CCA-508

541.18.041:546.185.791.6
Original Scientific Paper

Precipitation and Solubility of Uranyl-Orthophosphates. I.* Heterogeneous Equilibria in Solutions of: $UO_2(NO_3)_2$ — H_3PO_4

*N. Pavković,** M. Branica, and B. Težak*

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

Received April 6, 1968

The precipitation and dissolution of uranium(VI) from aqueous solutions of orthophosphoric acid (2×10^{-6} to 6 *M*) and uranyl nitrate (3×10^{-5} to 0.5 *M*) has been investigated by turbidimetric and chemical analyses, fluorescent and electron microscopy. The concentration ranges where $(UO_2)_3(PO_4)_2$ and UO_2HPO_4 precipitates were observed 24 hours and 30 days after mixing are represented by typical precipitation bodies. The morphology of the precipitated particles is shown by electron micrographs. At equilibrium conditions $(UO_2)_3(PO_4)_2$ is stable at concentrations of total phosphate in the mother liquor lower than 1.5×10^{-3} *M*. At total phosphate concentrations higher than 5×10^{-3} *M*, UO_2HPO_4 is stable.

INTRODUCTION

The formation of soluble and slightly soluble uranyl orthophosphates is highly important in the technology of uranium production, especially from low grade uranium phosphate ores and in fuel reprocessing[1-3]. These slightly soluble compounds are also used in analytical chemistry for the determination of uranium and phosphate[4-7].

The interaction of uranyl salts and orthophosphates in aqueous solutions has been the subject of considerable interest. The already published papers report on the precipitation conditions, dissolution[8-10], composition[8,9] and stability ranges of the solid phase[11], solubility products[12-15] and the formation and composition of uranium (VI) orthophosphate complexes[16-19].

Neutral uranyl orthophosphate ($(UO_2)_3(PO_4)_2$) crystallizes in the form of needle-like crystals which do not show fluorescence, while monohydrogen uranyl phosphate (UO_2HPO_4) shows an intensive green fluorescence and crystallizes in the form of tabular platelets, usually four-sided but occasionally as truncated squares[20-24]. The spectra of UO_2HPO_4 were determined and discussed[25] and sorption properties of this compound were studied in detail[26,27]. The method of preparation of $UO_2(H_2PO_4)_2$ was reported[28] and its crystal structure described[11].

However, most of the previously reported data on these subjects were obtained by solubility studies and thus cannot be applied to precipitation

---

* Presented in part at the 2nd Yugoslav Symposium on Reactor Materials, Herceg Novi, October 1965.

** Part of the Thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Chemistry at the Faculty of Science, University of Zagreb.

processes without reservation. Besides many studies are incomplete since the investigations were carried out in narrow concentration regions. In this paper a complete precipitation system within the solubility limits of both uranyl nitrate and orthophosphoric acid is presented. The formation and dissolution of the solid phase in broad concentration regions of both precipitating components are represented by means of typical precipitation bodies[29,30].

EXPERIMENTAL

Stock solutions of uranyl nitrate and orthophosphoric acid were prepared from analytical grade chemicals and bidistilled water. The concentration of uranyl nitrate was determined by precipitation of uranium with ammonium hydroxide and weighing as U_3O_8[31], and that of orthophosphoric acid by alkalimetric titration using thymolphtalein as indicator[32].

The precipitation systems were prepared by direct mixing of the solutions, containing the precipitation components in a chosen concentration, according to a published method[33].

For chemical analyses the systems were centrifuged 24 hours after mixing at 10.000—13.000 RPM. The mother liquor was then filtered off and uranium content determined by a. c. polarography in a supporting electrolyte containing 2 *M* H_3PO_4 and 5×10^{-4} % triton X-100. Phosphorus was determined colorimetrically[34,35].

Instruments used. — Reichert microscope with attachments for fluorescence microscopy, electrostatic electron microscope Trüb, Tauber and Comp. model KM 4, Zeiss tyndallometer in connection with a Pulfrich photometer, Serwall SS-4 centri-

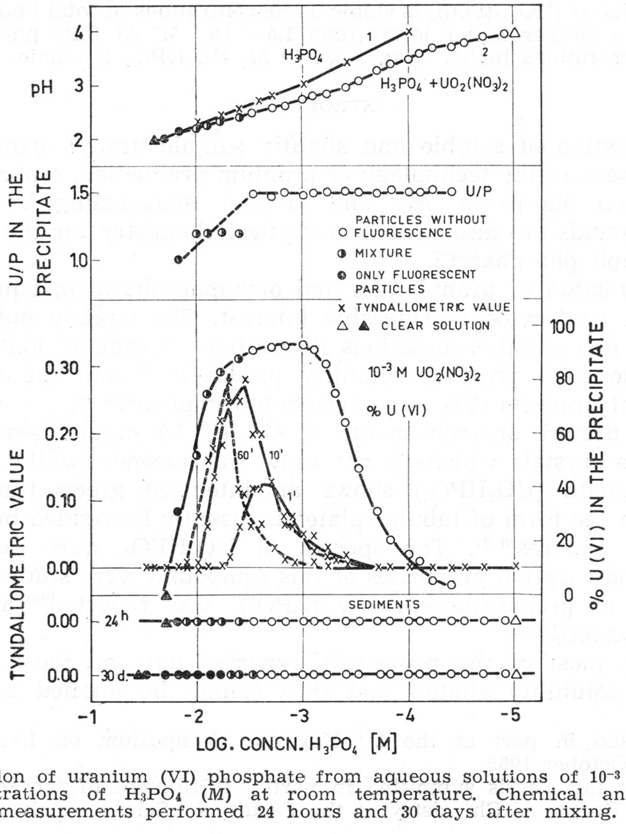
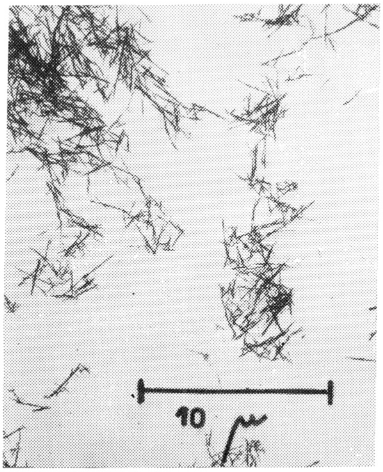


Fig. 1. Precipitation of uranium (VI) phosphate from aqueous solutions of 10^{-3} *M* $UO_2(NO_3)_2$ at different concentrations of H_3PO_4 (*M*) at room temperature. Chemical analyses and *p*H measurements performed 24 hours and 30 days after mixing.



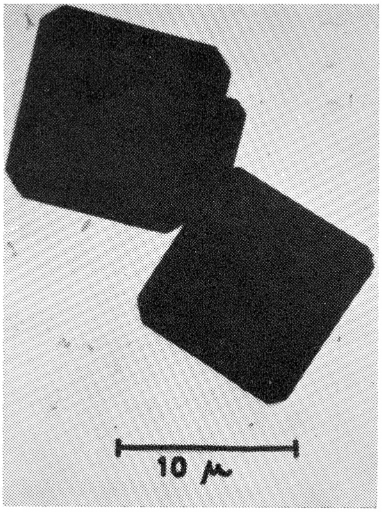


Fig. 2a. Electron micrographs of $(UO_2)_3(PO_4)_2$ precipitates obtained from the systems: 10^{-3} *M* $UO_2(NO_3)_2$ — 6×10^{-4} *M* H_3PO_4 made 30 days after mixing. The systems were aged at room temperature.

Fig. 2b. Electron micrographs of UO_2HPO_4 precipitates obtained from the systems: 10^{-3} *M* $UO_2(NO_3)_2$ — 6×10^{-3} *M* H_3PO_4 made 30 days after mixing. The systems were aged at room temperature.

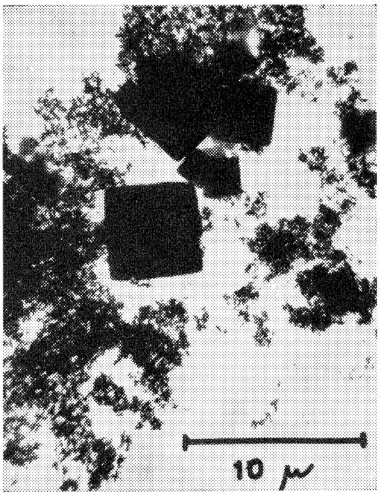


Fig. 2c. Electron micrographs of the mixture of $(UO_2)_3(PO_4)_2$ and UO_2HPO_4 particles of the precipitates obtained from systems: 2.5×10^{-4} *M* $UO_2(NO_3)_2$ — 3×10^{-3} *M* H_3PO_4 made 30 days after mixing. The systems were aged at room temperature.

fuge, Cambridge Pen recording polarograph in connection with the Univector Unit, Klett-Summerson photocolorimeter and a Pye *p*H meter with a glass and calomel electrode.

RESULTS

The formation of the precipitate from a 10^{-3} *M* uranyl nitrate solution with orthophosphoric acid (from 10^{-5} *M* to 10^{-1} *M*) is illustrated in Fig. 1. In the lower part of Fig. 1 are presented the time tyndallograms, the percentage of uranium precipitated (after 24 hours) and the composition (after 24 hours and 30 days) of the solid phase. In the upper part of the same figure the *p*H curve of the mother liquors and that of pure phosphoric acid of the same initial concentrations are shown. The middle part represents the molar ratio of uranium to phosphate in the precipitate (U/P curve). The particle shape of the precipitates can be seen from the electron micrographs depicted in Figs. 2a ($(UO_2)_3(PO_4)_2$), 2b (UO_2HPO_4), and 2c (the mixture of $(UO_2)_3(PO_4)_2$ and UO_2HPO_4). The particles of the $(UO_2)_3(PO_4)_2$ precipitate (molar ratio 1.5) appear as needle-like crystals and are not fluorescent, while those of UO_2HPO_4 precipitate (molar ratio 1.0) are rectangular crystals frequently appearing as truncated squares and show an intensive fluorescence.

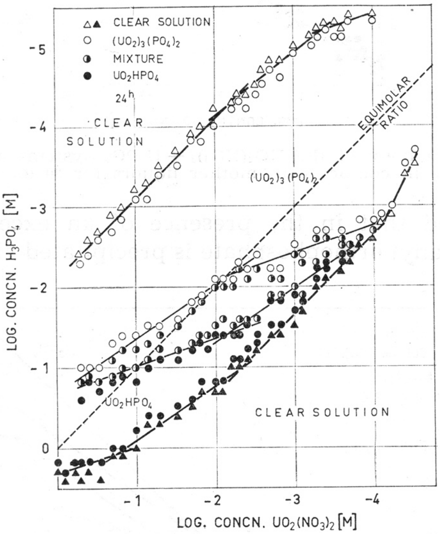


Fig. 3. Typical precipitation body of the $UO_2(NO_3)_2 — H_3PO_4$ systems at room temperature. The fluorescence microscopic examinations performed 24 hours after mixing (only the boundaries between different compositions are drawn). Intensively fluorescent clear solutions are denoted by full triangles.

Figs. 3 and 4 represent the typical precipitation bodies of the system uranyl nitrate—orthophosphoric acid after 24 hours and 30 days, respectively. The formation and dissolution of the uranyl orthophosphate precipitates in the concentration range from 3×10^{-5} *M* to 0.5 *M* uranyl nitrate and from 2×10^{-6} *M* to 6 *M* phosphoric acid are shown. The same diagram represents the boundaries of the precipitation body and those between the precipitation regions where solid phases of different composition appear. The presented data were obtained from fluorescent microscopic examinations of the solids

(Figs. 3 and 4) and were verified by chemical analyses (Fig. 6). Comparing Figs. 3 and 4 it can be seen which changes occured when the precipitates were in contact with the respective mother liquors for more than 24 hours. The equilibrium was practically attained after 14 days.

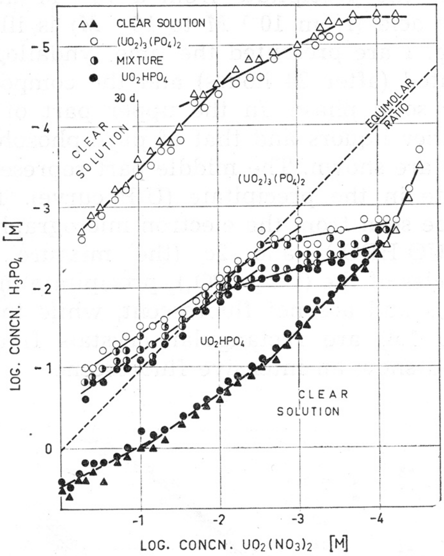


Fig. 4. Typical precipitation body of the $UO_2(NO_3)_2 - H_3PO_4$ systems at room temperature. The precipitates were in contact with mother liquors for 30 days after mixing.

It has been found that in the presence of an excess of uranyl nitrate exclusively neutral uranyl orthophosphate is precipitated along the precipitation

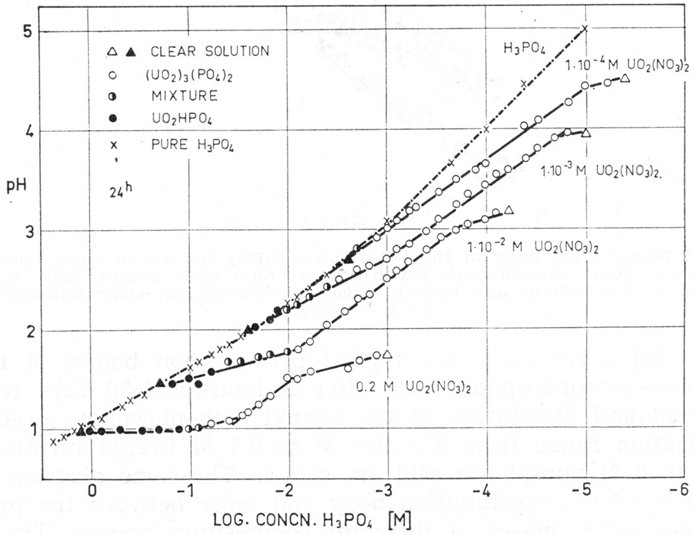


Fig. 5. *p*H curves of serval cross-sections through the typical precipitation body (Fig. 3) and the corresponding *p*H curve of orthophosphoric acid, at room temperature.

boundary. The fluorescence of the clear solutions along this boundary, excited by the UV light, is comparable to the fluorescence of the corresponding solutions of pure uranyl nitrate.

In the presence of an excess of phosphoric acid two species are precipitated along the precipitation boundary: the neutral uranyl orthophosphate and the monohydrogen uranyl phosphate. Only the clear solutions in the region close to the precipitation boundary where the monohydrogen uranyl phosphate precipitates, showed a more intensive fluorescence. The fluorescence intensity increased with increasing uranyl nitrate and phosphoric acid concentrations.

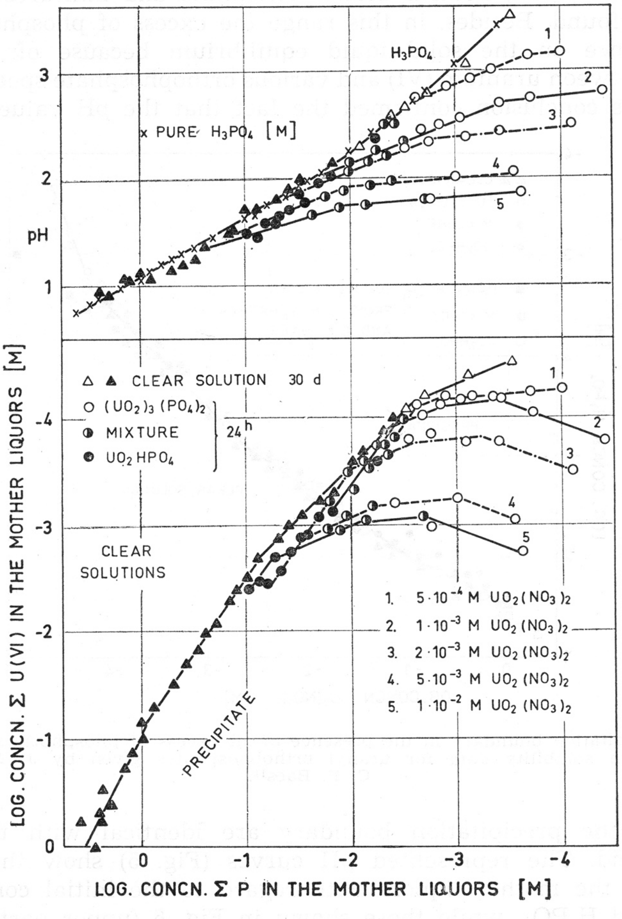


Fig. 6. The composition of precipitates obtained from solutions of different initial $UO_2(NO_3)_2$ (*M*) concentrations against total phosphate (Σ P) and uranium (VI) (Σ U) in the mother liquor (24 hours after mixing) lower curves 1—5, and *p*H — upper curves 1—5. The precipitation boundary in the presence of an excess of phosphoric acid (Fig. 4) is denoted by △▲ curve, at room temperature.

During the precipitation of $(UO_2)_3(PO_4)_2$ and UO_2HPO_4 the H^+ ions are liberated. The H^+ ion activity can be measured and give some information on the equilibrium conditions between the solid phase and the mother liquor. Some characteristic *p*H curves of various cross sections through the typical precipitation body (Fig. 3) are shown in Fig. 5, various uranyl phosphates being denoted by different dots. The corresponding *p*H curve of pure phosphoric acid is also given. In the range of excess of uranyl nitrate the *p*H curves of all systems have similar slopes. A break of the curves is observed at the transition into the region where phosphoric acid is in excess. The changes in the slopes of the *p*H curves seem to be dependent upon the changes in the composition of the solid phase and the corresponding mother liquor. Thus, in the range of excess of uranyl nitrate only neutral uranyl orthophosphate was precipitated. On the other hand in excess of phosphoric acid monohydrogen uranyl orthophosphate, neutral uranyl phosphate and mixtures of both compounds were found. Besides, in this range the excess of phosphate ions has a strong influence on the solid-liquid equilibrium because of the extensive complexing between uranium (VI) and various orthophosphate species in aqueous solutions. This conclusion confirmed the fact that the *p*H values of the clear solutions on the precipitation boundary are identical with those of pure phosphoric acid. The represented *p*H curves (Fig. 5) show the equilibrium *p*H values of the mother liquors with regard to the initial concentration of $UO_2(NO_3)_2$ and H_3PO_4, while those shown in Fig. 6 (upper part) refer to the equilibrium concentration of total phosphate and total U (VI) in the mother liquor.

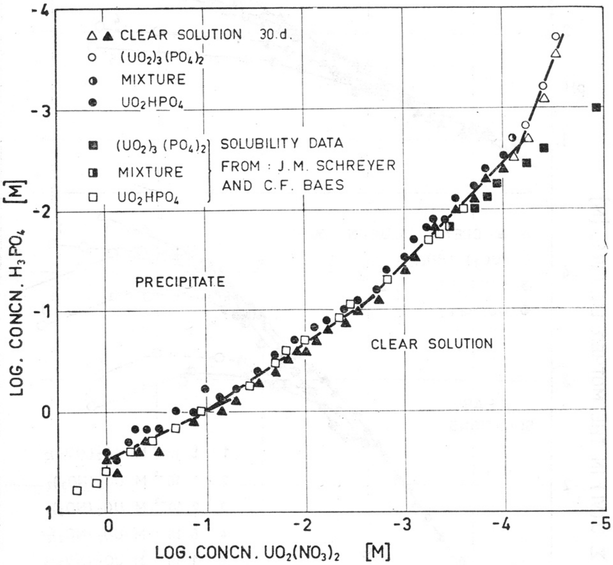


Fig. 7. The precipitation boundary in the presence of an excess of phosphoric acid (from Fig. 4) is compared with solubility data for uranyl orthophosphates given by J. M. Schreyer and C. F. Baes[11].

The equilibrium conditions (24 hours after mixing) between the solid phases and the mother liquor for a characteristic precipitation system, within the precipitation body (Fig. 3) are described in Fig. 6 in terms of total uranium (VI), total phosphate and *p*H. It is evident that all curves representing the composition of the mother liquor (lower part of Fig. 6) converge to the curve, which indicates the precipitation boundary in the presence of an excess of phosphoric acid, 30 days after mixing. It can also be seen that the *p*H curves (upper part of Fig. 6) converge to the *p*H curve of pure phosphoric acid. In addition curves 1—5 (Fig. 6, lower part) show that neutral uranyl orthophosphate is in equilibrium with the mother liquor, the total phosphate concentration being 3×10^{-3} *M* or less. At higher total phosphate concentrations the mixture of neutral and monohydrogen uranyl orhophosphate was in equilibrium after 24 hours. Within the period of 14 days the following changes were observed: (i) Transformation of the neutral uranyl orthophosphate into a mixture of neutral and monohydrogen uranyl phosphate at concentrations of the mother liquors higher than 1.5×10^{-3} *M;* (ii) At concentrations of the mother liquors higher than 5×10^{-3} *M* of total phosphate the primarily formed mixtures changed completely into monohydrogen uranyl phosphate.

DISCUSSION

The results described in the previous section can be summarised as follows:

a) The conditions for the precipitation and dissolution of $(UO_2)_3(PO_4)_2$ and UO_2HPO_4 (24 hours after mixing) in a broad concentration range of $UO_2(NO_3)_2$ and H_3PO_4 are represented by the typical precipitation body (Fig. 3).

b) In the investigated precipitation regions (Figs. 3 and 4) $UO_2(H_2PO_4)_2$ did not appear as a solid phase. This species was reported to be formed under special experimental conditions[28] and was found to be stable only in contact with extremely high concentrations of orthophosporic acid[11].

c) At the total phosphate concentrations higher than 1.5×10^{-3} *M* $(UO_2)_3(PO_4)_2$ transforms into UO_2HPO_4, therefore the area where only UO_2HPO_4 species appear is remarkably augmented after aging the precipitate in the mother liquor for a long time (Fig. 4 as compared with Fig. 3).

The slopes of the obtained precipitation boundaries in the concentration region of excess of uranium (VI) and phosphate can be explained by the formation of different soluble complex uranyl phosphates[16–19]. These species which were formed when monohydrogen uranyl orthophosphate was dissolved in an excess of phosphoric acid exhibited a very intensive fluorescence. From the data obtained the most probable complex species in equilibrium with the solid phase can be calculated. These calculations will be presented in one of the next papers of this series.

In Fig. 9 the precipitation boundary which was obtained in the range of excess of phosphoric acid (30 days after mixing) is compared with the solubility curve obtained by Schreyer[11]. Both curves overlap in the concentration range from 2×10^{-2} *M* to 2 *M* phosphoric acid where the equilibrium solid phase is monohydrogen uranyl phosphate. However, significant discrepancies exist at very low and very high concentrations of phosphoric acid. At phosphoric acid concentrations from 1×10^{-2} *M* to 2.5×10^{-3} *M,* UO_2HPO_4 was in equilibrium at the precipitation boundary, while according to Schreyer's solybility data, $(UO_2)_3(PO_4)_2$ is in iquilibrium with the mother liquor. At total phosphate concentrations lower than 2.5×10^{-3} *M,* neutral uranyl orthophosphate was found to be the stable solid phase in both cases, but the precipitation boundary is shifted. At concentrations of phosphoric acid higher than 6 *M,* which, according to Schreyer's data, the stability range of $UO_2(H_2PO_4)_2$, no crystals of any kind could be found by our method but stable clear solutions exhibiting intensive fluorescence were obtained.

Besides, the equilibrium conditions for $(UO_2)_3(PO_4)_2$ and UO_2HPO_4, as determined by chemical analyses and microscopic examinations (Fig. 6 and 3, 4), are also in disagreement with the stability ranges reported by Schreyer[11].

All these discrepancies are most probably due to the different experimental methods used (the determination of solubility[11] and the formation and transformation of precipitates in our investigations). Thus it is evident that the data obtained by both methods are not necessarily comparable, a fact that should be kept in mind when applying them in technology.

Acknowledgments. We wish to thank Dr. M. Wrischer for making the electron micrographs and Dr. H. Füredi for reading and discussing the manuscript.

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.
3. R. P. Linstead, F. M. Burstall, and T. V. Arden, *Brit. Pat.* 759900 (1956).
4. J. A. Atanasiu and A. Velculescu, *Z. Anal. Chem.* **102** (1935) 344.
5. I. M. Kolthoff and G. Cohn, *Ind. Eng. Anal. Ed.* **14** (1942) 412.
6. H. Krause, *Z. Anal. Chem.* **128** (1948) 98.
7. E. G. Cogbill, J. C. White and C. D. Susano, *Anal. Chem.* **27** (1955) 455.
8. A. Chretien and J. Kraft, *Bull. Soc. Chim. France* **5** (1938) 372.
9. M. Domine-Berges, *Compt. rend.* **236** (1953) 2242.
10. E. Matijević and N. Pavković, *Kolloid-Z.* **159** (1958) 1.
11. J. M. Schreyer and C. F. Baes, Jr., *J. Am. Chem. Soc.* **76** (1954) 354.
12. V. G. Chukhlantsev and S. I. Stepanov, *Zh. Neorg. Khim.* **1** (1956) 478.
13. V. G. Chukhlantsev and K. V. Alyamovskaya, *Izvestia Vyschikh. Ucheb. Zavedenii, Khim. i Khim. tehnol.* **4** (1961) 359.
14. V. I. Karpov, *Zh. Neorg. Khim.* **6** (1961) 531.
15. V. Vesely, V. Pekarek, and M. Abbrent, *J. Inorg. Nucl. Chem.* **27** (1965) 1159.
16. J. M. Schreyer and C. F. Baes, Jr., *J. Phys. Chem.* **59** (1955) 1179.
17. C. F. Baes, Jr., *J. Phys. Chem.* **60** (1956) 878.
18. B. J. Thamer, *J. Am. Chem. Soc.* **79** (1957) 4298.
19. Y. Marcus, *Proc. UN Intern. Conf. Peaceful Uses At. Energy,* 2^{nd}, Geneva **3** (1958) 465.
20. W. H. Zachariasen, *Report* CC-2768 (1945).
21. W. W. Harris and R. H. Scott, *Report* AECD-2746 (1949).
22. A. Weiss, K. Hartl, and U. Hofmann, *Z. Naturforsch.* **12 b** (1957) 669.
23. H. Lineau, *Dissertation,* Berlin (1898).
24. V. I. Karpov and Ts. L. Ambartsumyan, *Zh. Neorg .Khim.* **7** (1962) 1838.
25. K. V. Narasimham, *Indian J. Phys.* **34** (1960) 321.
26. V. Pekarek and M. Benešova, *J. Inorg. Nucl. Chem.* **26** (1964) 1743.
27. V. Pekarek and V. Vesely, *J. Inorg. Nucl. Chem.* **27** (1965) 1151.
28. G. Werther, *J. Prakt. Chem.* **43** (1848) 321.
29. B. Težak and collaborators, *Disc. Faraday Soc.* **42** (1966) 175.
30. H. Füredi, *Complex Precipitation Systems* Chapter 6 of *The Formation and Properties of Precipitates* by A. G. Walton, Interscience Publ., New York, 1967.
31. C. J. Rodden, *Analytical Chemistry of the Manhatan Project,* McGraw Hill Book Co., New York, 1950.
32. A. J. Vogel, *A Textbook of Quantitative Inorganic Analysis,* 2^{nd} Ed., Longmans, Green and Co., 1957, pp. 245.
33. B. Težak, E. Matijević, and K. Schultz, *J. Phys. Colloid Chem.* **55** (1951) 1557.

34. C. Urbach, *Biochem. Z.* **268** (1934) 457.
35. G. Charlot and D. Bezier, *Quantitative Inorganic Analysis,* London, Methuen and Co. Ltd., New York, 1957, pp. 533.

IZVOD

Taloženje i topljivost uranil ortofosfata I. Heterogena ravnoteža u otopinama: $UO_2(NO_3)_2$—H_3PO_4

N. Pavković, M. Branica i B. Težak

Taloženje i otapanje urana(VI) iz vodenih otopina uranil nitrata (3×10^{-5} do 0,5 *M*) i ortofosforne kiseline (2×10^{-6} do 6 *M*) ispitano je turbidimetrijskom i kemijskom analizom, fluorescentnom i elektronskom mikroskopijom. Općim precipitacionim dijagramima pokazana su koncentraciona područja gdje nakon 24 sata, odnosno 30 dana, od miješanja otopina nastaju talozi sastava $(UO_2)_3(PO_4)_2$ i UO_2HPO_4. Elektronskim mikrofotografijama prikazana je morfologija nastalih čestica taloga.

Kod manjih koncentracija od $1,5 \times 10^{-3}$ *M* totalnoga fosfata u matičnoj otopini kod ravnotežnih uvjeta stabilan je $(UO_2)_3(PO_4)_2$, dok je kod većih koncentracija od 5×10^{-3} *M* totalnoga fosfata stabilan UO_2HPO_4.

ODJEL FIZIČKE KEMIJE
INSTITUT »RUĐER BOŠKOVIĆ«
I
FIZIČKO-KEMIJSKI ZAVOD
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
SVEUČILIŠTE U ZAGREBU

Primljeno 6. travnja 1968.