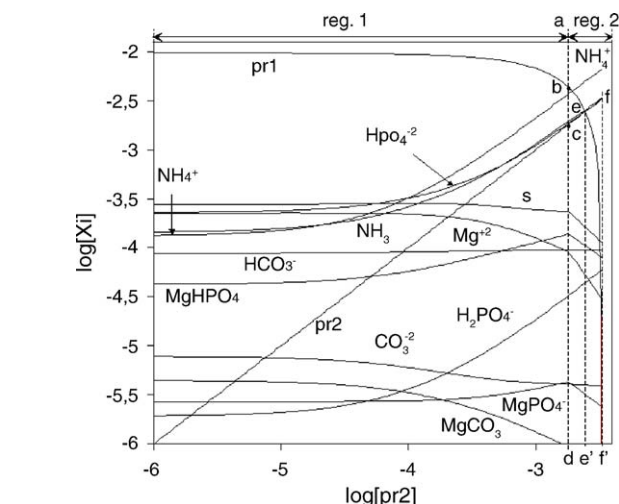
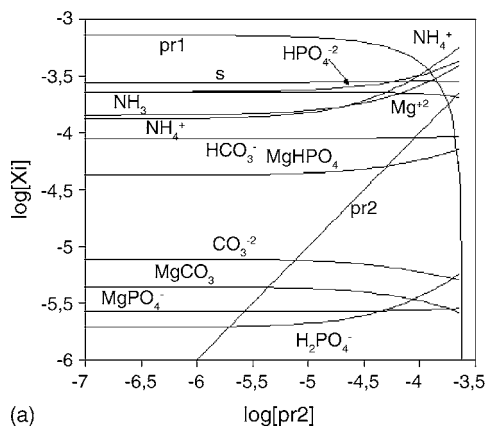


Fig. 3. Plots of $\log [X_i]$ vs. $\log [\text{pr}2]$ for the indicated species X_i (speciation) and collective ($\log s$ vs. $\log [\text{pr}2]$) relationships obtained at $C_0 = 10^{-2}$ and $C_{\text{CO}_2} = 10^{-4}$. Notations: ad = abcd, bordering line (perpendicular to $\log [\text{pr}2]$ axis) where $Q_1 = K_{\text{sp}1}$ and $Q_2 = K_{\text{sp}2}$ simultaneously; ad separates the region 1 (where $Q_1 < K_{\text{sp}1}$ and $Q_2 = K_{\text{sp}2}$) and region 2 (where $Q_1 = K_{\text{sp}1}$ and $Q_2 < K_{\text{sp}2}$); b defines $[\text{pr}1]$ at $Q_1 = K_{\text{sp}1}$ and $Q_2 = K_{\text{sp}2}$; c defines $[\text{pr}2]$ at $Q_1 = K_{\text{sp}1}$ and $Q_2 = K_{\text{sp}2}$; e refers to the point where $[\text{pr}2] = [\text{pr}1]$; f (together with its projection f') refers to $[\text{pr}1] = 0$.

grow monotonically, see Figs. 3 and 4. At nearly constant solubility (s) (Eqs. (11a) and (11b)), the concentration of soluble complex MgHPO_4 grows also, although in a limited degree.

- Fig. 3 consists (informally) of two parts (region 1 and region 2) combined together and divided by straight line $\text{ad} = \text{abcd}$, perpendicular to the x -axis (with $\log [\text{pr}2]$ values). At the end of the region 2 ($[\text{pr}2] > [\text{pr}2]_c$), it is assumed that pr2, with concentration $[\text{pr}2]_f$ (at $Q_1 = K_{\text{sp}1}$ and $Q_2 < K_{\text{sp}2}$) is present in the system. Dissolution of pr2 is accompanied by growth in concentration of pr1 expressed by the line $f'b$ —up to the point where the solubility product $K_{\text{sp}2}$ for pr2 is attained, i.e., $Q_2 = K_{\text{sp}2}$. At this option, $[\text{Mg}^{2+}]$ has been involved in the relation $[\text{Mg}^{2+}] = K_{\text{sp}1}/([\text{NH}_4^+][\text{PO}_4^{3-}])$. The growth in pr1 con-

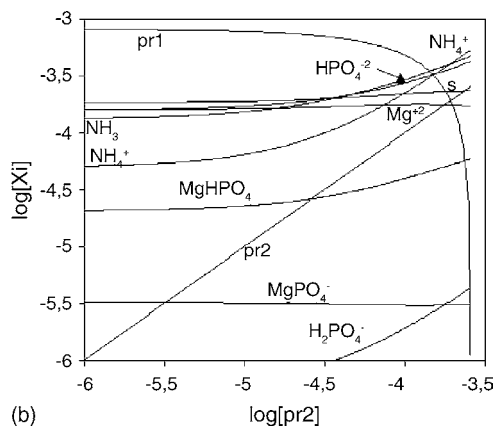


Fig. 4. The $\log [X_i]$ vs. $\log [\text{pr}2]$ relationships plotted for the indicated species X_i and for $\log s$ vs. $\log [\text{pr}2]$ relationship (see Eqs. (11a) and (11b)) obtained at $C_0 = 10^{-3}$ mol/l and (a) $C_{\text{CO}_2} = 10^{-4}$; (b) $C_{\text{CO}_2} = 0$.

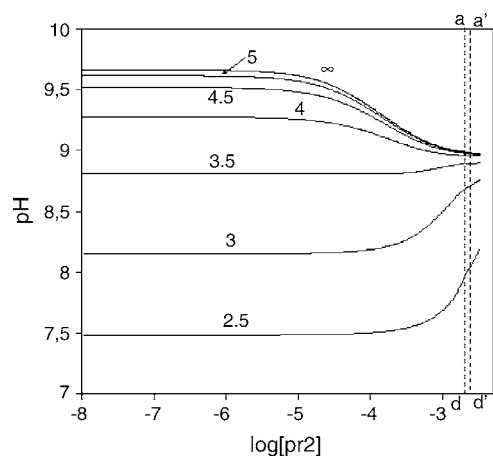


Fig. 5. The pH changes accompanying the precipitation of pr2 at $C_0 = 10^{-2}$ mol/l and indicated pC_{CO_2} values. The line ad (with abscissa $\log [pr2] = 2.746$) corresponds to the line ad in Fig. 3 and refers to $pC_{CO_2} \geq 3.453$. The line $a'd'$ (with abscissa $\log [pr2] = 2.655$) refers to $pC_{CO_2} \geq 2.5$.

centration, expressed by the line fb , is then accompanied by pr2 dissolution along the line fc . Note that the speciation curves (and s-curves) on both parts of the line ad form continuous (at $[pr2] = [pr2]_d$) but not necessarily smooth lines.

- At the points on the line ad in Fig. 3, the solution (formerly saturated towards pr2) becomes saturated against pr1, as well; this way, further dissolution of pr1 stops at $\log [pr2]_d = -2.743$. If $C_0 < C_0^* = 10^{-2.246}$ (where C_0^* – limiting C_0 value at $C_{CO_2} = 0$), pr2 remains as the only solid phase in the system; pr1 is totally depleted, i.e., the K_{sp1} value for pr1 is not crossed ($Q_1 < K_{sp1}$), see Fig. 4a and b. The $C_0^* = 10^{-2.246}$ ($pC_0^* = 2.246$ with accuracy to the third decimal figure) value, obtained at $pC_{CO_2} > 3.5$, is the limiting C_0 value where pr1 dissolves wholly. For greater C_{CO_2} values we have, for example $pC_0^* = 2.117$ at $C_{CO_2} = 10^{-2.5}$ and $pC_0^* = 1.878$ at $C_0 = C_{CO_2} = 10^{-2}$.
- Plots of individual (speciation) and collective (s, Eqs. (11a) and (11b)) species obtained at $C_0 = 10^{-3}$ and $C_{CO_2} = 10^{-4}$ are presented in Fig. 4a. The curves are distorted in comparison with ones obtained for the system where $C_{CO_2} = 0$ (Fig. 4b). For example the pH drop (Fig. 5) affected by pr1 dissolution at $C_{CO_2} = 10^{-4}$ causes a growth in $[NH_3]$, greater than for $[NH_4^+]$, i.e., $d[NH_3]/d[pr2] > d[NH_4^+]/d[pr2]$ and both curves intersect, i.e., $[NH_4^+] = [NH_3]$, at $pH = pk_1 = 9.24$.
- The curves of pH versus $\log [pr2]$ relationship (Fig. 5) obtained at different pC_{CO_2} values are changed in shape and distorted when compared with one obtained at $C_{CO_2} = 0$ ($pC_{CO_2} = \infty$). The presence of carbonate shifts pH towards lower pH values. What is more, a monotonic drop at low C_{CO_2} values is changed into monotonic growth at higher C_{CO_2} values.
- At first sight, from Eq. (1) it is expected that the value of ϑ (Eq. (12)) should be close to 3, i.e., three molecules of pr1 are needed to form one molecule of pr2. However, pr1

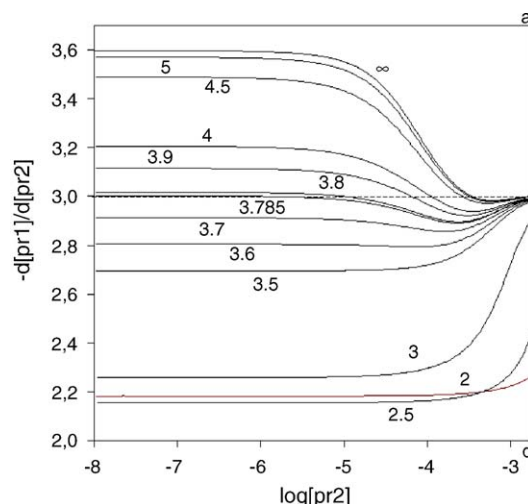


Fig. 6. The $\vartheta = -d[pr1]/d[pr2]$ vs. $\log [pr2]$ relationships plotted at indicated pC_{CO_2} values. Right bordering line ad corresponds to the line ad in Fig. 3.

is moderately soluble in water media and concentrations of some other (soluble) species (mainly Mg^{2+} , HPO_4^{2-} , NH_3 , NH_4^+ , $MgHPO_4$) involved in the system are comparable with $[pr1]$ and $[pr2]$, see Figs. 3, 4a and 4b; then the ϑ -values on the resulting plots differ from $\vartheta = 3$ (Fig. 6). Generally, $\vartheta > 3$ at higher pC_{CO_2} (low C_{CO_2}), particularly at initial step of pr1 dissolution; a distinct change occurs at the final step of pr1 dissolution. At higher C_{CO_2} , the ϑ -values are lower than 3. The $\vartheta \approx 3$ value is obtained at $pC_{CO_2} = 3.785$ at initial stage of pr1 dissolution. Moreover, at higher C_{CO_2} values, a kind of inversion in ϑ is stated. Namely the ϑ -values obtained at $C_{CO_2} = 10^{-2}$ are higher than ones referred to $C_{CO_2} = 10^{-2.5}$. Such effects are accompanied by a decrease in pH value (Fig. 5), down to ca. 6.5–7, i.e., close to the region $pH < 6.36$ where weakly soluble form H_2CO_3 predominates among other carbonate species. For these reasons, greater C_{CO_2} values can be obtained in pressurised systems (i.e., ones affected by high pCO_2 value).

5. Final comments

The struvite + water is an interesting example of the two-phase system where the pure substance introduced is not in equilibrium with water. On a defined step of struvite (pr1) dissolution, the solubility product of another precipitate, namely $Mg_3(PO_4)_2$ (pr2), is crossed, before the saturation state towards struvite is attained. This process leads to total (at $pC_0 > 2.247$) or partial (at $pC_0 < 2.247$) transformation of struvite into magnesium orthophosphate. The problem of pr1 transformation, although known from the end of 19th century [17], was ‘unnoticed’ by ones trying to calculate the solubility (s) of pr1 in water. Namely considering the solubility (s) of pr1, one should note that the incorrect formula:

$$s = (K_{sp1})^{1/3} \quad (13)$$

obtained on the basis of the reaction notation $\text{MgNH}_4\text{PO}_4 = \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-}$, is still in use. The formula (13) assumes tacitly that (1) the solution is saturated towards pr1, (2) pr1 dissociates into the species distinctly predominating within the related pH values of the solution.

Both assumptions are invalid. First of all, pr2 (not pr1) is the equilibrium precipitate, i.e., the solution is undersaturated towards pr1. Moreover, at pH ca. 9–9.5 (see Fig. 5), where HPO_4^{2-} is the predominating phosphate species, the fraction $[\text{HPO}_4^{2-}]/[\text{PO}_4^{3-}] \approx 10^3$; i.e., the value $s = [\text{PO}_4^{3-}]$ cannot be considered, by no means, as a valid approximation; even $[\text{H}_2\text{PO}_4^-] > [\text{PO}_4^{3-}]$, see Fig. 3. Moreover, all other species formed in the system are omitted in expression for s , given by Eqs. (11a) and (11b) where full physicochemical knowledge about the system in question is involved. Huge discrepancies between the values: calculated and obtained experimentally were attributed in [14] to the activity and ionic strength values of the (saturated, as is tacitly supposed) solution, although ionic strength of the solution in equilibrium with the precipitate is low, per se. Also the approximation [33] done by the equations $s = [\text{Mg}^{2+}] = [\text{NH}_4^+] + [\text{NH}_3] = \sum_{i=0}^3 [\text{H}_i\text{PO}_4^{+i-3}]$ is insufficient. Moreover, the ‘quantitative’ considerations were helped by experimental pH value, i.e., pH of the solution was not obtained from calculations. To explain the resulting discrepancies, the activity concept has been raised too.

All the s -calculations, applied above in close connection with Eq. (13), were referred to the system where struvite (pr1) is not the equilibrium solid phase. It is obvious that this requirement is the *conditio sine qua non* for correct calculations. What is more, another precipitate (pr2) or the mixture (pr2 + pr1) appears to be an equilibrium solid phase. Note that struvite (pr1) is wholly dissolvable at $C_0 = 10^{-3}$ mol/l (Fig. 4a and b). All the more, this process occurred at lower C_0 -values (i.e., $C_0 < 10^{-3}$), particularly at $C_0 = 10^{-4.2}$ value calculated from the formula (13). Assuming that pr1 does not exist (it is the virtual assumption only) this could lead to the homogeneous system. All the facts specified above testify about incorrectness of the approach done in [14,33] and elsewhere.

It should also be noticed that application of the activity concept for a deficient (incomplete) model needs is a common (‘filling’) procedure practised in many papers involved with ionic equilibria in aqueous solutions or in thermodynamics of gases, where the fugacity concept is widely considered. The two papers [14,33] cited above provide evident examples of such an inadmissible approach that cannot be tolerated. In many instances, such a procedure may be considered only as a ‘smoke screen’ applied in many theoretical considerations trying to explain the diversities between theoretical and experimental data. This mystification is usually supported by emphasising diversity in equilibrium constant values found in literature.

Formation of pr2 in mixture prepared from MgSO_4 , NH_4Cl and Na_2HPO_4 solutions at Mg:N:P = 1:1:1 was also

confirmed experimentally in [13], where excessive contents of ammonium remaining in the solution has been stated. It testifies that pr2 (not pr1) is the equilibrium solid phase in the system at Mg:N:P = 1:1:1. The systems obtained (a) after mixing equimolar quantities of the corresponding reagents and (b) after introducing pure pr1 into pure water are comparable, in principle. The difference lies only in presence of new (non-complexing, except SO_4^{2-}) ions, affecting ionic strength and then the activity coefficients values. However, this effect is small—provided that concentrations of the composing salts are low. On the other hand, it was also stated [13,34] that a due relative excess of NH_4^+ (e.g. Mg:N:P = 1:1.6:1 [13]) makes possible the precipitation of struvite as the equilibrium solid phase.

This paper testifies in favour of the opinion that the equilibrium (thermodynamic) analysis is the valuable tool for introspection and explanation of processes occurred in complex electrolytic media. The calculating procedure, suggested in [25], enables concentrations of all species (speciation) in batch and dynamic systems to be calculated. The dynamic systems are realised mainly in titrimetric procedures. The (current) values for ionic strength (I) and activity coefficients can then be calculated—provided that the (doubtful) calculating procedure based on extended Debye–Hückel model (e.g. Davies equation) is valid, particularly at high I -values.

Some troubles arised in finding the solubility product ($K_{\text{sp}5}$) for $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. However, $\text{p}K_{\text{sp}5}$ can be evaluated from the solubility value equal 0.25 g/l (20 °C) and the stability constant $K_1 = 10^{2.91} = 0.813 \times 10^3$ of the soluble complex MgHPO_4 . Neglecting the complexes MgOH^+ , $\text{MgH}_2\text{PO}_4^+$ and MgPO_4^- at pH ca. 9–9.5, and applying a primitive approach assuming $[\text{Mg}^{2+}] = [\text{HPO}_4^{2-}] = K_{\text{sp}5}^{1/2}$, one can calculate, by turns: $s = 0.25/174.3 = 1.434 \times 10^{-3}$, $[\text{MgHPO}_4] = K_1[\text{Mg}^{2+}][\text{HPO}_4^{2-}] = K_1 K_{\text{sp}5}$, we write:

$$s = [\text{Mg}^{2+}] + [\text{MgHPO}_4] = K_{\text{sp}5}^{1/2} + K_1 K_{\text{sp}5}$$

Setting $K_{\text{sp}5}^{1/2} = x$ and resolving the quadratic equation we get $K_{\text{sp}5} = x^2 = 2.9 \times 10^{-6}$, i.e. $\text{p}K_{\text{sp}5} = 5.54$. This value coincides well with the value $\text{p}K_{\text{sp}5} = 5.5$ found in literature [22].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2005.04.052.

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