

Spontaneous Precipitation in the System Uranyl(2+)nitrate — Potassium Hydroxide — Phosphoric Acid — Water

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The precipitation system $\text{UO}_2(\text{NO}_3)_2$ — KOH — H_3PO_4 — H_2O (at 298 K) aged for 1 day and for 30 days is examined ($[\text{UO}_2(\text{NO}_3)_2] = 1 \cdot 10^{-3}$ mol dm^{-3} , $[\text{KOH}]$ varied from $1 \cdot 10^{-6}$ to $6 \cdot 10^{-1}$ mol dm^{-3} , $[\text{H}_3\text{PO}_4]$ from $2 \cdot 10^{-4}$ to $6 \cdot 10^{-1}$ mol dm^{-3} and $1.5 < \text{pH} < 11.5$). The precipitation and phase boundaries are determined.

The solid phases $\text{UO}_2\text{HPO}_4 \cdot 4 \text{H}_2\text{O}(\text{s})$ and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ are stable at $[\text{KOH}] < 1 \cdot 10^{-3}$ mol dm^{-3} , $1.5 < \text{pH} < 4.0$. Uranates precipitate at $\text{pH} > 9.5$. The stability region of $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}(\text{s})$ is found at high concentrations of KOH and H_3PO_4 . X-ray diffraction pattern of this compound is given. According to the precipitation boundary after 30 days (equilibrium conditions) the solubility product of $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ is determined: $\log ([\text{K}^+] \cdot [\text{UO}_2^{2+}] [\text{PO}_4^{3-}]) = -26.28$ (at $I = 0$ mol dm^{-3}).

INTRODUCTION

The formation of the uranyl salts by spontaneous precipitation from the phosphate solutions has been exhaustively described¹⁻³. In the precipitation system $\text{UO}_2(\text{NO}_3)_2$ — H_3PO_4 — H_2O the stable solid phases $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (tetragonal polymorph, type I according to Moroz et al.⁴) and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ were found². Solubility of both salts was examined³ and stability constants of uranyl phosphato complexes were calculated^{3,5}.

The spontaneous precipitation of potassiumuranyl(2+)phosphate has not been systematically examined. The formation of $\text{KUO}_2\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($n = 2, 3, 3.5$) from solutions was described⁶⁻⁸. KUO_2PO_4 and $\text{K}_4[\text{UO}_2(\text{PO}_4)_2]$ were prepared by thermal synthesis^{8,9}.

The spontaneous precipitation in the system $\text{UO}_2(\text{NO}_3)_2$ — KOH — H_3PO_4 — H_2O and the identification of solid phases are presented in this paper. The solubility product of $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ is determined (at $I = 0$ to 0.15 mol dm^{-3} , $T = 298$ K) and compared with literature data^{6,10,11}. The solubility data of $\text{KUO}_2\text{PO}_4 \cdot n\text{H}_2\text{O}$ (at $I = 0.23$ mol dm^{-3} , $T = 293$ K) obtained by Vesely, Pekarek and Abbrent¹¹ are recalculated and discussed.

EXPERIMENTAL

Stock solutions were prepared by dissolving the following p.a. chemicals in tridistilled water: $\text{UO}_2(\text{NO}_3)_2$, H_3PO_4 , KOH (Merck, Darmstadt). Standardization of solutions was performed according to classical analytical methods.

The precipitation systems were prepared by the mixing¹² of uranyl(2+)nitrate solution with an equal volume of potassiumphosphate solution ($\text{H}_3\text{PO}_4 + \text{KOH}$) and aged 1 and 30 days at temperature of 298 K. The pH was measured with the electrode GK 2302 C, using Radiometer Mo 26 pH-meter. The morphology of the precipitates was examined in white, polarized and UV light under an Orthoplan microscope (Leitz, Wetzlar) and by electron microscopy (Elmiskop I, Siemens). A charge of potassiumuranyl(2+)phosphate colloidal particles was determined by using micro-electrophoretic apparatus equipped with Smith-Lisse double cell¹³.

Selected precipitates were characterized by means of chemical and thermogravimetric analyses, X-ray powder diffraction patterns and IR spectra. After dissolution in perchloric acid solid phase was chemically analysed for uranium, phosphorus and potassium. Uranium was precipitated with $(\text{NH}_4)_2\text{HPO}_4$, heated at 1373 K and weighed as $\text{U}_2\text{O}_3\text{P}_2\text{O}_7$ ¹⁴. Phosphorus was determined gravimetrically by precipitation with ammonium molybdate¹⁵ and spectrophotometrically as phosphovanadatomolybdate complex¹⁵. Potassium was determined by flame photometry.¹⁵ Water was determined by thermogravimetric analysis (Cahn RG recording electromicrobalance, sensitivity 10^{-6} g, rate 4 K in minute, heating to 1050 K).

X-ray diffraction patterns were recorded on a Philips X-ray diffractometer with a proportional counter, using graphite monochromated $\text{CuK}\alpha$ radiation. X-ray patterns were calibrated with an internal standard, graphite, with a unit cell $a = 2.463$, $c = 6.714$ Å ($\lambda = 1.54178$ Å)¹⁶. Relative intensities, I_{rel} , are given as a peak height. IR spectra were carried out on Mo-221 spectrophotometer (Perkin-Elmer) by the standard KBr platelets technique.

RESULTS

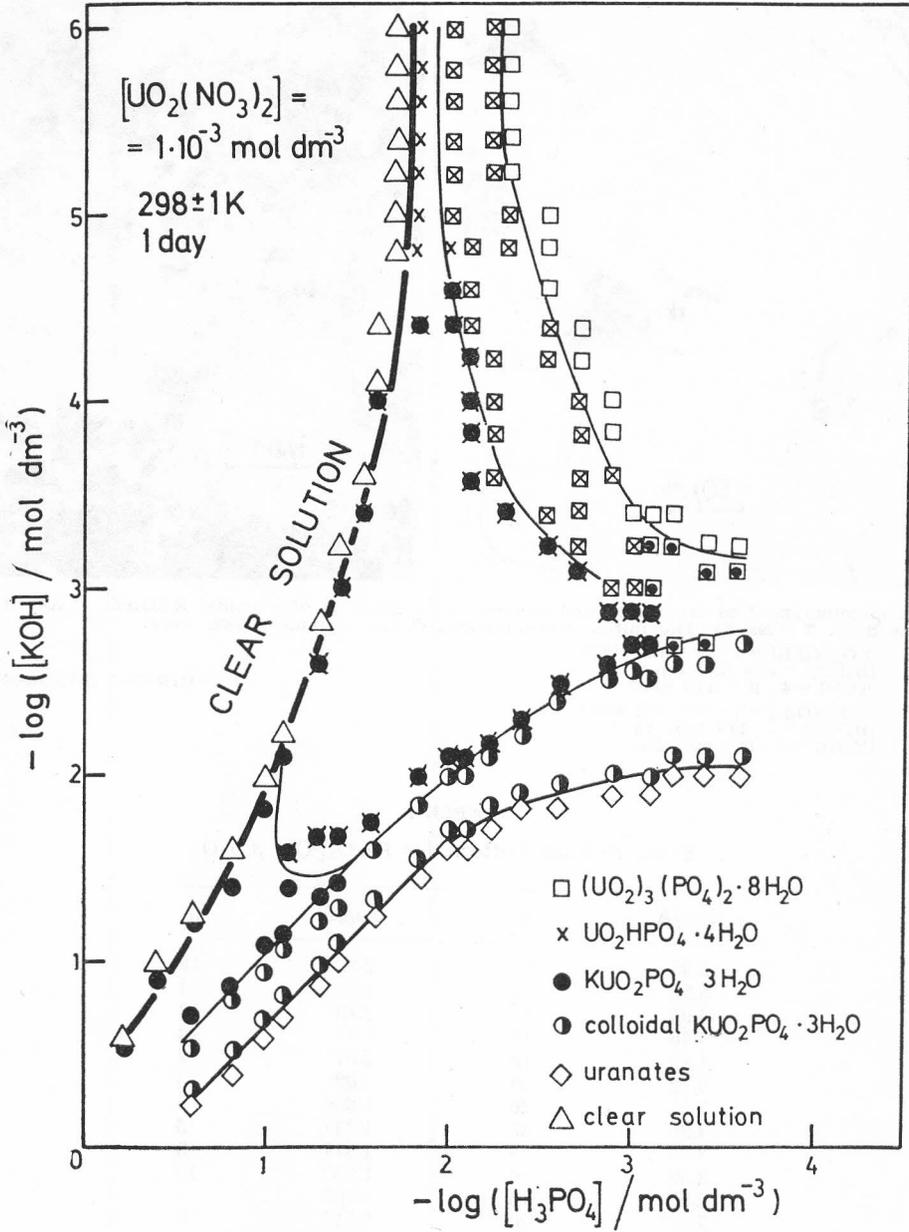
The spontaneous precipitation in the system $\text{UO}_2(\text{NO}_3)_2 - \text{KOH} - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ (at 298 K) was performed at constant uranyl(2+)nitrate concentration, $1 \cdot 10^{-3}$ mol dm^{-3} ; the concentrations of KOH varied from $1 \cdot 10^{-6}$ to $6 \cdot 10^{-1}$ mol dm^{-3} and phosphoric acid from $2 \cdot 10^{-4}$ to $6 \cdot 10^{-1}$ mol dm^{-3} .

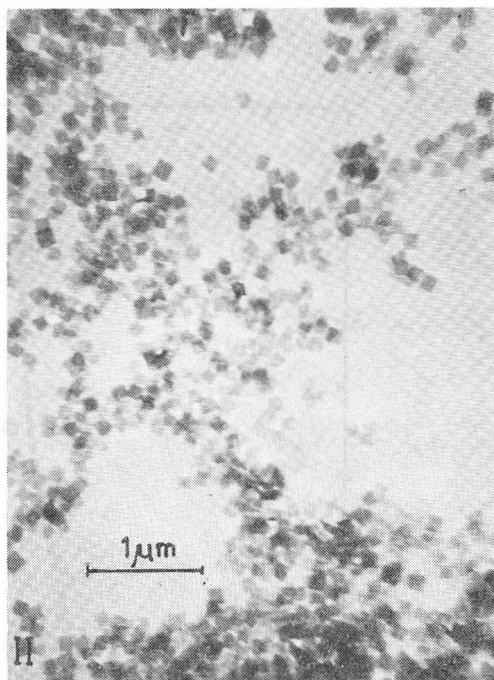
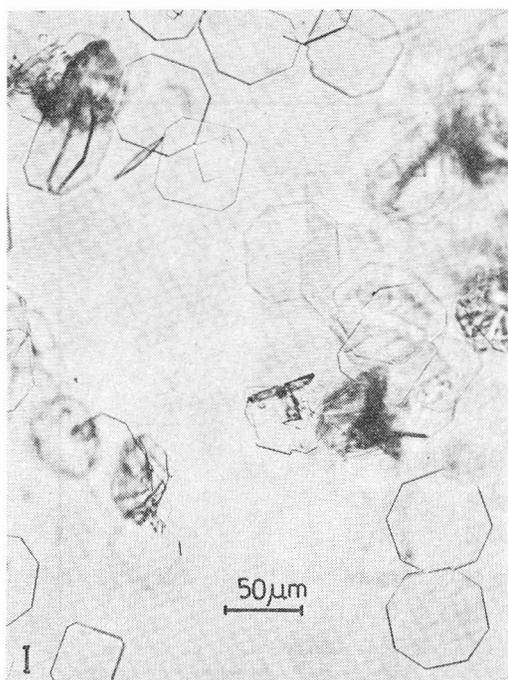
The precipitation diagram of this system, a day after the mixing of the components, is presented in Figure 1. The precipitation boundary was detected tyndallogometrically and microscopically (visible, UV and electron microscopy). The solid phases were identified by X-ray powder diffraction patterns and IR spectroscopy. The phase boundaries were determined on the basis of these data and light microscopy. For the sake of clarity only the dots near the precipitation and phase boundaries are marked.

In the region of the precipitation of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ an influence of KOH can be neglected. The stability region of $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ in this system can be compared with those found in the $\text{UO}_2(\text{NO}_3)_2 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ system² at analogous conditions (reactant concentrations, pH).

Uranates are precipitated in the extremely base conditions, $\text{pH} > 9.5$ ($[\text{KOH}] \gg [\text{H}_3\text{PO}_4]$).

The boundary between $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and its mixture with $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ was determined according to the identified solid phases by means of an X-ray powder diffraction and chemical analysis. The X-ray powder diffraction pattern of $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ is given in Table I. The crystalline $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (microphotograph I) appears at high concentrations of KOH and H_3PO_4 ($[\text{KOH}] \approx [\text{H}_3\text{PO}_4] \gg [\text{UO}_2(\text{NO}_3)_2]$ at $\text{pH} = 1.5 - 3.5$). However, the


 Figure 1. Precipitation diagram of 1 day aged system $\text{UO}_2(\text{NO}_3)_2\text{--KOH--H}_3\text{PO}_4\text{--H}_2\text{O}$.



Microphotograph I of crystalline and electron micrograph II of colloidal $K_2UO_2PO_4 \cdot 3H_2O$ ($t = 30$ days, $T = 298$ K). The initial concentrations at the systems shown were:

I — $[UO_2(NO_3)_2] = 1 \cdot 10^{-3}$ mol dm^{-3}
 $[H_2PO_4] = 0.15$ mol dm^{-3}
 $[KOH] = 4 \cdot 10^{-2}$ mol dm^{-3}

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II — $[UO_2(NO_3)_2] = 1 \cdot 10^{-3}$ mol dm^{-3}
 $[H_2PO_4] = 3 \cdot 10^{-3}$ mol dm^{-3}
 $[KOH] = 6 \cdot 10^{-3}$ mol dm^{-3}

TABLE I

X-ray Powder Pattern for $K_2UO_2PO_4 \cdot 3H_2O$

$d_{obs}/\text{Å}$	I_{rel}	$d_{obs}/\text{Å}$	I_{rel}
8.95	100	2.23	15
5.52	20	2.21	11
4.95	18	2.16	14
4.46	18	2.13	10
4.33	18	2.07	9
3.72	55	2.03	8
3.51	26	1.896	5
3.26	28	1.837	6
3.15	5	1.817	5
3.09	4	1.782	10
2.95	15	1.752	5
2.74	20	1.717	4
2.56	8	1.679	11
2.48	7	1.627	6
2.39	9	1.589	8
2.26	6	1.568	6

formation of colloidal particles (electron micrograph II) is accompanied by a high concentration of KOH ($[\text{KOH}] > [\text{H}_3\text{PO}_4]$, $\text{pH} > 3.5$).

In Figure 2 diagram of 30 day aged system is presented.

Figure 3 illustrates relations between $[\text{KOH}]$ and pH at various $[\text{H}_3\text{PO}_4]$ (crosssection through precipitation diagram in Figure 2).

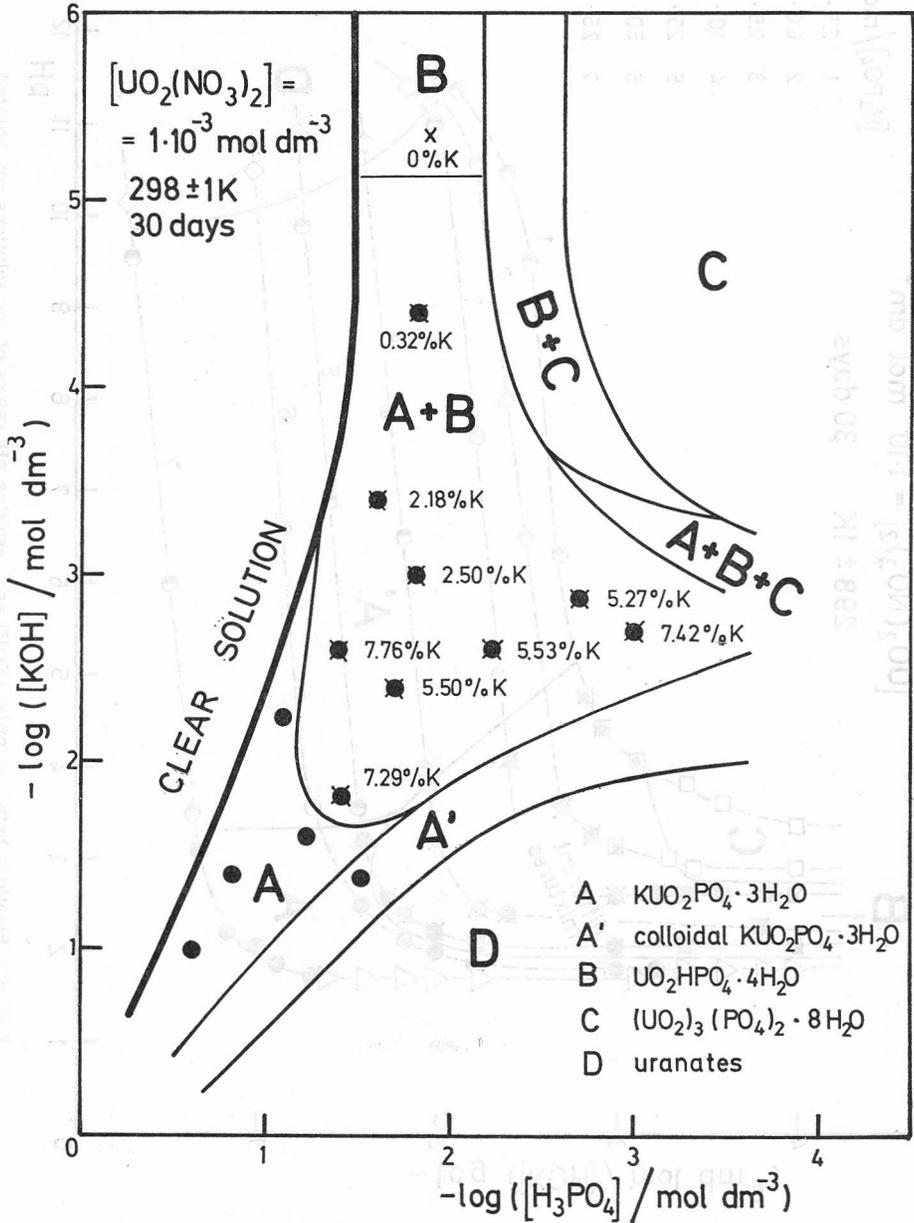


Figure 2. Precipitation and phase boundaries in the 30 day aged system defined in Figure 1. In the assigned samples the percentage of potassium in the precipitate is determined. The solid phase in the region A (filled circles) is identified as $\text{KUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$.

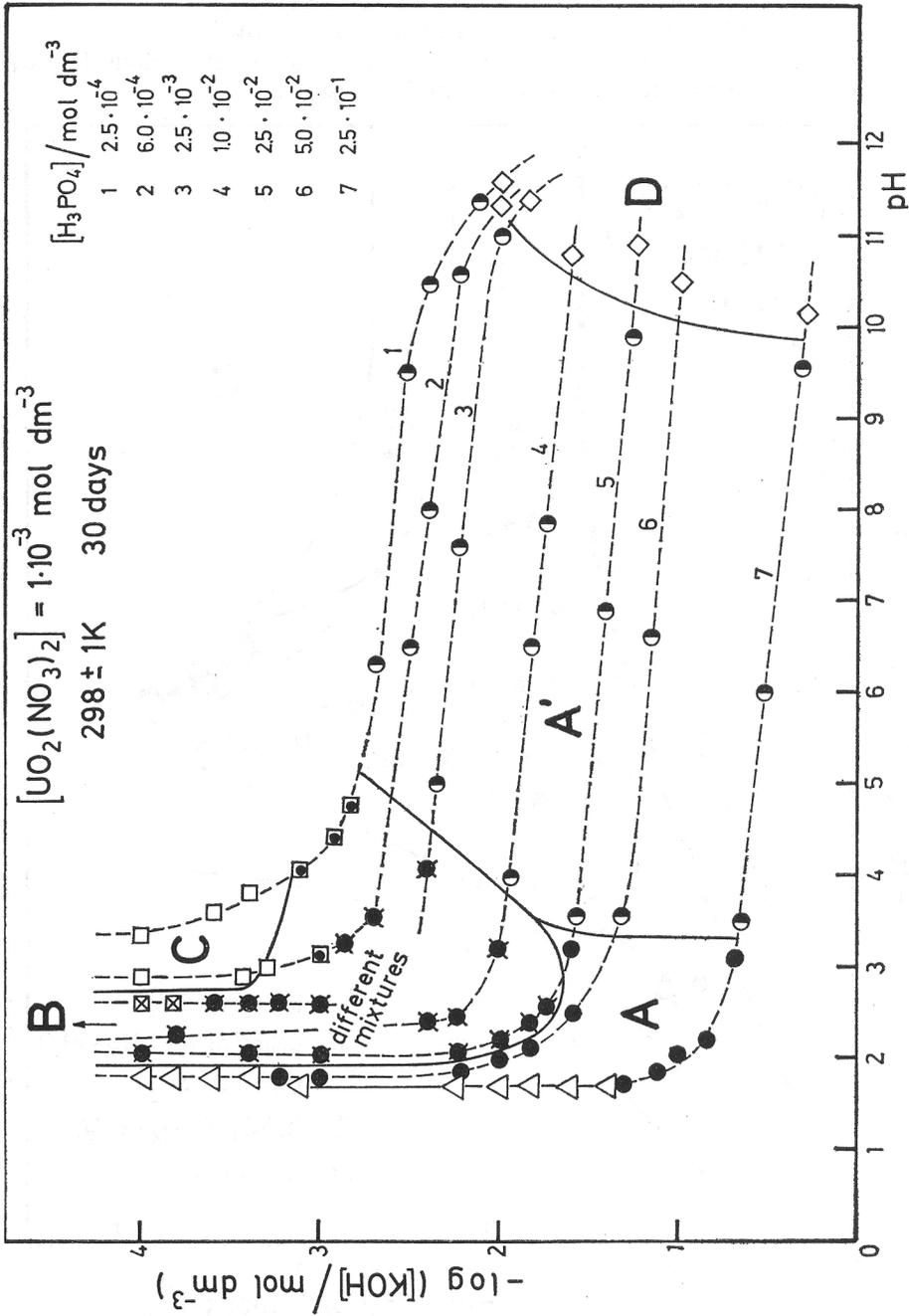


Figure 3. Relations between initial [KOH] and resulting pH values of the solutions equilibrated with different solid phase at various initial $[\text{H}_3\text{PO}_4]$ (crosssections through precipitation diagram in Figure 2).

The precipitates marked by dots (Figure 2) were chemically analysed. In the mixture region of KUO₂PO₄ · 3H₂O and UO₂HPO₄ · 4H₂O (Figure 2, region A + B) the percentage of K in the precipitates was determined indicating the amount of the particular solid phase in the mixture. Chemical analyses of the precipitates in the region A (at marked dots) revealed the following values:

	%U	%P	%K	% weight loss
Found:	51.14—51.95	6.66—6.88	8.29—8.63	11.33—11.85
Calculated:	51.95	6.76	8.53	11.80

giving an evidence of KUO₂PO₄ · 3H₂O. A TGA curve shows the loss of 2.5 mol H₂O till 353 K and the additional 0.5 mol loss up to 408 K.

The stability of colloidal KUO₂PO₄ · 3H₂O depends on [KOH]/[H₃PO₄] and pH. The colloid formation occurs simultaneously with the jump of the pH values in the system (Figure 3, curves 1—7). The colloidal particles are stable in the region of [KOH] > [H₃PO₄] and pH > 3.5 with domination of H_nPO₄ⁿ⁻³ (n = 0 to 2) anions. The microelectrophoretic measurements detected negatively charged colloidal particles.

Table II gives the experimental values of all components in the solutions determined according to the precipitation boundary: equilibrium concentrations of [UO₂]_{sol}, [PO₄]_{sol} and [K]_{sol}, pH values and ionic strengths.

The concentration of [UO₂]_{sol} is the sum of all uranyl species in solution and is given by equation:

$$[UO_2]_{sol} = \sum_{i=0} \sum_{j=0} [UO_2(H_3PO_4)_i (H_2PO_4)_j^{i-2j}] \tag{1}$$

The concentration of [PO₄]_{sol} is the sum of free phosphates (H₃PO₄, H₂PO₄⁻) and phosphates incorporated in uranyl complexes,

$$[PO_4]_{sol} = [H_3PO_4]_{free} + [H_2PO_4^-]_{free} + [PO_4]_{complex} \tag{2}$$

The concentration of [K]_{sol} is equal to the concentration of [K⁺].

The equilibrium constants of uranyl phosphate complex species are defined as:

TABLE II

Equilibrium Concentrations Determined According to Precipitation Boundary and Calculated K_s Values for KUO₂PO₄ · 3H₂O

	$\frac{[PO_4]_{sol} \cdot 10^3}{mol\ dm^{-3}}$	$\frac{[K]_{sol} \cdot 10^3}{mol\ dm^{-3}}$	pH	$\frac{I \cdot 10^3}{mol\ dm^{-3}}$	logK _s	log K _{s0} (corr.)
1	40	0.45	1.95	11	-25.86	-26.50
2	50	0.50	1.83	17	-25.59	-26.35
3	80	2.00	1.71	23	-25.29	-26.14
4	100	5.00	1.61	27	-25.08	-26.03
5	150	12.50	1.56	38	-25.40	-26.42
6	250	35.00	1.67	64	-24.32	
7	400	112.50	1.75	150	-23.76	

In all systems [UO₂]_{sol} = 1 · 10⁻³ mol dm⁻³

$$\beta_{ij} = \frac{[\text{UO}_2^{2+}] [\text{H}_3\text{PO}_4]^{i+j}}{[\text{UO}_2(\text{H}_3\text{PO}_4)_i (\text{H}_2\text{PO}_4)_{j-2}^{2-j}] [\text{H}^+]^j} \quad (3)$$

According to the equations (1) and (3) the solubility product of $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ ($K_s = [\text{K}^+] [\text{UO}_2^{2+}] [\text{PO}_4^{3-}]$) is expressed as:

$$K_s = \frac{[\text{UO}_2]_{\text{sol}} [\text{K}^+] [\text{H}_3\text{PO}_4]_{\text{free}}}{K_{13} K_{12} K_1 [\text{H}^+]^3} \left(\sum_{i=0} \sum_{j=0} \frac{\beta_{ij} [\text{H}_3\text{PO}_4]_{\text{free}}^{i+j}}{[\text{H}^+]^j} \right)^{-1} \quad (4)$$

The values of association constants of phosphoric acid¹⁷⁻¹⁹ ($\log K_{13} = 2.148$, $\log K_{12} = 7.199$, $\log K_1 = 12.35$) and the equilibrium constants for different uranyl phosphato complex species³ ($\beta_{01} = 1.50$, $\log \beta_{10} = 1.30$, $\log \beta_{02} = 1.30$, $\log \beta_{12} = 2.30$) were used in the calculations (at $I = 0 \text{ mol dm}^{-3}$). The values of constants are corrected to the corresponding ionic strength using the Davies equation²⁰ (for $I < 0.05 \text{ mol dm}^{-3}$) and according to the activity coefficients of uranyl ions^{21,22} (for $I > 0.05 \text{ mol dm}^{-3}$).

The solubility product for each system at corresponding ionic strength ($\log K_s$) and the values corrected to $I = 0$ ($\log K_{s0}$) are presented in Table II. The mean value of $\log K_{s0} = -26.28 \pm 0.25$.

DISCUSSION

Certain structural relations can be found between the $\text{UO}_2\text{HPO}_4 \cdot 4 \text{H}_2\text{O}$ and $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$. An X-ray crystal structure determination²³ and thermal stability,^{2,24} and conductivity measurements²⁵ of $\text{UO}_2\text{HPO}_4 \cdot 4 \text{H}_2\text{O}$ established the H_3O^+ in the structure, thus the correct structural formula is $\text{H}_3\text{O}[\text{UO}_2\text{PO}_4] \cdot 3 \text{H}_2\text{O}$. An analogous structural formula of $\text{K}[\text{UO}_2\text{PO}_4] \cdot 3 \text{H}_2\text{O}$ suggests a similar octahedral coordination around uranium composed of four phosphato groups and two oxo atoms²³. Three water molecules are involved in hydrogen bonding although some differences can be expected in crystal packing due to the different size of H_3O^+ and K^+ . Rather similar X-ray powder patterns of these compounds confirm close structural relationship.

The transformation of $\text{UO}_2\text{HPO}_4 \cdot 4 \text{H}_2\text{O}$ to $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ in the system aged from 1 to 30 days was observed explaining the shifts of phase boundaries (Figures 1 and 2, $[\text{KOH}] > 3 \cdot 10^{-3} \text{ mol dm}^{-3}$). During the aging of the system (Figures 1 and 2, $[\text{KOH}] < 1 \cdot 10^{-3} \text{ mol dm}^{-3}$) transformation of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ to $\text{UO}_2\text{HPO}_4 \cdot 4 \text{H}_2\text{O}$ was detected. The same transformation was occurred also in the system without KOH^2 .

After one day the precipitation boundary is shifted to the lower concentrations of reactants in the 30 day aged system.

The value of solubility product ($\log K_{s0} = -26.28$) is in disagreement with the value given by Chukhlantsev et al.¹⁰ and Muraveva et al.⁶ ($\log K_{s0} = 23.1$) because these authors did not consider the uranyl phosphato complex formation. Vesely et al.¹¹ determined solubility product of $\text{KUO}_2\text{PO}_4 \cdot n \text{H}_2\text{O}$ at $I = 0.23 \text{ mol dm}^{-3}$ ($\log K_s = -25.50$) using literature association constants of H_3PO_4 at $I = 0 \text{ mol dm}^{-3}$ and literature constants of uranyl complexes at $I = 1 \text{ mol dm}^{-3}$, without correction to the corresponding ionic strength ($I = 0.23 \text{ mol dm}^{-3}$). The values of equilibrium constants corrected to $I = 0.23 \text{ mol dm}^{-3}$ are: for uranyl complexes³ $\log \beta_{01} = 1.30$, $\log \beta_{10} = 1.30$, $\log \beta_{02} = 1.03$, $\log \beta_{12} = 2.03$ and for phosphoric acid^{26,27} $\log K_{13} = 1.90$, $K_{12} = 6.65$, $\log K_1 = 11.59$. The experimental solubility data from Vesely et al.¹¹ for $\text{KUO}_2\text{PO}_4 \cdot n \text{H}_2\text{O}$ and our solubility data for $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ are presented in Figure 4, an inter-

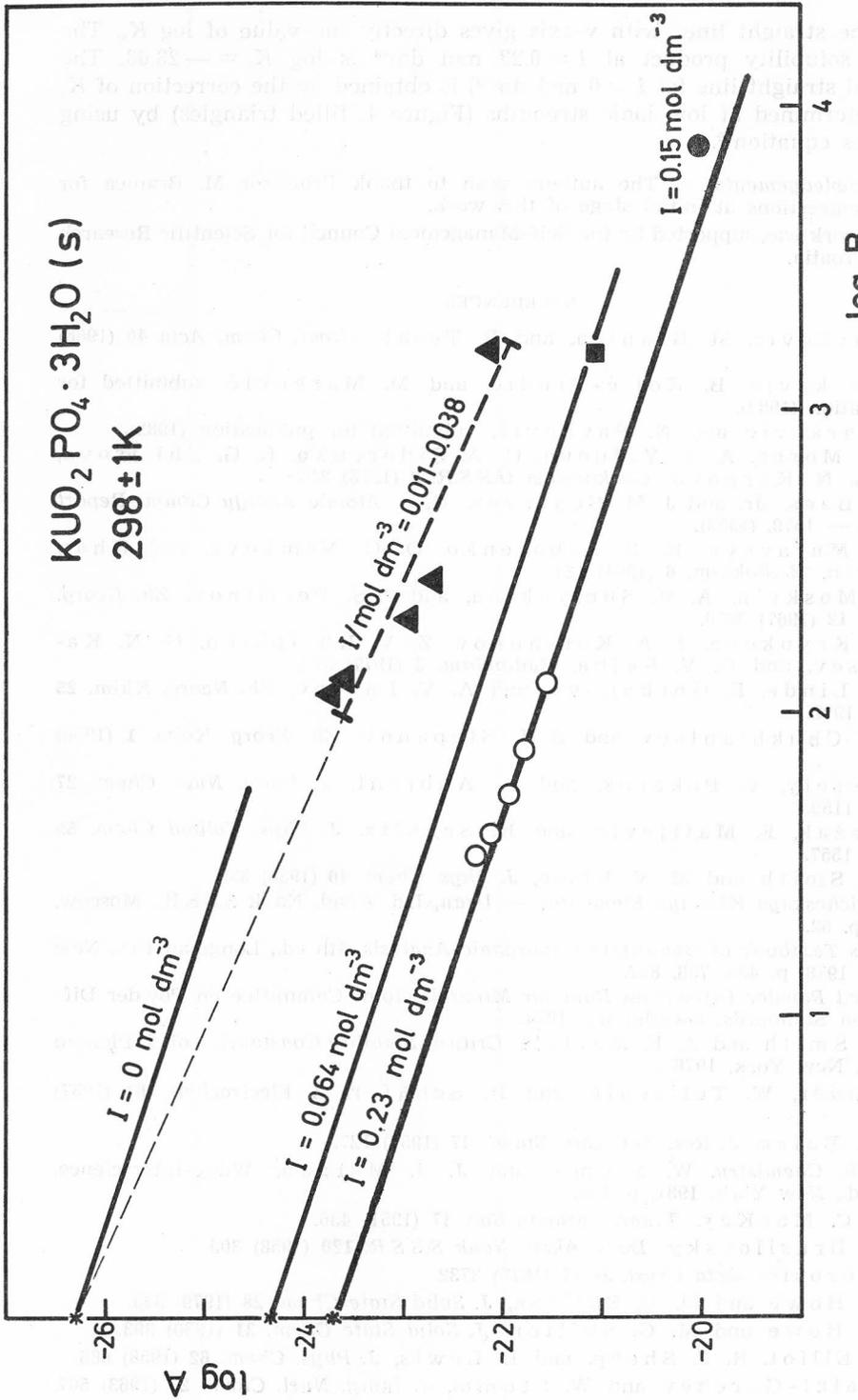


Figure 4. Determination of $\log K_s$ for $KUO_2PO_4 \cdot 3H_2O(s)$ at $I/mol\ dm^{-3} = 0$ to 0.15 (filled triangles, square and circle — our data) and at $I = 0.23\ mol\ dm^{-3}$ (open circles — reinterpreted literature data). The values of K_s are determined according to equation (4):
 $A = [UO_2]_{sol} [K^+] [H_3PO_4]_{free} K_{13}^{-1} K_{12}^{-1} K_{11}^{-1} [H^+]^3$
 $B = \sum_{i=0}^{i=3} \beta_{ij} [H_3PO_4]_{free} [H^+]^{-i}$
 $\log K_s = \log A - \log B$

cept of the straight lines with y-axis gives directly the value of $\log K_s$. The value of solubility product at $I = 0.23 \text{ mol dm}^{-3}$ is $\log K_s = -23.68$. The theoretical straight line (at $I = 0 \text{ mol dm}^{-3}$) is obtained by the correction of K_s values determined at low ionic strengths (Figure 4, filled triangles) by using the Davies equation²⁰.

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SAŽETAK

Spontano taloženje u sistemu $\text{UO}_2(\text{NO}_3)_2\text{—KOH—H}_3\text{PO}_4\text{—H}_2\text{O}$ *N. Pavković, M. Marković i B. Kojić-Prodić*

Ispitan je taložni sistem $\text{UO}_2(\text{NO}_3)_2\text{—KOH—H}_3\text{PO}_4\text{—H}_2\text{O}$ (pri 298 K) staren 1 dan i 30 dana ($[\text{UO}_2(\text{NO}_3)_2] = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$, varirani su $[\text{KOH}]$ od $1 \cdot 10^{-6}$ do $6 \cdot 10^{-1}$ i $[\text{H}_3\text{PO}_4]$ od $2 \cdot 10^{-4}$ do $6 \cdot 10^{-1} \text{ mol dm}^{-3}$, $1.5 < \text{pH} < 11.5$). Određene su taložne i fazne granice.

$\text{UO}_2\text{HPO}_4 \cdot 4 \text{H}_2\text{O(s)}$ i $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ su stabilni kod $[\text{KOH}] < 1 \cdot 10^{-3} \text{ mol dm}^{-3}$, $1.5 < \text{pH} < 4.0$. Uranati talože kod $\text{pH} > 9.5$. Područje stabilnosti $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O(s)}$ nalazi se kod visokih koncentracija KOH i H_3PO_4 .

Navedeni su međuplošni razmaci i intenziteti $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ dobiveni rendgenskom difrakcijom na praškastom uzorku.

Produkt topljivosti $\text{KUO}_2\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ određen je iz podataka s taložne granice nakon 30 dana (ravnotežni uvjeti) i iznosi $\log([\text{K}^+][\text{UO}_2^{2+}][\text{PO}_4^{3-}]) = -26.28$ (kod $I = 0 \text{ mol dm}^{-3}$).