Precipitation and Characterization of Strontium Phosphates

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Spontaneous precipitation of strontium phosphates was studied over a wide concentration range of strontium chloride ($2 \cdot 10^{-4} \text{–} 8 \cdot 10^{-1} \text{ mol dm}^{-3}$) and of sodium phosphate ($4 \cdot 10^{-4} \text{–} 3 \cdot 10^{-1} \text{ mol dm}^{-3}$) solutions. In all systems, initial pH was 7.4 and sodium chloride concentration was 0.15 mol dm$^{-3}$. The precipitates aged for 1 day and 30 days at 298 K and 310 K were characterized by light microscopy and X-ray powder diffraction. Solid phases $\text{SrHPo}_4$ (α and β modifications), $\text{Sr}_{16} \text{(PO}_4\text{)}_{6} \text{(OH)}_2$, $\text{H}_3 \text{Sr}_4 \text{(PO}_4\text{)}_6 \cdot 2\text{H}_2\text{O}$, and $\text{Na}[\text{Sr(H}_2\text{O)}_9] \text{PO}_4$ were determined. According to the precipitation boundary after 30 days (equilibrium conditions) the solubility product of $\text{Na}[\text{Sr(H}_2\text{O)}_9] \text{PO}_4$ is determined as follows:

$$\log ([\text{Na}^+] [\text{Sr}^{2+}] [\text{PO}_4^{-3}]) = -9.98 \pm 0.11 \text{ (at } I = 0.25 \text{ mol dm}^{-3}, 298 \text{ K).}$$

INTRODUCTION

The investigation of the system strontium chloride — sodium phosphate — sodium chloride (0.15 mol dm$^{-3}$), reported in this paper is a part of a general study on the spontaneous precipitation of the alkaline earth phosphates. An early phase rule study of the system $\text{SrO-P}_2\text{O}_5-H_2\text{O}$ at 298 K in the acid region indicated the existence of two solid phases, $\text{Sr(H}_2\text{PO}_4\text{)}$ and $\text{SrHPO}_4$.\(^1\)

In the system $\text{SrCl}_2-K\text{H}_2\text{PO}_4-H_2\text{O}$ ($6 < \text{pH} < 10$), $\text{SrHPO}_4$ and $\text{Sr}_6\text{(PO}_4\text{)}_6\text{(OH)}_2$ were detected.\(^2\) $\text{SrHPO}_4$ may be precipitated from solutions in two different crystalline modifications (α and β), the formation of which depends on several conditions, temperature being the most critical.\(^3\)

This paper deals with spontaneous precipitation in the system $\text{SrCl}_2-\text{H}_2\text{PO}_4-\text{NaOH-H}_2\text{O}$ occurring under physiological conditions (NaCl = 0.15 mol dm$^{-3}$, pH = 7.4) at 298 K and 310 K.

Investigation of precipitation phenomena of strontium phosphates is important in biological mineralization due to the isomorphous replacement of calcium by strontium in hydroxyapatite\(^4\) and the similar biological metabolism of these elements.\(^5\) The role of strontium in pathological calcification has been reported by several authors.\(^6-9\) It can produce rickets in bone\(^8\) and increase the bone abnormalities caused by scurvy.\(^10\) Its effect on caries has also been observed.\(^11\) Low concentrations of strontium make easier the transformation of carbonate-containing hydroxyapatite (a constituent of bones and tooth enamel) into β-tricalcium phosphate by heat treatment.\(^12\)
Solutions were prepared by dissolving analytical grade chemicals in triply distilled water. Stock solutions of SrCl₂ and NaCl were standardized by ion exchange (Dowex 50-W resin). The concentration of H₃PO₄ was determined by titration, using thymolphthalein as indicator. The precipitates were prepared by mixing a SrCl₂ solution with an equal volume of a sodium phosphate solution (H₃PO₄ + NaOH, adjusted to a chosen initial pH, and NaCl to give a constant concentration of 0.30 mol dm⁻³). The systems were aged for 1 day and 30 days at temperatures of 298 K and 310 K. The pH was measured with a GK 2302C electrode using a Radiometer pH-meter.

The morphology of the precipitates was examined in white and polarized light in an Orthoplan microscope supplied with an automatic Orthomat-W camera (Leitz, Wetzlar). The X-ray powder patterns of selected samples were recorded by means of a Philips diffractometer with a proportional counter, using graphite monochromated Cu Kα radiation. The d-spacings were compared with the values reported by Ropp et al. and Powder Diffraction File. The composition of Na[Sr(H₂O)₉]PO₄ was determined by precipitating strontium with KH₂PO₄, drying at 393 K and weighing as SrHPO₄. Phosphorus was precipitated with ammonium molybdate and after drying at 476–673 K, it was weighed as (NH₄)₆PMO₁₂O₄₀. Sodium was determined by atomic absorption spectrometry and water by thermogravimetric analysis.

RESULTS AND DISCUSSION

Spontaneous precipitation of strontium phosphates was carried out over concentration ranges of strontium chloride from 2 × 10⁻⁴ to 8.0 × 10⁻¹ mol dm⁻³ and total phosphates from 4 × 10⁻⁴ to 3.0 × 10⁻¹ mol dm⁻³. The concentration of sodium chloride was 0.15 mol dm⁻³ in all systems.

Figure 1. Precipitation diagrams of the system strontium chloride—sodium phosphate—sodium chloride—water at pH_i = 7.4, 298 K:

(a) aged 1 day
(b) aged 30 days.

The precipitation and phase boundaries are assigned by full lines and iso-pH curves by dashed lines.
The precipitation diagrams of strontium phosphates, 1 day and 30 days after mixing the components are presented in Figure 1. The precipitation and phase boundaries were detected microscopically. The solid phases were identified by X-ray powder diffraction patterns.

The precipitation region of pure Sr$_{10}$(PO$_4$)$_6$(OH)$_2$ appears in excess of strontium chloride (resulting pH range 4 < pH < 7) and also in excess of phosphate (resulting pH range 6.5 < pH < 7.4). The precipitates of Sr$_{10}$(PO$_4$)$_6$(OH)$_2$ are submicroscopic sized crystals of crystal aggregates (microphotograph I).

The mixture of two modifications (α and β) of SrHPO$_4$ precipitates at high reactant concentrations (3 < pH < 4). The α-modification prevails in excess of phosphate. SrHPO$_4$ crystallizes in the prismatic shape (microphotograph II) or as spherulitic agglomerates (microphotograph III).

Solid Na[SR(H$_2$O)$_9$]PO$_4$ precipitates at [PO$_4$]$^-$ to [Sr]$_{tot}$, as tetrahedral crystals (microphotograph IV). Chemical analysis of this compound revealed the following values:

<table>
<thead>
<tr>
<th></th>
<th>% Sr</th>
<th>% P</th>
<th>% Na</th>
<th>loss</th>
<th>weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found:</td>
<td>23.65 ± 0.30</td>
<td>8.49 ± 0.15</td>
<td>6.27 ± 0.05</td>
<td>43.8 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>Calculated:</td>
<td>23.83</td>
<td>8.42</td>
<td>6.25</td>
<td>44.09</td>
<td></td>
</tr>
</tbody>
</table>

TGA showed continuous dehydration from 313 K up to 390 K. Under conditions close to the precipitation boundary Na[SR(H$_2$O)$_9$]PO$_4$ precipitates alone (7.6 > pH > 7.4). At higher [Sr]$_{tot}$ it appears in the mixture with SrHPO$_4$ and/or Sr$_{10}$(PO$_4$)$_6$(OH)$_2$.

The precipitation boundary of Sr$_{10}$(PO$_4$)$_6$(OH)$_2$ in excess of [Sr]$_{tot}$ (Figures 1a, b; [SrCl]$_{tot}$ > 1 · 10$^{-2}$ mol dm$^{-3}$, [PO$_4$]$_{tot}$ < 2 · 10$^{-3}$ mol dm$^{-3}$) does not change with time. In the concentration region of [SrCl]$_{tot}$ < 1 · 10$^{-2}$ mol dm$^{-3}$, 2 · 10$^{-3}$ mol dm$^{-3}$ < [PO$_4$]$_{tot}$ < 1 · 10$^{-2}$ mol dm$^{-3}$ the precipitation boundary at 30 days is shifted to lower reactant concentrations (Figures 1a, b). Systems exhibiting clear solutions after 1 day, on being aged for 30 days showed precipitates containing β-SrHPO$_4$ or a mixture of β-SrHPO$_4$ and H$_2$Sr$_6$(PO$_4$)$_5$ · 2H$_2$O. The formation of SrHPO$_4$ at these conditions can be either a spontaneous process, or it can be connected with the precipitation of Sr$_{10}$(PO$_4$)$_6$(OH)$_2$ as the precursor, which converts to SrHPO$_4$ and H$_3$Sr$_6$(PO$_4$)$_5$ · 2H$_2$O. The reaction of transformation can be given as:

$$ \text{Sr}_{10}$(PO$_4$)$_6$(OH)$_2$ + 9H$^+$ + 3PO$_4^{2-}$ → H$_3$Sr$_6$(PO$_4$)$_5$ + 4SrHPO$_4$ + 2H$_2$O

In the precipitation region characterized by crystallization of Na[SR(H$_2$O)$_9$]PO$_4$ the precipitation boundary is shifted to lower concentrations with time. The solubility product of Na[SR(H$_2$O)$_9$]PO$_4$ is determined according to the precipitation boundary after 30 days (Figure 1b). In Table I (systems 1—6) the equilibrium concentrations of all components in the solutions are listed: [Sr]$_{eq}$, [PO$_4$]$_{eq}$, [Na]$_{eq}$, pH values, and ionic strengths.

The concentration of [Sr]$_{eq}$ is the sum of [Sr$^{2+}$] and [SrHPO$_4$]$^-$, while [SRH$_2$PO$_4$]$^-$ is negligible at corresponding [PO$_4$]$_{eq}$ and pH. The concentration of [PO$_4$]$_{eq}$ is the sum of free phosphates (HPO$_4^{2-}$ ions prevail, H$_3$PO$_4$ being negligible). Phosphates incorporated in the strontium complex (SrHPO$_4$) can be neglected at [Sr]$_{eq}$ << [PO$_4$]$_{eq}$. The concentration of [Na]$_{eq}$ is equal to the
Microphotographs I–IV of strontium phosphate precipitates: I – Sr$_{16}$(PO$_4$)$_4$(OH)$_2$, II and III SrHPO$_4$, IV – Na[SR(H$_2$O)$_6$]PO$_4$. The experimental conditions for all systems shown were: pH 7.4, $T = 298$ K, $t = 30$ days. The initial concentrations of strontium chloride and sodium phosphate, and the final pH for particular systems were:

I – [SrCl$_2$]$_{tot}$ = $4 \cdot 10^{-3}$ mol dm$^{-3}$, [PO$_4$]$_{tot}$ = $6 \cdot 10^{-2}$ mol dm$^{-3}$, pH 6.52

II – [SrCl$_2$]$_{tot}$ = $4 \cdot 10^{-2}$ mol dm$^{-3}$, [PO$_4$]$_{tot}$ = $3 \cdot 10^{-2}$ mol dm$^{-3}$, pH 5.28

III – [SrCl$_2$]$_{tot}$ = $1 \cdot 10^{-3}$ mol dm$^{-3}$, [PO$_4$]$_{tot}$ = $1 \cdot 10^{-3}$ mol dm$^{-3}$, pH 7.35

IV – [SrCl$_2$]$_{tot}$ = $1 \cdot 10^{-3}$ mol dm$^{-3}$, [PO$_4$]$_{tot}$ = $8 \cdot 10^{-3}$ mol dm$^{-3}$, pH 7.55
TABLE I
Equilibrium Concentration Determined According to Precipitation Boundary and Calculated $K_\text{s}$ Values for $\text{Na}[\text{Sr}(\text{H}_2\text{O})_n]\text{PO}_4(s)$

<table>
<thead>
<tr>
<th>$-\log [\text{Sr}]_{eq}$</th>
<th>$-\log [\text{PO}<em>4]</em>{eq}$</th>
<th>$-\log [\text{Na}]_{eq}$</th>
<th>pH</th>
<th>$I$/mol dm$^{-3}$</th>
<th>$\log K_\text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.11</td>
<td>1.82</td>
<td>0.75</td>
<td>7.50</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>3.16</td>
<td>1.70</td>
<td>0.73</td>
<td>7.47</td>
<td>0.21</td>
</tr>
<tr>
<td>3</td>
<td>3.35</td>
<td>1.52</td>
<td>0.66</td>
<td>7.49</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>3.50</td>
<td>1.40</td>
<td>0.65</td>
<td>7.42</td>
<td>0.26</td>
</tr>
<tr>
<td>5</td>
<td>3.55</td>
<td>1.30</td>
<td>0.61</td>
<td>7.52</td>
<td>0.29</td>
</tr>
<tr>
<td>6</td>
<td>3.70</td>
<td>1.22</td>
<td>0.58</td>
<td>7.54</td>
<td>0.30</td>
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</tbody>
</table>

The precipitation boundary was determined at $I = 0.1$ mol dm$^{-3}$ and $I = 0.4$ mol dm$^{-3}$ (Table II eqs. 1 and 2). The constant of strontium phosphate complex is determined$^{18}$ at $I = 0.2$ mol dm$^{-3}$ (Table II, eq. 3). The values of association constants at $I = 0.2$ and 0.3 mol dm$^{-3}$ calculated from the values of constants at $I = 0.1$ and 0.4 mol dm$^{-3}$ (using Davies equation$^{19}$) are close (see deviations of constants at $I = 0.25 \pm 0.05$ in Table II). Therefore the set of constants corrected to $I = 0.25$ mol dm$^{-3}$ (mean value of ionic strengths in systems 1—6) is used (Table II, eqs. 1—3). The solubility product of $\text{Na}[\text{Sr}(\text{H}_2\text{O})_n]\text{PO}_4$ ($K_\text{s} = [\text{Na}^+] [\text{Sr}^{2+}] [\text{PO}_4^{3-}]$) is expressed as:

$$K_\text{s} = \frac{[\text{Na}^+] [\text{Sr}^{2+}] [\text{PO}_4^{3-}]}{[\text{Na}[\text{Sr}(\text{H}_2\text{O})_n]\text{PO}_4]}$$

Figure 2. Precipitation diagrams of the system strontium chloride—sodium phosphate—sodium chloride—water at pH$_1$ = 7.4, 310 K:
(a) aged 1 day
(b) aged 30 days.
The precipitation and phase boundaries are assigned by full lines and iso-pH curves by dashed lines.
### Table II

<table>
<thead>
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<th>Eq.</th>
<th>Homogeneous Equilibria</th>
<th>Literature Value</th>
<th>Corrected Value</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( H^+ + HPO_4^{2-} = H_2PO_4^- )</td>
<td>( K_1 )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( H^+ + PO_4^{3-} = HPO_4^{2-} )</td>
<td>( K_2 )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( Sr^{2+} + HPO_4^{2-} = SrHPO_4^- )</td>
<td>( K_3 )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Heterogeneous Equilibria</th>
<th>Literature Value</th>
<th>Corrected Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>( Na[Na(H_2O)_9]PO_4(\omega) = Na^+ + Sr^{2+} + PO_4^{3-} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The solubility products calculated for each system are presented in Table I. The mean value of log $K_s$ is given in Table II (eq. 4).

The diagrams of precipitation systems aged one day and 30 days at 310 K are shown in Figure 2. Solutions which were clear after one day (Figure 2a). \(2 \cdot 10^{-3} \text{ mol dm}^{-3} < [\text{PO}_4]_{\text{tot}} < 2 \cdot 10^{-2} \text{ mol dm}^{-3}\), when aged for 30 days (Figure 2b) contained mixed precipitates: $\alpha$-SrHPO$_4$ and Sr$_{10}$(PO$_4$)$_6$(OH)$_2$, $\alpha$-SrHPO$_4$ and H$_3$Sr$_6$(PO$_4$)$_5$ · 2H$_2$O. In the high excess of phosphates \([\text{PO}_4]_{\text{tot}} > 2 \cdot 10^{-2} \text{ mol dm}^{-3}\) pure Na[Sr(H$_2$O)$_9$]PO$_4$ was formed during the same period of time. The phase boundaries of SrHPO$_4$ (mixture of $\alpha$ and $\beta$ modifications) and of Sr$_{10}$(PO$_4$)$_6$(OH)$_2$ are also shown in Figure 2.

Figure 3. Relation between final pH and reactant concentrations during precipitation at initial pH of 5.6, 6.5, 7.4, and 8.5. The symbols indicate the various compositions of precipitated solid phases.
A comparison of the precipitation and phase boundaries in Figure 1b (at 298 K) and Figure 2b (at 310 K) indicates the influence of temperature on the processes involved. The precipitation boundary of \( \text{Sr}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_2 \) at 310 K is at lower reactant concentrations than is the case at 298 K. The precipitation boundary of \( \text{Na}[\text{Sr}\left(\text{H}_2\text{O}\right)_3]\text{PO}_4 \) at 310 K is at higher reactant concentrations. The stability region of the latter solid is narrow at 310 K due to the dehydration of this compound starting at 313 K (thermogravimetric data). Lowering the temperature to \(< 298 \text{ K} \) favors the precipitation of \( \text{Na}[\text{Sr}\left(\text{H}_2\text{O}\right)_9]\text{PO}_4 \).

In the region where mixtures of \( \text{Na}[\text{Sr}\left(\text{H}_2\text{O}\right)_9]\text{PO}_4 , \text{SrHPO}_4 \) and \( \text{Sr}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_2 \) were found at 298 K (Figure 1b), only \( \text{Na}[\text{Sr}\left(\text{H}_2\text{O}\right)_9]\text{PO}_4 \) precipitated at 291 K. In the concentration region between precipitation boundaries of one day and 30 days, \( \beta\)-\( \text{SrHPO}_4 \) precipitates at 298 K, and \( \alpha\)-\( \text{SrHPO}_4 \) at 310 K. This result is in accordance with Mooney et al.3

The formation of strontium phosphates at various initial pH values at \( [\text{PO}_4]_{\text{tot}} = 6 \cdot 10^{-4} \text{ mol dm}^{-3} \) is indicated in Figure 3. At the expense of \( \text{Na}[\text{Sr}\left(\text{H}_2\text{O}\right)_9]\text{PO}_4 \) the broadening of the precipitation region for \( \text{Sr}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_2 \) occurs in the system at \( \text{pH} = 8.5 \). At \( \text{pH} = 6.5 \) and 5.6, only \( \alpha\)-\( \text{SrHPO}_4 \) is precipitated over the entire region.

A comparison of precipitation of strontium phosphates with that of calcium phosphates20-23 shows that analogous solids are formed (\( \text{SrHPO}_4 \) and \( \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}, \text{Sr}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_2 \) and \( \text{Ca}_{10} \left( \text{PO}_4 \right)_{6} \left( \text{OH} \right)_2 \)). In the former case an additional solid phase, \( \text{Na}[\text{Sr}\left(\text{H}_2\text{O}\right)_9]\text{PO}_4 \) (at high phosphate concentrations and \( \text{pH} \approx 7.4 \)) was found.

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REFERENCES


SAZETAK
Taloženje i karakterizacija stroncej-fosfata

Nevenka Pavković, Biserka Kojić-Prodić, Milenko Marković i Dejan Plavšić

Proučavan je proces spontanog taloženja stroncej-fosfata u širokom koncentracijskom području stroncej-klorida (2·10⁻⁴—8·10⁻¹ mol dm⁻³) i natrij-fosfata (4·10⁻⁴—3·10⁻¹ mol dm⁻³). Početni pH u svim sistemima bio je 7,4, a koncentracija natrij-klorida 0,15 mol dm⁻³. Ispitani su talozi staren 1 dan i 30 dana pri 298 K i 310 K. Karakterizacija taloga načinjena je optičkom mikroskopijom i rendgenskom difrakcijom na praškastim uzorcima. Nađene su slijedeće čvrste faze: SrHPO₄ (α i β modifikacija), Sr₁₀(Po₄)₈(OH)₈, H₂Sr₉(Po₄)₅·2H₂O i Na[Sr(H₂O)₉]PO₄. Produkt topljivosti Na[Sr(H₂O)₉]PO₄ određen je iz podataka s taložne grani ce nakon 30 dana (ravnatežni uvjeti) i iznosi log ([Na⁺][Sr²⁺][PO₄³⁻]) = -9.98 ± 0.11 (I = 0.25 mol dm⁻³, T = 298 K).