Struvite as a Non-Equilibrium Solid Phase in Electrolytic Systems (Aqueous Media)

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Abstract
Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is not the equilibrium solid phase when introduced into pure water or into an aqueous CO_2 solution, with or without KOH added as the pH-modifying component. In some instances, the dissolution process consists of several steps where different solid phases are formed. It results from a simulating procedure, where the entire physicochemical knowledge on the system in question is involved in the iterative computer program. The results of calculations are put in context with formation of struvite renal calculi in urinary tracts.

Keywords: Struvite, Equilibrium Analysis, Computer Simulation, Renal Calculi

Notations
pri – precipitate of i–th kind (i = 1,...,5) with molar concentration [pri];
pr1 = **$MgNH_4PO_4$**, pr2 = **$Mg_3(PO_4)_2$**, pr3 = **$MgHPO_4$**, pr4 = **$Mg(OH)_2$**, pr5 = **$MgCO_3$** ;
K_{spi} – solubility product for pri (i= 1,..., 5);
$pC_0 = -\log C_0$; $pC_{CO2} = -\log C_{CO2}$, $pC_b = -\log C_b$;
ppri = $-\log$[pri].
Precipitates pri are written in bold letters.

Introduction
Struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$, written as **$MgNH_4PO_4$** (for brevity) and denoted later as pr1, is of great importance from medical, technical, environmental and agricultural viewpoints. Particularly, it is the main component of kidney stones (*renal calculi*) developed in human and animal urinary tracts infected by bacteria producing urease (*urea amidohydrolase*). Although clinical occurrence and presentation of kidney stones has already been described in the *Aphorisms* of Hippocrates, its behavior in aqueous media was not known until recently sufficiently well, as is seen on example of struvite [1].

This paper follows the article issued 2006 and provides the novel approach to simulated dissolution of pure struvite in aqueous media containing CO_2 (C_{CO2} mol/L) and KOH (C_b mol/L) [2]. It is proved that pr1 is not a stable solid species in such media. The approach is based on charge and concentration balances, together with expressions for equilibrium constants, involving all physicochemical knowledge on the system in question [2]. The calculations were made with use of DELPHI iterative computer program.

Some Remarks
Struvite (pr1) is not the equilibrium solid phase (C_0, mol/L) when introduced into pure water or aqueous solution of CO_2, modified (or not) by free strong acid HB or base MOH. Although the fact that NH_3 evolves from the system obtained after leaving pure pr1 in pure water [2].

$$3pr1 = pr2 + HPO_4^{-2} + 2NH_4^{+1} + NH_3 \qquad (1)$$

has already been known at the end of 19th century (see [2-6]) the solubility (s, mol/L) of pr1was commonly calculated from the approximate formula s = $(K_{sp1})^{1/3}$ (see e.g. [7]), based on an assumption that pr1 is the equilibrium solid phase in such a system.

In the past, it was noticed that mixing $MgCl_2$ and $NH_4H_2PO_4$ solutions, at the molar ratio 1:1 of the salts, gives a two-phase system containing an excess of ammonium species remaining in the solution, and the precipitate that "was not struvite, but was probably composed of magnesium phosphates" [7]. Such inferences were confirmed later on the basis of X-ray diffraction analysis of the crystallographic structure of the solid phase thus obtained [7, 8].

It was also stated [8,9] that the precipitation of pr1 requires a significant excess of ammonium species, e.g. Mg:N:P = 1:1.6:1. The co-precipitation of other phosphate species can occur on the stage of pr1 washing [3].

Formulation of Struvite + Aqueous Solution System
We refer first to the system where pure struvite (pr1) is introduced into aqueous solution with dissolved CO_2 (C_{CO2} mol/L) + KOH (C_b mol/L) + HCl (C_a mol/L); initial (t=0) concentration of pr1 in the system equals C_0 mol/L. The species involved in such systems are interrelated in the corresponding concentration (Eqs. 2, 4, 6) and charge (Eq. 5) balances:

$f1 = [pr1] + 3[pr2] + [pr3] + [pr4] + [Mg^{+2}] + [MgOH^{+1}] + [MgH_2PO_4^{+1}] + [MgHPO_4] + [MgPO_4^{-1}] + [MgNH_3^{+2}] + [Mg(NH_3)_2^{+2}] + [Mg(NH_3)_3^{+2}] + [MgHCO_3^{+1}] + [MgCO_3] - C_0 = 0$ (2)

$f2 = [pr1] + [NH_4^{+1}] + [NH_3] + [MgNH_3^{+2}] + 2[Mg(NH_3)_2^{+2}] + 3[Mg(NH_3)_3^{+2}] - C_0 = 0$ (3)

$f3 = [pr1] + 2[pr2] + [pr3] + [H_3PO_4] + [H_2PO_4^{-1}] + [HPO_4^{-2}] + [PO_4^{-3}] + [MgH_2PO_4^{+1}] + [MgHPO_4] + [MgPO_4^{-1}] - C_0 = 0$ (4)

$f4 = [H^{+1}] - [OH^{-1}] + \Delta + [NH_4^{+1}] + 2[Mg^{+2}] + [MgOH^{+1}] - [HCO_3^{-1}] - 2[CO_3^{-2}] + [MgH_2PO_4^{+1}] - [MgPO_4^{-1}] + [MgHCO_3^{+1}] + 2[MgNH_3^{+2}] + 2[Mg(NH_3)_2^{+2}] + 2[Mg(NH_3)_3^{+2}] - [H_2PO_4^{-1}] - 2[HPO_4^{-2}] - 3[PO_4^{-3}] = 0$ (5)

$f5 = [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] + [MgHCO_3^{+1}] + [MgCO_3] - C_{CO2} = 0$ (6)

where (in equation 5)
$\Delta = C_b - C_a$ (7)

and [pri] is the concentration of pri (see the list of notations). On defined stage of pr1 dissolution, concentrations of some (or all) solid phases are assumed zero. To check it, the qi values for different potentially perceptible species pri (i=1,..., 5) were 'peered' in computer program applied for this purpose.

The concentration of **MgCO_3**, i.e. [pr5], has not been included in the concentration balances specified above. Simply, at any case considered below, pr5 does not exist as the equilibrium solid phase, as results from preliminary calculations.

The manner of calculations was similar to one presented in [2]. The equilibrium data are collected in Table 1. At the start for calculations, four or five fundamental/independent variables were chosen, namely:

$x_1 = pMg = -\log[Mg^{+2}], x_2 = pNH_3 = -\log[NH_3], x_3 = pHPO_4 = -\log[HPO_4^{-2}], x_4 = pH$ at $C_{CO2} = 0$ or (8)

$x_1 = pMg = -\log[Mg^{+2}], x_2 = pNH_3 = -\log[NH_3], x_3 = pHPO_4 = -\log[HPO_4^{-2}], x_4 = pH, x_5 = pHCO_3 = -\log[HCO_3^{-1}]$ at $C_{CO2} > 0$ (9)

Note, for example, that $C_{CO2} = 0 \Leftrightarrow pC_{CO2} = \infty$, $C_{CO2} = 10^{-4} \Leftrightarrow pC_{CO2} = 4$; $C_b = 0 \Leftrightarrow pC_b = \infty$, $C_b = 10^{-2} \Leftrightarrow pC_b = 2$.

At further steps of pr1 dissolution in defined medium, the variable ppri = $-\log$ [pri] related to concentration [pri] of the precipitate pri formed in the system was introduced against the old variable (e.g. pMg) when the solubility product K_{spi} for the precipitate pri was attained; some changes in the algorithm were also made. Decision on introducing the new variable has been done on the basis of 'peering' the $\log q_i$ values, where:

$q_1 = [Mg^{+2}] \cdot [NH_4^{+1}] \cdot [PO_4^{-3}]/K_{sp1}$, $q_2 = [Mg^{+2}]^3 \cdot [PO_4^{-3}]^2/K_{sp2}$, $q_3 = [Mg^{+2}] \cdot [HPO_4^{-2}]/K_{sp3}$
$q_4 = [Mg^{+2}] \cdot [OH^{-1}]^2/K_{sp4}$, $q_5 = [Mg^{+2}] \cdot [CO_3^{-2}]/K_{sp5}$ (10)

This way, we were confirmed that the solid species pri is (or is not) formed in the system, i.e. $\log q_i = 0$ or $\log q_i < 0$.

Table 1: The logK values for equilibrium constants (K) related to the system tested; $K = K_{spi}$ (i = 1,...,5) – solubility product of the i–th precipitate (pri); $pK_w = 14.0$ for $K_w = [H^{+1}][OH^{-1}]$.

Reaction	logK	Reaction	logK		
$Mg^{+2} + OH^{-1} = MgOH^{+1}$	2.57	$Mg^{+2} + HCO_3^{-1} = MgHCO_3^{+1}$	1.16		
$NH_3 + H^{+1} = NH_4^{+1}$	9.24	$Mg^{+2} + CO_3^{-2} = MgCO_3$	3.4		
$H^{+1} + PO_4^{-3} = HPO_4^{-2}$	12.35	$Mg^{+2} + NH_3 = MgNH_3^{+2}$	0.24		
$2H^{+1} + PO_4^{-3} = H_2PO_4^{-1}$	19.55	$Mg^{+2} + 2NH_3 = Mg(NH_3)2^{+2}$	0.2		
$3H^{+1} + PO_4^{-3} = H_3PO_4$	21.70	$Mg^{+2} + 3NH_3 = Mg(NH_3)_3^{+2}$	-0.3		
$H^{+1} + CO_3^{-2} = HCO_3^{-1}$	10.33	$\mathbf{MgNH_4PO_4} = Mg^{+2} + NH_4^{+1} + PO_4^{-3}$	−12.6	$K=K_{sp1}$	
$2H^{+1} + CO_3^{-2} = H_2CO_3$	16.71	$\mathbf{Mg_3(PO_4)_2} = 3Mg^{+2} + 2PO_4^{-3}$	−24.38	$K=K_{sp2}$	
$Mg^{+2} + H_2PO_4^{-1} = MgH_2PO_4^{+1}$	0.45	$\mathbf{MgHPO_4} = Mg^{+2} + HPO_4^{-2}$	−5.5	$K=K_{sp3}$	
$Mg^{+2} + HPO_4^{-2} = MgHPO_4$	2.91	$\mathbf{Mg(OH)_2} = Mg^{+2} + 2 OH^{-1}$	−10.74	$K=K_{sp4}$	
$Mg^{+2} + PO_4^{-3} = MgPO_4^{-1}$	4.8	$\mathbf{MgCO_3} = Mg^{+2} + CO_3^{-2}$	−5.17	$K=K_{sp5}$	

All concentrations in the system were expressed in terms of fundamental variables. Then the equations (2) – (6), applicable for $C_{CO2} > 0$, can be written as follows:

$fi = fi(x) = 0$ (i = 1,...,5) (11)

and the sum of squares
$SS = \Sigma_{i=1}^5 [fi(x)]^2$ (12)

is taken as the minimized function. Generally, the calculation procedure and graphical presentation was similar to one described in [2]. It concerns also speciation plots as formulations for the solubility or dissolution (s, mol/L) of pr1, expressed by the formula

$s = [Mg^{+2}] + [MgOH^{+1}] + [MgH_2PO_4^{+1}] + [MgHPO_4] + [MgPO_4^{-1}] + [MgNH_3^{+2}] + [Mg(NH_3)_2^{+2}] + [Mg(NH_3)_3^{+2}]$ (13)

at $C_{CO2} = 0$, or
$s' = s + [MgHCO_3^{+1}] + [MgCO_3]$ (14)

at $C_{CO2} > 0$, were calculated on the basis of the optimized variables xi considered (compare with eqs 2 and 3).

The Struvite Dissolution – Graphical Presentation
The results of calculations, referred to $C_a = 0$, $(pC_0, pC_{CO2}, pC_b) = (3, 4, \infty)$ and $(pC_0, pC_{CO2}, pC_b) = (2, 4, 2)$, are presented in Figures 1 and 2, respectively.
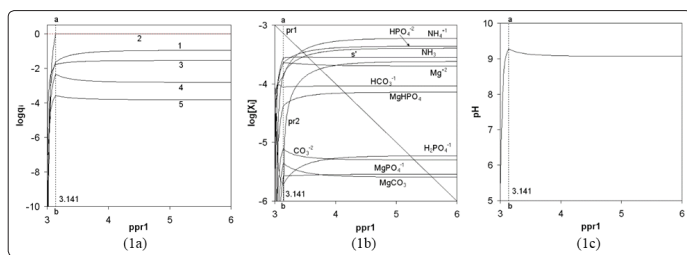
Figure 1: The relationships: (1a) $\log q_i$ vs. ppr1, (1b) $\log[X_i]$ vs. ppr1, (1c) pH vs. ppr1 plotted at $(pC_0, pC_{CO2}, pC_b) = (3, 4, \infty)$, at $C_a = 0$. The solubility s' in (1b) is expressed by Eq. 14.
The curves in Figure 1 are plotted at $(pC_0, pC_{CO2}, pC_b) = (3, 4, \infty)$.

In Figure (1a), is pr2, forming from the point where ppr1 = 3,141. For ppr1 > 3,141, pr1 transforms into pr2, until pr1 is completely depleted/ exhausted.

At $(pC_0, pC_{CO2}, pC_b) = (3, 4, \infty)$, the solubility product K_{sp2} for pr2 is attained at ppr1 = 3.141 (Figure 1a), and then pr2 is precipitated (Eq. 1) as the equilibrium solid phase. This lasts up to total depletion of pr1 (Figure 2a), i.e. the solubility product K_{sp1} for pr1 is not attained ($q_1 < 1$). The pH vs. ppr1 relationship is presented in Figure (1c). The course of speciation curves (Figures 2a, 2b) testifies in favour of the validity of the reaction notation (Eq.1), involving the predominating species in the system.
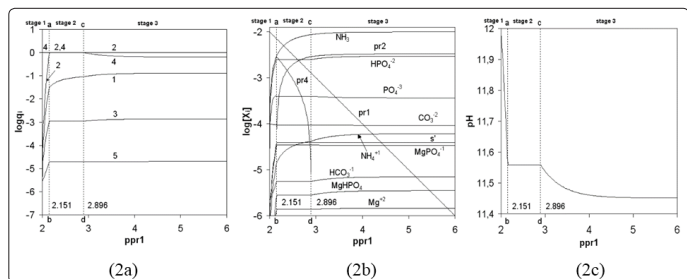
Figure 2 The relationships: (2a) $\log q_i$ vs. ppr1, (2b) $\log[X_i]$ vs. ppr1, (2c) pH vs. ppr1 plotted at $(pC_0, pC_{CO2}, pC_b) = (2, 4, 2)$. The solubility s' in (2b) is expressed by Eq. 14.

At $(pC_0, pC_{CO2}, pC_b) = (2, 4, 2)$, the process is more complicated and consists on three stages (Figure 2). The pr4 precipitates
$$pr1 + 2OH^{-1} = pr4 + NH_3 + HPO_4^{-2} \qquad (15)$$

nearly from the very start of pr1 dissolution, ppr1 = 3.000102 in Figure (2a), i.e., the pr4 is the equilibrium solid phase, almost from the very beginning of pr1 dissolution, up to ppr1 = 2,151 (stage 1), where Ksp2 for pr2 is attained. At ppr1 $\in$ <2.151, 2.896>, pr2 forms, next to pr4, the second equilibrium solid phase (stage 2), i.e. the solution is saturated toward pr2 and pr4. On this stage, the reaction

$$2pr1 + pr4 = pr2 + 2NH_3 + 2H_2O \qquad (16)$$

occurs up to total depletion of pr4 (at ppr1 = 2.896), see Figure (2a). For ppr1 > 2.896, the equilibrium solid phase is pr2 (stage 3), wherein the solution is in a state close to saturation with respect to pr4. On the stage 3, the reaction
$$3pr1 + 2OH^{-1} = pr2 + 3NH_3 + HPO_4^{-2} + 2H_2O \qquad (17)$$

occurs up to total depletion of pr1, i.e. solubility product (K_{sp1}) for pr1 is not crossed. The pH changes, occurring during this process,

are presented in Figure (2c).

All the reaction notations specified above involve predominating species of the related systems. All them were formulated on the basis of the related speciation plots (Figure 2b) and confronted with the related plot in Figure (2c). Particularly, OH^{-1} ions participate the reactions (15) and (17) as substrates and then pH of the solution decreases during the dissolution process on the stages 1 and 3 (see Figure 2c). On the stage 2 we have pH $\cong$ constant (see Eq. 16 and Figure 2c). A growth in concentration of NH_3 and HPO_4^{-2} is also reflected in the reactions (15)-(17) notation.

Struvite Versus Kidney Stones
The urinary system is one of the most important regulatory systems for body's waste removal (excretion). It consists of two kidneys that clean the body's fluids, as well as the bladder and urethra, which store and eliminate waste.

An infection of urinary tract may concern bladder and kidney [10]. Kidney infection, if it occurs, usually follows a bladder infection. Symptoms from a bladder infection include pain while urination, and frequent urination. Rarely, the urine may appear to be bloody (hematuria). This infection is more common in women than men, and occurs more often at the age of 16 to 35 years.

The most common cause of infection is uropathogenic bacteria *Escherichia coli* (*E. Coli*) from the gut. After entering the bladder via the urethra, *E. Coli* are able to attach to the bladder wall and form a biofilm that resists the body's immune response. When the kidneys, bladder, or ureters become inflamed by this infection, formation of bladder stones may occur. The stones can move through ureters and get out from urethra with urine. Some kidney stones can also get stuck in urinary tract and block urine from getting through. The flow of large kidney stones can be very painful in this case. Kidney stone disease is known as urolithiasis [11]. At present, urolithiasis is one of the leading urological diseases and, irrespective of the method of removal of kidney stones; there are serious complications and relapses.

Formation of kidney stones deposits is relatively common ailment in human's organisms. A few percent of people in the world experience this ailment in their lifetime [12]. The list of known people suffering from this ailment is long [13, 14].

The kidney stones are formed mainly from crystallized, moderately soluble calcium and/or magnesium salts [15, 16]. Formation of the kidney stones results from combination of genetic and environmental factors [17]. Nearly 80 – 90% of urolithiasis cases involve concretions composed of calcium oxalates: whewellite and weddellite, and 10–15% cases involve struvite stones [18].

Struvite stones are almost always caused by urinary tract infections. Struvite stones are formed in presence of urease-producing bacteria (most commonly *Proteus* and *Klebsiella*), resulting from the infection [19-24]. Ureases are metalloenzymes catalyzing the hydrolysis of urea into carbon dioxide and ammonia [25-29]
$$(NH_2)_2CO + H_2O = CO_2 + 2NH_3 \qquad (18)$$

This reaction occurs effectively at pH ca. 7, where $[NH_4^{+1}]/[NH_3] >>$ 1. Normal urine is under-saturated with ammonium and phosphate species and, therefore, the solubility product of struvite is not crossed.

The stone formation (crystallization) occurs only from supersaturated solution. Reaction (18) does not occur in presence of acetohydroxamic acid ($CH_3CO-NH-OH$), used in drugs as the irreversible urease inhibitor, in combination with antibiotics. Some inhibiting substances (e.g. citrate) are able to prevent the stone formation in urine. An essential role in the inhibiting plays pH of the solution.

To diagnose this ailment accurately in hospital (radiology department), and provide the most effective treatment, the following diagnostic techniques are used: computerized tomography (CT) with X-ray scans for adults, or ultrasound bladder scan (sonogram) to monitor kidney stones in children/young people or an unborn baby in pregnant women.

Another option is cytoscopy, where a cytoscope (a specialized tube with camera at the end) is inserted into the body through the urethra in order to view the inside of the bladder and urethra.

On the treatment step, non-invasive techniques: lithotripsy or extracorporeal shockwave lithotripsy (ESWL) are most frequently applied [30-36]. Shock waves break up the stones into smaller sand-like fragments which can then pass on their own.

Final Comments
The paper concerns the behavior of struvite $MgNH_4PO_4 \cdot 6H_2O$ introduced into either pure water or an aqueous solution of CO_2, with or without KOH applied as the pH-modifying component. A simulating procedure, involving the entire physicochemical knowledge on the system in question, enables us to state that struvite is not the equilibrium solid phase in such systems. Struvite is one of the main components of infection stones, i.e. *renal calculi* developed in hu-man and animal urinary tracts infected by bacteria producing urease.

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