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Original Scientific Paper

**Precipitation and Solubility of Uranyl Orthophosphates. II.\***  
**Heterogeneous Equilibria in Solutions of:**  
 **$\text{UO}_2(\text{NO}_3)_2$  —  $\text{H}_3\text{PO}_4$  —  $\text{HNO}_3$**

N. Pavković,\*\* M. Wrischer, and M. Branica

*Department of Physical Chemistry, Institute »Ruđer Bošković«, and Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia*

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The precipitation and dissolution of uranium(VI) from aqueous solutions containing  $10^{-3}$  M uranyl nitrate and various concentrations of orthophosphoric and nitric acid is surveyed. The concentration regions where  $(\text{UO}_2)_3(\text{PO}_4)_2$  and  $\text{UO}_2\text{HPO}_4$  are precipitated and/or dissolved are presented by means of typical precipitation bodies. The influence of the initial concentration ratio of nitric/orthophosphoric acid in the precipitation system on the morphology of  $(\text{UO}_2)_3(\text{PO}_4)_2$  particles formed is shown by electron micrographs.

#### INTRODUCTION

The precipitation and dissolution of  $(\text{UO}_2)_3(\text{PO}_4)_2$  and  $\text{UO}_2\text{HPO}_4$  in solutions containing nitric acid has found its application in the uranium production technology<sup>1-2</sup>.

Up to now only the solubility behaviour of  $\text{UO}_2\text{HPO}_4$  in nitric and perchloric acid has been reported<sup>3,4</sup>. However, there is not much information available on the precipitation of both  $(\text{UO}_2)_3(\text{PO}_4)_2$  and  $\text{UO}_2\text{HPO}_4$  and on the solubility behaviour of  $(\text{UO}_2)_3(\text{PO}_4)_2$  in solutions containing nitric acid<sup>5,6</sup>.

In our previous paper<sup>7</sup> the influence of changes in concentrations of uranyl nitrate and orthophosphoric acid on the precipitation and dissolution processes of uranium (VI) has been shown. In the present work the concentration of uranyl nitrate was kept constant ( $1 \times 10^{-3}$  M) and the influence of changes in the concentrations of orthophosphoric and nitric acid on the mentioned processes was studied.

#### EXPERIMENTAL

All chemicals were reagent grade. The systems were obtained by mixing equal volumes of solutions of uranyl nitrate and phosphoric acid, the solutions of phosphoric acid contained different amounts of nitric acid. The method of the preparation of the systems, their analyses and the instruments used have been the same as in the previous work<sup>7</sup>.

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## RESULTS

The precipitation of uranium (VI) from solutions containing  $10^{-3}$  M uranyl nitrate and varying concentrations of phosphoric acid (from  $2 \times 10^{-5}$  M to  $4 \times 10^{-2}$  M) and nitric acid (from  $10^{-6}$  to  $10^{-1}$  M) is surveyed by means of the typical precipitation bodies<sup>8,9</sup> which are represented in the lower parts of Figs. 1 and 2. The distribution of  $(\text{UO}_2)_3(\text{PO}_4)_2$  and  $\text{UO}_2\text{PHO}_4$  species, as detected by fluorescent microscopy and verified by chemical analyses is presented as a function of the concentrations of phosphoric and nitric acids. The systems were aged in contact with the mother liquor for 24 hours (Fig. 1) and 30 days (Fig. 2) respectively. On the upper parts of Figs. 1 and 2 two kinds of pH curves are shown. The first one (curves 1) denotes the pH values

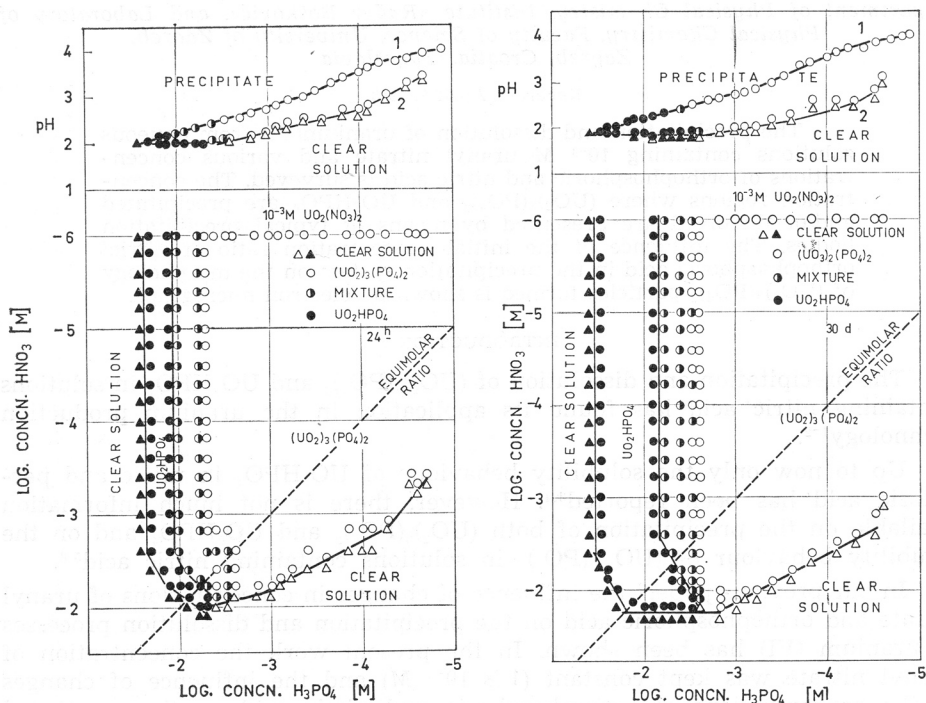
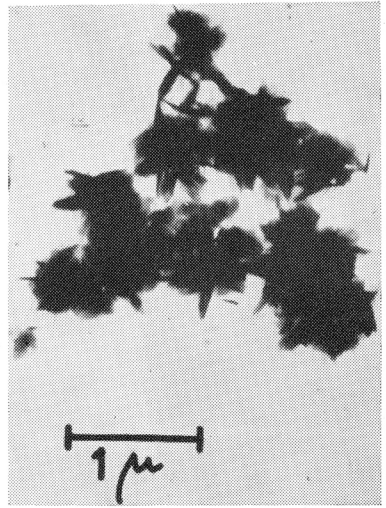
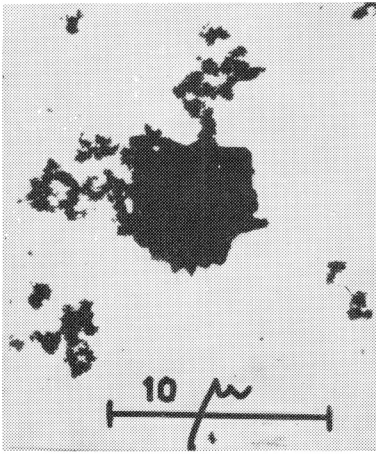
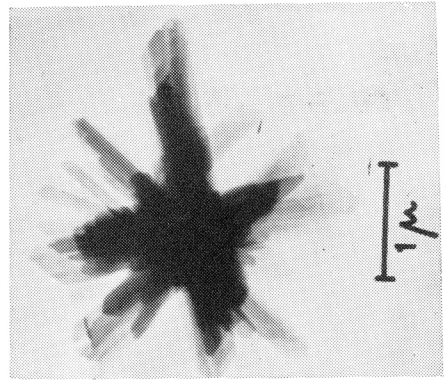
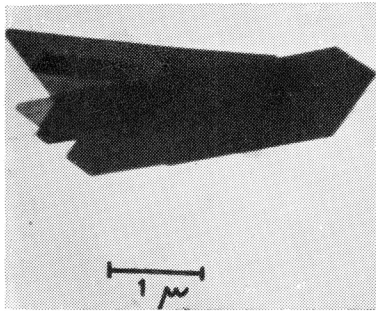
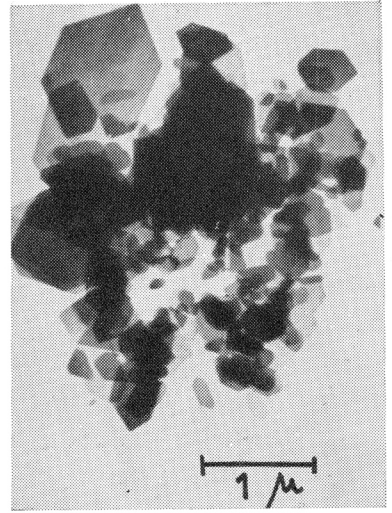
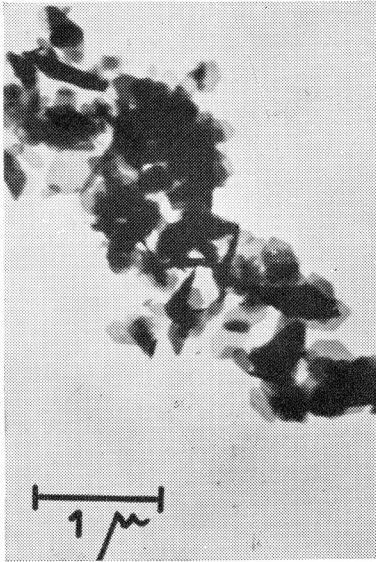


Fig. 1. Lower part. Typical precipitation body of the system:  $1 \times 10^{-3}$  M  $\text{UO}_2(\text{NO}_3)_2 - \text{H}_3\text{PO}_4$  (var.) -  $\text{HNO}_3$  (var.) 24 hours after mixing, at room temperature. Upper part: pH curve 1 corresponds to the system:  $1 \times 10^{-3}$  M  $\text{UO}_2(\text{NO}_3)_2 - \text{H}_3\text{PO}_4$  (var.) and pH curve 2 to the system:  $1 \times 10^{-3}$  M  $\text{UO}_2(\text{NO}_3)_2 - \text{H}_3\text{PO}_4$  (var.) -  $\text{HNO}_3$  (var.) Full triangles demonstrate the clear solutions which show a more intensive fluorescence than the solutions of uranyl nitrate of the same concentrations. Fig. 2. Typical precipitation body of the  $1 \times 10^{-3}$  M  $\text{UO}_2(\text{NO}_3)_2 - \text{H}_3\text{PO}_4$  (var.) -  $\text{HNO}_3$  (var.) systems at room temperature. The precipitates were in contact with the mother liquor for 30 days.

for the mother liquor of the systems:  $\text{UO}_2(\text{NO}_3)_2$  ( $10^{-3}$  M) -  $\text{H}_3\text{PO}_4$  (var.) without any addition of nitric acid (corresponding to the pH curve in Fig. 1, paper No. I<sup>7</sup>). The second one (curves 2, Figs. 1 and 2) denotes the pH values for the solutions of corresponding composition but with different amounts of nitric acid added to the systems at the precipitation boundary. Comparing Figs. 1 and 2 changes of the solid with time can be seen. Observations on a great



Figs. 3a—b. Electron micrographs of the precipitates obtained from the systems listed in Table I made 24 hours after mixing. The systems were aged at room temperature.



Figs. 4a—d. Electron micrographs of the precipitates obtained from the systems listed in Table I made 24 hours after mixing. The systems were aged at room temperature.

number of systems have shown that complete equilibrium between the solid phase and the mother liquor is attained after 10 to 14 days.

At the precipitation boundary in the range of excess of phosphoric acid  $\text{UO}_2\text{HPO}_4$  is the stable form and the clear solutions in these concentration regions exhibit very intensive fluorescence when excited by UV light. In the range of excess of uranyl nitrate  $(\text{UO}_2)_3(\text{PO}_4)_2$  was found to be the stable solid phase (Fig. 2). The fluorescence of the clear solutions in this part of the precipitation boundary has an comparable intensity to intensity of the fluorescence of a  $10^{-3}$  M uranyl nitrate solution.

The electron micrographs 3a and 3b show the morphology of particles which precipitate in the uranyl nitrate—orthophosphoric acid system without addition of nitric acid. In Fig. 3a a mixture of particles of  $(\text{UO}_2)_3(\text{PO}_4)_2$  (small crystals) and of  $\text{UO}_2\text{HPO}_4$  (much bigger rectangular crystals) is shown while in Fig. 3b only crystals of  $(\text{UO}_2)_3(\text{PO}_4)_2$  can be optically selected. From the electron-micrographs 4a—d the influence of the addition of increasing concentrations of nitric acid on the morphology of the  $(\text{UO}_2)_3(\text{PO}_4)_2$  particles can be seen. In Table I are listed the concentrations of orthophosphoric acid, nitric acid, their ratio and the pH of the mother liquor of the corresponding precipitation systems.

It is evident (Figs. 4a—d) that the crystals become larger with increasing concentrations of nitric acid in the systems. At extreme concentrations of nitric acid large, rod-like crystals were formed (Figs. 4c, d). The influence of nitric acid on the growth of  $\text{UO}_2\text{HPO}_4$  crystals was less evident.

TABLE I

Fig. No.	Initial concn. (M) of $\text{H}_3\text{PO}_4$	Initial concn. (M) of $\text{HNO}_3$	Ratio of the conc. $\text{HNO}_3/\text{H}_3\text{PO}_4$	pH of the mother liquor	Composition of the ppt. 24 hours after mixing
3 a	$3 \times 10^{-3}$	—	—	2.50	$(\text{UO}_2)_3(\text{PO}_4)_2$ and $\text{UO}_2\text{HPO}_4$
3 b	$3 \times 10^{-3}$	—	—	2.50	$(\text{UO}_2)_3(\text{PO}_4)_2$
4 a	$3 \times 10^{-3}$	$1 \times 10^{-4}$	0.033	2.50	$(\text{UO}_2)_3(\text{PO}_4)_2$
4 b	$3 \times 10^{-3}$	$3.0 \times 10^{-3}$	1.0	2.31	$(\text{UO}_2)_3(\text{PO}_4)_2$
4 c	$3 \times 10^{-3}$	$6.6 \times 10^{-3}$	2.2	2.14	$(\text{UO}_2)_3(\text{PO}_4)_2$
4 d	$2 \times 10^{-4}$	$2.8 \times 10^{-3}$	1.4	2.55	$(\text{UO}_2)_3(\text{PO}_4)_2$

In all systems uranyl nitrate concentration was kept constant at  $1 \times 10^{-3}$  M.

## DISCUSSION

Comparing the results described in this and the previous paper<sup>7</sup> we may draw some conclusions as to the influence of changes in the initial pH (as achieved by the addition of nitric acid) on the precipitation and dissolution processes in the system  $\text{UO}_2(\text{NO}_3)_2$  ( $1 \times 10^{-3}$  M) —  $\text{H}_3\text{PO}_4$  (*var.*) —  $\text{HNO}_3$  (*var.*). Similarly as in the system without nitric acid in the entire concentration range investigated only precipitates of  $(\text{UO}_2)_3(\text{PO}_4)_2$  and  $\text{UO}_2\text{HPO}_4$  were formed. Their distribution was independent of the initial pH, *i. e.* of the concentration of nitric acid added (Fig. 2) up to approximately equimolar concentrations of nitric and phosphoric acid.

The slopes of the precipitation boundaries at nitric acid concentrations higher than  $3 \times 10^{-3}$  M indicate the formation of several different soluble

complex uranyl orthophosphates whose hydrogen to phosphate ratios differ from the hydrogen to phosphate ratios of the respective solid phases. It is also obvious from these data, as well as from the different fluorescence behaviour of the mother liquors which were in equilibrium with  $(\text{UO}_2)_3(\text{PO}_4)_2$  and  $\text{UO}_2\text{HPO}_4$ , that different complex species are in equilibrium with these two solids.

Of interest is also the significant effect of the initial concentration ratio of nitric/orthophosphoric acid in the systems on the morphology of the precipitated  $(\text{UO}_2)_3(\text{PO}_4)_2$  particles. This effect is especially pronounced in the vicinity of the precipitation boundary and thus might be due to highly prolonged precipitation processes.

The calculation of more probable soluble species and their equilibrium constants will be done in one of the following paper.

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#### REFERENCES

1. *Processing of Low-Grade Uranium Ores, Proceedings of Panel*, Vienna, 27 June—1 July 1966, International Atomic Energy Agency, Vienna, 1967.
2. C. D. Harrington and A. E. Ruehle, *Uranium Production Technology*, D. V. Nostrand Company, Inc., New York, 1959 pp. 15—17, 24—25.
3. G. R. Leader, *Report CN-2195* (1944).
4. J. M. Schreyer and C. F. Baes Jr., *J. Phys. Chem.* **59** (1955) 1179.
5. A. D. Ryon and D. W. Kuhn, *Report Y-315* (1949).
6. A. D. Ryon and D. W. Kuhn, *Report Y-381* (1949).
7. N. Pavković, M. Branica, and B. Težak, *Croat. Chem. Acta* **40** (1968) 117.
8. B. Težak and collaborators, *Disc. Faraday Soc.* **42** (1966) 175.
9. H. Füredi, *Complex Precipitation Systems, Chapter 6 of The Formation and Properties of Precipitates* by A. G. Walton, Interscience Publ., New York, 1967.

#### IZVOD

### Taloženje i topljivost uranil ortofosfata II. Heterogena ravnoteža u otopinama: $\text{UO}_2(\text{NO}_3)_2\text{—H}_3\text{PO}_4\text{—HNO}_3$ .

N. Pavković, M. Wrischer i M. Branica

Ispitano je taloženje i otapanje urana(VI) iz vodenih otopina koje su sadržavale  $10^{-3}$  M uranil nitrat i razne koncentracije ortofosforne i dušične kiseline. Koncentraciona područja, gdje se talože ili otapaju talozi sastava  $(\text{UO}_2)_3(\text{PO}_4)_2$  i  $\text{UO}_2\text{HPO}_4$  prikazana su općim precipitacionim dijagramima.

Elektronskim mikrofotografijama prikazan je utjecaj početnoga koncentracionog odnosa dušična/ortofosforna kiselina na morfologiju nastalih čestica taloga  $(\text{UO}_2)_3(\text{PO}_4)_2$ .

ODJEL FIZIČKE KEMIJE  
INSTITUT »RUDER BOŠKOVIĆ«

I  
FIZIČKO-KEMIJSKI ZAVOD  
PRIRODOSLOVNO-MATEMATIČKI FAKULTET  
SVEUČILIŠTE U ZAGREBU

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