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Original Scientific Paper

Precipitation and Hydrolysis of Uranium(VI) in Aqueous Solutions. V. The Composition of Precipitates From Uranyl Nitrate — Potassium Hydroxide — K, Ca, Sr, Ba, and Eu — Nitrate Solutions*

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The appearance of the solid phase in the precipitation system: uranyl nitrate-potassium hydroxide depends on the concentration of uranyl nitrate. The lower the concentration of uranyl nitrate the higher is the ratio $Z = [KOH] / [UO_2(NO_3)_2]$ (M/M) at which the precipitation of uranates occurs. In a narrow concentration range of potassium hydroxide the decrease of the precipitation of uranium can be attributed to the formation of negatively charged colloid particles. The effect of various neutral electrolytes on the precipitation of uranium in the system: 10^{-3} *M* uranyl nitrate-potassium hydroxide *var.* has the following common characteristics:

— The precipitation begins at a minimum ratio $Z = 1.6$; the presence of neutral electrolyte lowers the colloidal stability of the system.

— A neutral electrolyte exerts the same action as the corresponding hydroxide, resulting in a formation of the corresponding uranates. The neutral electrolytes display coagulation and constitution effects.

— »Heptauranates« are formed at the Z value 2—2.5. The logarithm of the solubility product constant for potassium heptauranate is calculated as:

$$\log K_{So} = -23.5 \pm 0.4$$

By further increase of the Z value, the ratio Me^{I}/U is increased; the final products are probably diuranates.

— By a prolonged contact between the precipitate and the mother liquor the precipitation increases; this is accompanied by an increase in the acidity of the mother liquor. The precipitates formed have a colloidal structure. The microcrystalline structure is observed between $2 < Z < 10$ only.

INTRODUCTION

There is disagreement in the literature data on the precipitation products formed by the hydrolysis of uranium (VI). The precipitate appears at the ratio base/uranium which varies from 0.8 to 3.5[1-5]. It is a well-known fact that the hydrolysis and hydrolytic precipitation of uranium (VI) are relatively

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slow processes[1-7]. Unsystematic investigations of authors which disregard such parameters as concentration of uranyl ion, time of reaction, way of preparing systems, temperature and ionic media, lead to different conclusions. The composition of the precipitates formed leads to further disagreement; some authors suppose that the first precipitation product corresponds to the pure uranyl hydroxide. Their conclusions are based on potentiometric[1,8,9], conductometric[8] and thermometric[9] data only. Some other authors proved from the results of analyses that uranates are formed in such systems[6,9-14]. In the formed uranates, the ratio Me/U increases with increase of the *p*H value of the system. It has been shown that different treatment, *i. e.* washing of the precipitates, leads to different results of the analyses which can be attributed to the considerable sensitivity of the precipitates to solvolysis[9,12]. Therefore, different mechanisms of precipitation of uranium are proposed[2,7,12].

Studying the hydrolysis of uranium, Swedish authors performed measurements in a medium of high constant ionic strength (up to 3 M in $NaClO_4$) assuming that this »neutral« electrolyte has no influence on the precipitation and hydrolysis of uranium[15-17]. However, in previous papers from this Laboratory, the specific effect of various neutral electrolytes is described[5]. It is shown that neutral electrolytes cause the precipitation in the optically clear system: 10^{-3} M uranyl nitrate — 2×10^{-3} M potassium hydroxide. Some authors stated that the presence of neutral electrolytes causes the coagulation and precipitation of uranyl hydroxide[18]. Great differences in the critical precipitation concentrations of alkaline-earth nitrates indicate that coagulation is not the only mechanism which causes precipitation in the system mentioned. The aim of this paper is to try to explain the role of neutral electrolytes (K, Ca, Sr, Ba and Eu-nitrate) and to propose the mechanism of the precipitation of uranium (VI).

EXPERIMENTAL

All solutions were prepared by dissolving analytically pure chemicals in twice — distilled water. The concentration of uranium was determined by precipitation of uranium with ammonium hydroxide and weighing as U_3O_8 after ignition[19]. The concentration of potassium hydroxide was determined by titration with standardized hydrochloric acid. The concentration of neutral electrolytes were determined by the ion exchange method (*Dowex-50 X8*, 50/100 mesh)[20]. All the precipitation systems were prepared by mixing the corresponding pairs of equal volumes of precipitation components; the final volumes were 50 and 500 ml. respectively, the concentration being given for the whole volume. The solution of potassium hydroxide was added to the mixture of uranyl nitrate and neutral electrolyte and the mixing was repeated 9 or 11 times during 30 and 35 seconds for the volume of 50 and 500 ml. respectively. The precipitates formed were separated by centrifugation at 3000 RPM. Some of the systems which remained turbid were separated by centrifugation at 17000 RPM in a *Serwall SS-4* centrifuge (rotor *SM-24*). In order to prevent solvolysis, the precipitates were not washed. Aliquots of the clear supernatant liquid were taken to determine the percentage of uranium precipitated. The uranium analyses were carried out polarographically[21] with a *Cambridge Instrument* Pen Recording polarograph. A. c. polarographic measurements were performed with the same *Cambridge* polarograph in connection with the Univector Unit. To determine the quantity of potassium, or cations of neutral electrolytes precipitated with uranium, the whole of the precipitate was dissolved in concentrated redistilled nitric acid, and uranium was removed by means of continuous extraction with tetrahydropyrane[22]. Potassium was determined by the a. c. polarographic method[23]. The mixture of 0.075 N $(CH_3)_4NOH$ + + 0.075 N $(CH_3)_4NCl$ served as a supporting electrolyte. Barium was determined by means of conductometric titration with lithium sulphate[24]. A *PYE* Conductance Bridge (cat. No 11700) was used and the titrations were carried out in thermostated conductance cells. Calcium and strontium were determined by complexometric titration with 0.01 *M* titriplex solution[25]. In order to determine accurately calcium and strontium, uranium had to be completely removed. The precipitates containing europium were dissolved in the supporting electrolyte: 1 *M* H_3PO_4 and 5×10^{-4} % *Triton — X — 100.* The content of europium was determined by means of a. c. polarography. The acidity measurements were performed with a compensation *p*H-meter *Radiometer Copenhagen,* type pH *M 4,* and the corresponding electrodes.

Microscopic characterisations of precipitates were performed with a *Reichert* microscope with attachments for fluorescence and polarisation microscopy. Photomicrograms were made with an electrostatic electron microscope *Trüb, Tauber & Comp.* model *KM 4.*

RESULTS

The precipitation of U (VI) with KOH

In Table I the values $Z = [KOH]/[UO_2(NO_3)_2]$ (M/M) are presented at which the precipitation occurs for the first time. The appearance of the precipitate in the system depends on the concentration of uranyl nitrate. The precipitates are separated for analysis four days after mixing. Results of the analyses are presented in Figs. 1., 2. and 3. In the concentration interval of uranyl nitrate investigated, the amount of initial precipitation decreases with the increase of the *Z* value. The position of the precipitation minimum is characteristic for the concentration of uranyl nitrate and the corresponding *Z'* values are given in Table I. The precipitates are visually different on the two sides of the precipitation minimum.

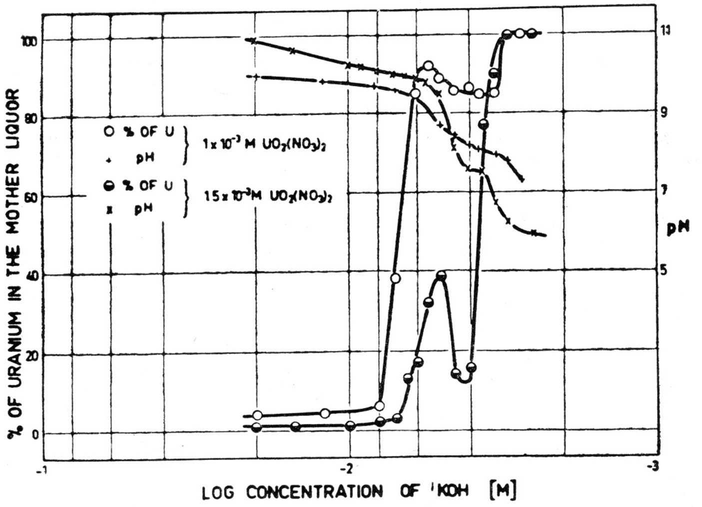

Fig. 1. Uranium precipitation from solutions:
— 10^{-3} *M* $UO_2(NO_3)_2$ — KOH varied
— 1.5×10^{-3} *M* $UO_2(NO_3)_2$ — KOH varied
Separated four days after mixing. Room temperature.

Phase I, formed at lower *p*H values, is a greenish-yellow amorphous precipitate. Phase II, formed at higher *p*H values on the left hand side of the precipitation minimum, is yellow-orange amorphous precipitate. For the concentrations of uranyl nitrate lower than 1×10^{-3} *M*, no formation of phase I. is

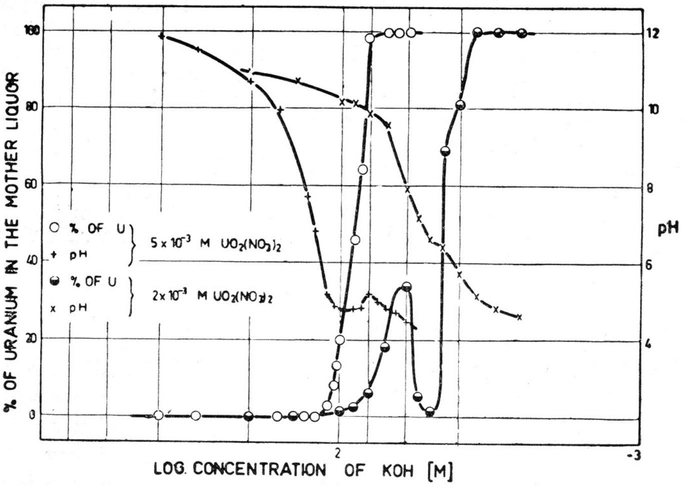

Fig. 2. Uranium precipitation from solutions:
— 2×10^{-3} M $UO_2(NO_3)_2$ — KOH varied
— 5×10^{-3} M $UO_2(NO_3)_2$ — KOH varied
Separated four days after mixing. Room temperature.

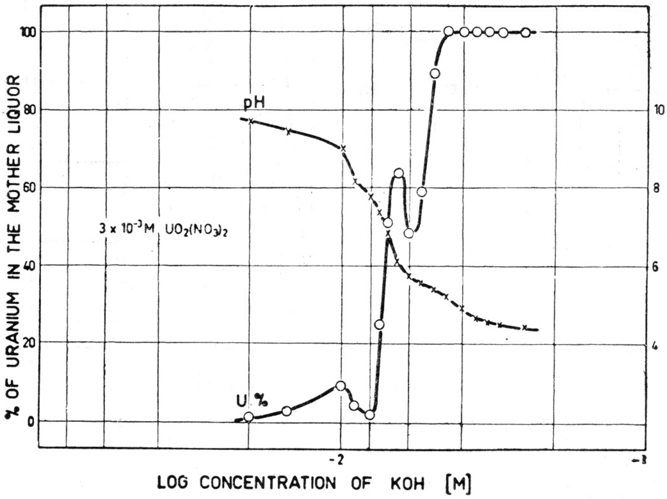

Fig. 3. Uranium precipitation from solutions:
— 3×10^{-3} M $UO_2(NO_3)_2$ — KOH varied
Separated four days after mixing. Room temperature.

noticed. In concentrations above 5×10^{-3} M uranyl nitrate, the precipitation minimum does not exist. Two distinct points on the precipitation curves are chosen for the analytical characterisation of the precipitates. The first point corresponds to the place of the first maximum precipitation of uranium (phase I); the second one corresponds to the systems where potassium hydroxide is present in excess, causing complete precipitation of phase II. From Table II it can be seen that the first phase formed at the *p*H values 4.5 corresponds to a compound known as heptauranate $K_2U_7O_{22} \cdot nH_2O$. The phase II, obtained from the systems with Z value = 8 at pH values about 11, corresponds to diuranate $K_2U_2O_7 \cdot mH_2O$. No uranyl hydroxide is isolated from this precipitation system as some authors suggested[1,4,8].

A slight discrepancy from the stoichiometric composition can be explained in terms of partial hydrolysis of the formed precipitates or in terms of formation of mixed uranates, which ratio is sensitive to the quantity of potassium hydroxide present.

TABLE I

Precipitation of the Uranate from the Solutions: $UO_2(NO_3)_2$ — KOH. Room Temperature. Precipitates Separated Four Days after Mixing

$UO_2(NO_3)_2$ (M)	The ratio $Z = [KOH]/[UO_2(NO_3)_2]$ (M/M) denoting the initial precipitation	pH	Colour of precipitate	Z' where precipitation minimum exist	pH
1.0×10^{-3}	3.3	7.9	orange yellow	5.5	9.2
1.5×10^{-3}	2.20	6.4	yelow	3.33	9.4
2.0×10^{-3}	2.0	5.1	green yellow	3.0	7.9
3.0×10^{-3}	1.66	5.3	green yellow	2.16	6.1
5.0×10^{-3}	1.6	5.2	greenish	—	—

TABLE II

Precipitation of the Uranate from the Solutions: $UO_2(NO_3)_2$ — KOH. Room Temperature Precipitates Separated Four Days after Mixing

$UO_2(NO_3)_2$ M	Z	pH	Uranium precipitated %	Molar ratio U : K in the precipitate
2×10^{-3}	2.5	6.5	100	3.0 : 1
2×10^{-3}	8.0	11.2	100	6.0 : 5
3×10^{-3}	2.0	4.6	80	3.7 : 1
3×10^{-3}	8.0	11.4	100	6.0 : 5
4×10^{-3}	2.0	4.5	82.2	3.3 : 1
4×10^{-3}	8.0	10.7	100	1.0 : 1
5×10^{-3}	2.0	4.5	81.3	3.4 : 1
5×10^{-3}	8.0	11.8	100	6.0 : 5

The precipitation of U(VI) with KOH in the presence of neutral electrolyte

From Fig. 1 it can be seen that precipitation in the system: 10^{-3} M uranyl nitrate — potassium hydroxide begins at the value $Z = 3.3$. It is known from previous investigations carried out in this Laboratory, that the presence of various neutral electrolytes causes the precipitation in the optically clear system: 10^{-3} M uranyl nitrate — 2×10^{-3} M potassium hydroxide[5]. The critical precipitation concentrations of neutral electrolytes differ due to the kind and valency of the corresponding cation.

Several mechanisms including coagulation, salting out and formation of mixed uranates have been proposed. The analyses of the precipitates should give an indication of the mechanism of the precipitation in the system. Systematic investigations and analyses were carried out on the precipitation systems: 10^{-3} *M* uranyl nitrate — potassium hydroxide *var.* and concentration of $Me(NO_3)_n$ *var.* (Me = K, Ca, Sr, Ba and Eu). By changing the acidity of the systems (at various *Z* values), the percentage of precipitation varies; the form, colour and composition of the precipitate are also changed. The results of the analyses are shown in Figs. 4., 5., 6., 7., and 8. All investigated systems were separated for analysis 24 hours after mixing. The percentage of uranium precipitated and the ratio of uranium and cation of neutral electrolyte in the precipitate are presented as functions of the acidity of the system.

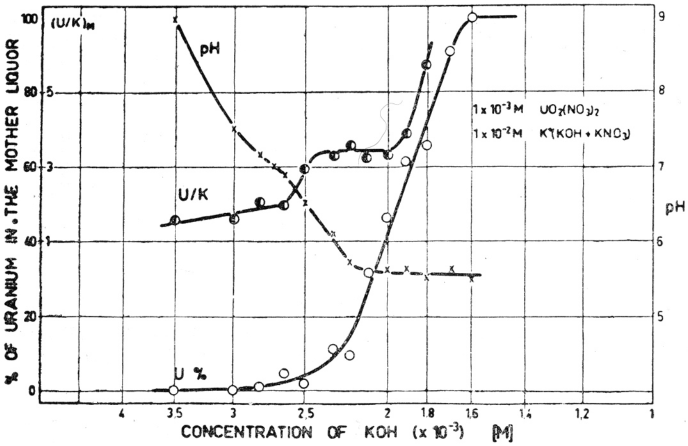

Fig. 4. Uranium precipitation from solutions:
— 10^{-3} *M* $UO_2(NO_3)_2$ — 10^{-2} *M* K^+ $(KOH + KNO_3)$
Separated 24 hours after mixing. Room temperature.

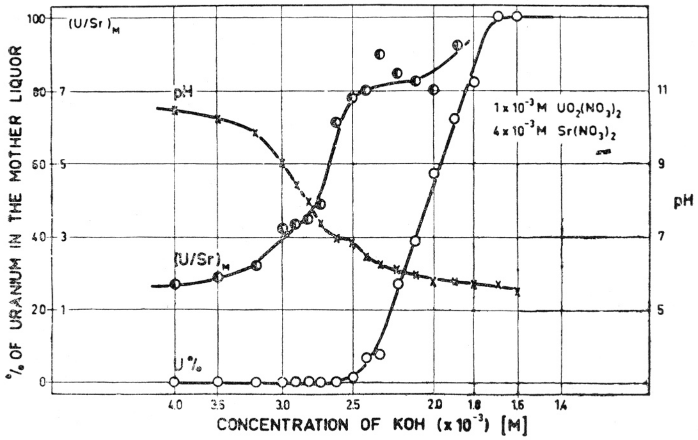

Fig. 5. Uranium precipitation from solutions:
— 10^{-3} *M* $UO_2(NO_3)_2$ — KOH varied — 4×10^{-3} *M* $Ca(NO_3)_2$
Separated 24 hours after mixing. Room temperature.

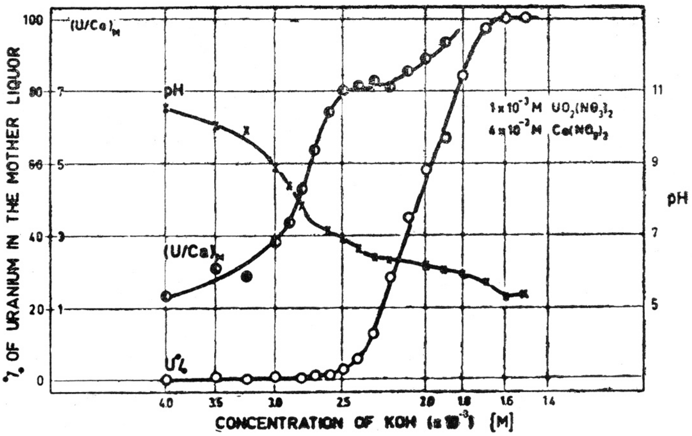

Fig. 6. Uranium precipitation from solutions:
— 10^{-3} *M* $UO_2(NO_3)_2$ — KOH varied — 4 × 10^{-3} *M* $Sr(NO_3)_2$
Separated 24 hours after mixing. Room temperature.

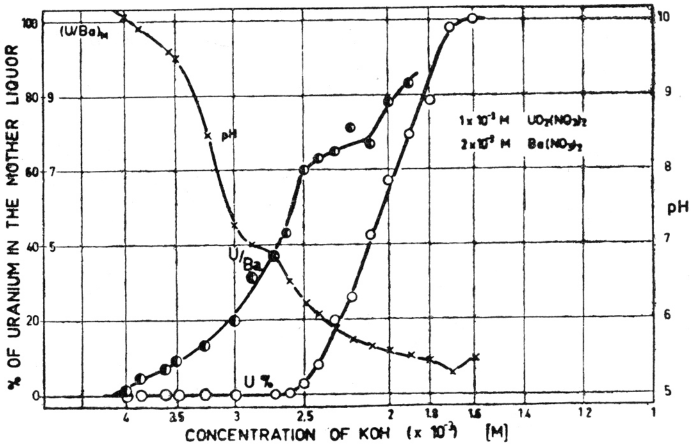

Fig. 7. Uranium precipitation from solutions:
— 10^{-3} *M* $UO_2(NO_3)_2$ — KOH varied — 2 × 10^{-3} *M* $Ba(NO_3)_2$
Separated 24 hours after mixing. Room temperature.

The presented diagrams show that due to the presence of neutral electrolyte, all investigated systems have some common characteristics. The precipitation of uranium is accelerated and the appearance of the percipitate is observed at the value $Z = 1.6$. The precipitation is increased with the increase of *p*H and it is completed at the value $Z = 2.5$—3.0, while in the system without neutral electrolyte, the precipitation begins at $Z = 3.3$. The precipitation minimum is suppressed by the action of neutral electrolytes. The content of cations in the uranates formed increases with increasing *p*H. The analyses show that uranates formed from the solutions containing calcium, strontium, barium and europium nitrate do not contain more than 3 molar percents of potassium. The curve representing the ratio U/Me shows characteristic plateaus at the values

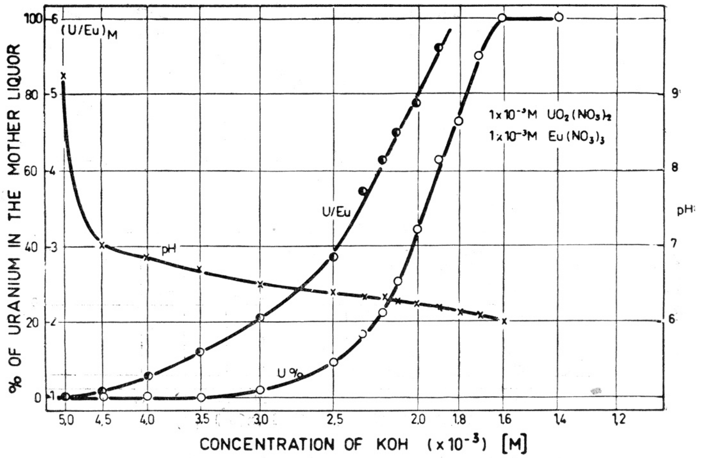

Fig. 8. Uranium precipitation from solutions:
— 10^{-3} *M* $UO_2(NO_3)_2$ — KOH varied — 10^{-3} *M* $Eu(NO_3)_3$
Separated 24 hours after mixing. Room temperature.

U : K = 3.5 : 1 and U : Me^{II} = 7 : 1. This can be explained by the formation of the corresponding »heptauranates« at the values *Z* = 2.0—2.5. The *p*H values in this interval do not change by more than one unit, which indicates that in this interval of *Z* values the systems behave as buffers, which results in a formation of the uniform phase. The slight discrepancy from the stoichiometric composition of »heptauranates« can be attributed to partial hydrolysis of the formed precipitate. Assuming that the reaction of the formation of potassium heptauranate is:

$$7\,UO_2^{++} + 2\,K^+ + 16\,OH^- \rightarrow K_2U_7O_{22} + 8\,H_2O \qquad (1)$$

one can write the equation defining the solubility product:

$$K'_{So} = [UO_2^{++}]^7 \cdot [OH^-]^{16} \cdot [K^+]^2 \qquad (2)$$

and

$$K_{So} = [UO_2^{++}] \cdot [OH^-]^{2.29} \cdot [K^+]^{0.29} \qquad (3)$$

This expression can be written in logarithmic form:

$$\log K_{So} = \log\,[UO_2^{++}] + 0.29 \log\,[K^+] + 2.29 \log\,[OH^-] \qquad (4)$$

Using eq. (4), the logarithmic value of the solubility product constant of potassium heptauranate is calculated. The data are presented in Table III.

By further addition of potassium hydroxide (*i. e.* increasing of *Z* values), the ratio of U/Me in the precipitate is decreased. The final products are probably diuranates $K_2U_2O_7 \cdot mH_2O$ and $Me^{II}U_2O_7 \cdot mH_2O$. From Figs. 6. and 7. it can be concluded that even monouranates $Me^{II}UO_4$ are formed; however, it is more probable that at *p*H values above 9 the partial formation of strontium and barium carbonates can occur.

The precipitation diagram of uranium in the presence of europium nitrate differs from the above described since the curve representing the change of U/Eu ratio is continuous and no flat part (indicating the formation of »heptau-

TABLE III

Data for the Calculation of Solubility Product log K_{So} of Potassium Diuranate at Constant Concentration of Potassium 10^{-2} M. *Room Temperature. Precipitates Separated 24 Hours after Mixing*

Z	% U pptd.	U/K ratio in the precipitate	*p*H	log K_{So}
1.9	39.0	3.85	5.6	—23.4
2.0	53.0	3.33	5.6	—23.3
2.1	68.4	3.24	5.5	—23.4
2.2	90.5	3.54	5.7	—23.8
2.3	89.5	3.31	6.1	—23.7
			log K_{So} =	— 23.5 ± 0.4

ranate«) is obtained. Besides, the *p*H curve is slightly changed with increase of *Z* value, indicating a relatively strong buffer capacity of this system. When the whole of the europium from the solution is consumed, a rapid increase of the *p*H value is noticed.

By prolonged contact of the precipitates with the mother liquor, the uranium precipitation and acidity of the mother liquors are increased. For comparison, some results obtained with the aged systems are presented in Table IV. The aged precipitates undergo recrystallization and, after a few days, a part of the precipitate is found to adhere strongly to the walls of the reaction vessel.

TABLE IV

Precipitation of U(VI) from a Solution of 10^{-3} M $UO_2(NO_3)_2$ *— KOH (varied) —* 4×10^{-3} M $Ca(NO_3)_2$. *Room Temperature. 24 Hours and 6 Weeks after Mixing*

Separated after	24 hours			6 weeks		
$Z = \frac{[KOH]}{[UO_2(NO_3)_2]}$ (*M/M*)	% U pptd.	*p*H	U : Ca : K	% U pptd.	*p*H	U : Ca : K
2.0	42.0	6.1	7.9 : 1 : 0.09	74.5	5.2	7.6 : 1 : 0.22
2.1	55.0	6.2	7.6 : 1 : 0.07	94.5*	5.4	6.7 : 1 : 0.43
2.2	71.5	6.3	7.1 : 1 : 0.07	96.1*	5.6	7.0 : 1 : 0.30
2.3	87.0	6.4	7.3 : 1 : 0.03	98.0*	5.7	7.4 : 1 : 0.25
2.4	94.5	6.6	7.2 : 1 : 0.06	100.0	5.9	6.8 : 1 : 0.30
2.5	97.7	6.9	7.0 : 1 : 0.14	100.0	6.2	6.1 : 1 : 0.40

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* The whole of the precipitate is strongly adhering to the walls of the reaction vessel.

By aging of the precipitates, the content of potassium in the precipitates increases. The same change is established for the solution with strontium and barium nitrate. Some of the precipitates (after aging for 6 weeks) were investigated microscopically. The properties of the particles, such as crystallinity, fluorescence and optical activity, depend on the *Z* value of the system. Typical results of microscopic observations of the precipitates formed in the system: 10^{-3} *M* uranyl nitrate — potassium hydroxide var. — 4×10^{-3} *M* strontium nitrate are presented in Table V.

Crystallinity of the particles formed is not observed in systems with a *Z* value lower than 2 or higher than 10, where colloidal precipitates are formed. The crystals formed have positive optical activity. The system with $Z = 10$ contains optically negative crystals, owing to the presence of strontium carbo-

TABLE V

Microscopically Observed Uranates from Solutions: 10^{-3} M $UO_2(NO_3)_2$ — KOH (varied) — 4 × 10^{-3} M $Sr(NO_3)_2$. Separated Six Weeks After Mixing. Room Temperature

Z	Light field image	Fluorescence microscopy	Polaryzing microscopy	Electron microscopy
2.0	Clusters of loose colloidal particles	Fluorescence light with a continuous spectrum in yellow to green region	The precipitate is optically isotropic	Clusters of fine particles and scarce chain-like aggregates
2.3	Dense aggregates of rod-like particles	Intensive fluorescence light with a continuous spectrum in green region	The crystals are optically positive in respect to the long axis	Very dense spherical clusters 2—5 μ in diameter composed of fine particles
2.5	Fine rod-like crystal particles	Fluorescence light with a continuous spectrum in green region	The crystals are optically positive in respect to the long axis	Aggregates of fine crystals, up to 0.015 μ in diameter
10.0	Needle-like crystals with characteristic divergent orientation and dense aggregates of submicroscopic particles	Very weak fluorescence	I. Optically negative crystals in respect to the long axis. II. Optically isotropic precipitate	Aggregates of fine particles and big needle-like crystals with characteristic divergent orientation

nate — which forms at high *p*H values of the system. The remainder of the uranate precipitate is amorphous and optically inactive. In the corresponding system with potassium nitrate, only the amorphous precipitate is present, as the formation of optically negative alkaline-earth carbonates does not take place. The continuous fluorescence of particles decreases with increase of the *Z* value. The electron microscopic photographs of the precipitates described in Table V are given in Figs. 9. The microcrystalline character of the precipitates makes possible the application of *X*-ray analysis and comparison with published *X*-ray data on uranates[9,26].

DISCUSSION

The results obtained show that only uranates are formed by precipitation from uranium (VI) solution with potassium hydroxide. The same conclusion is given by Chernyaew[27] although he postulated from theoretical considerations that the formation of uranyl hydroxide, which is a member of the genetic series of uranyl hydroxo complexes, must take place. The fact that uranyl hydroxide is not isolated as the solid phase is ascribed to the possibility of local presaturation and formation of highly insoluble sodium »uranylates« $Na[(UO_2)_2(OH)_5]$ and $Na[UO_2(OH)_3(H_2O)_n]$. However, as the formation of the precipitates from low concentration solutions is a fairly slow process, the local presaturation is almost impossible.

Also Brusilowski noticed the phenomenon of decreased precipitation in the system uranyl nitrate-potassium hydroxide[1]. He assumed that the metastable colloidal hydroxide exists in a ΔZ region depending on the initial

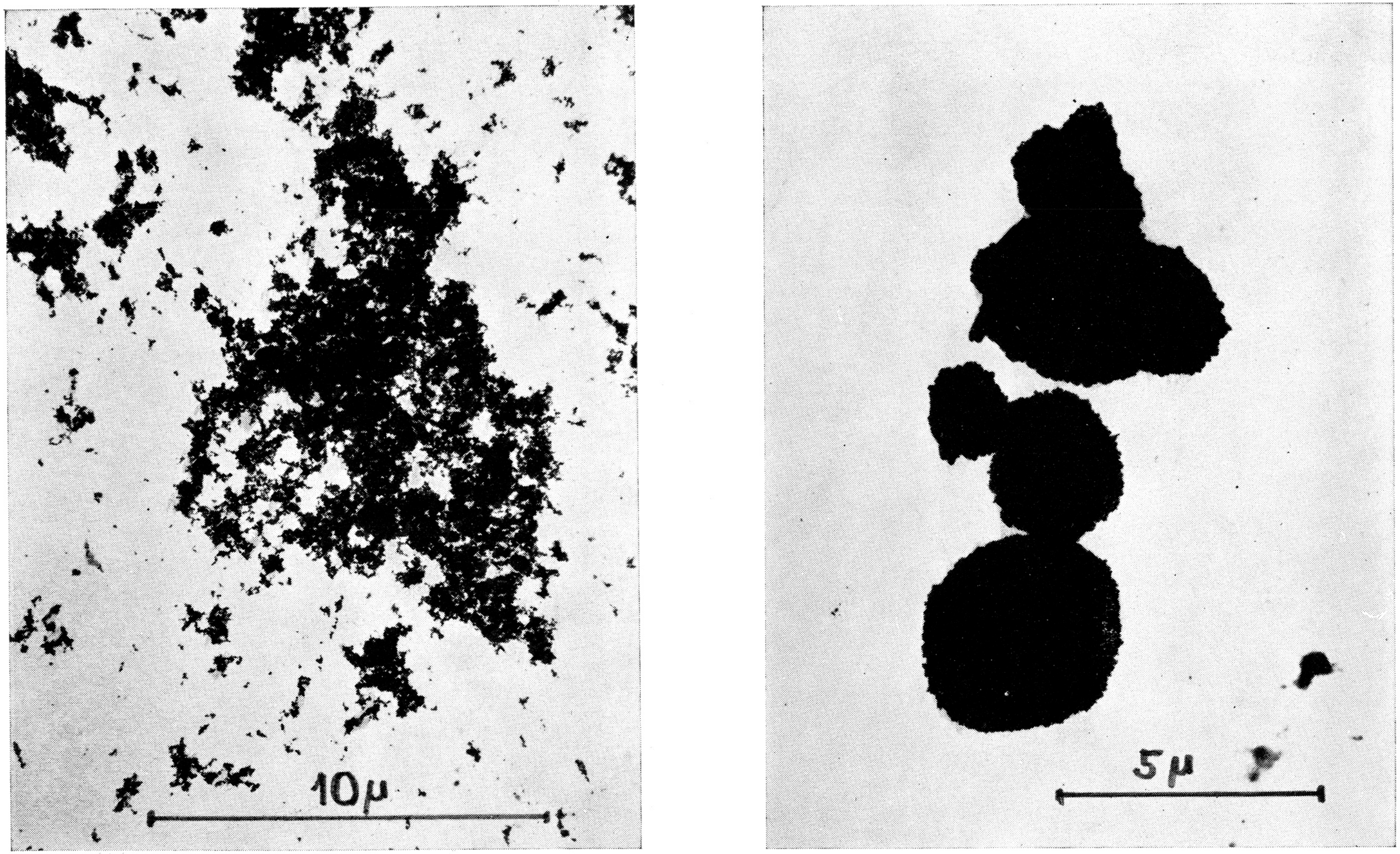


Fig. 9. Electron micrograms of strontium uranate formed from the solutions: —10^{-3} *M* $UO_2(NO_3)_2$ — KOH — 4×10^{-3} *M* $Sr(NO_3)_2$, six weeks after mixing. a) Z = 2.0 (left), b) Z = 2.3 (right). Room temperature.

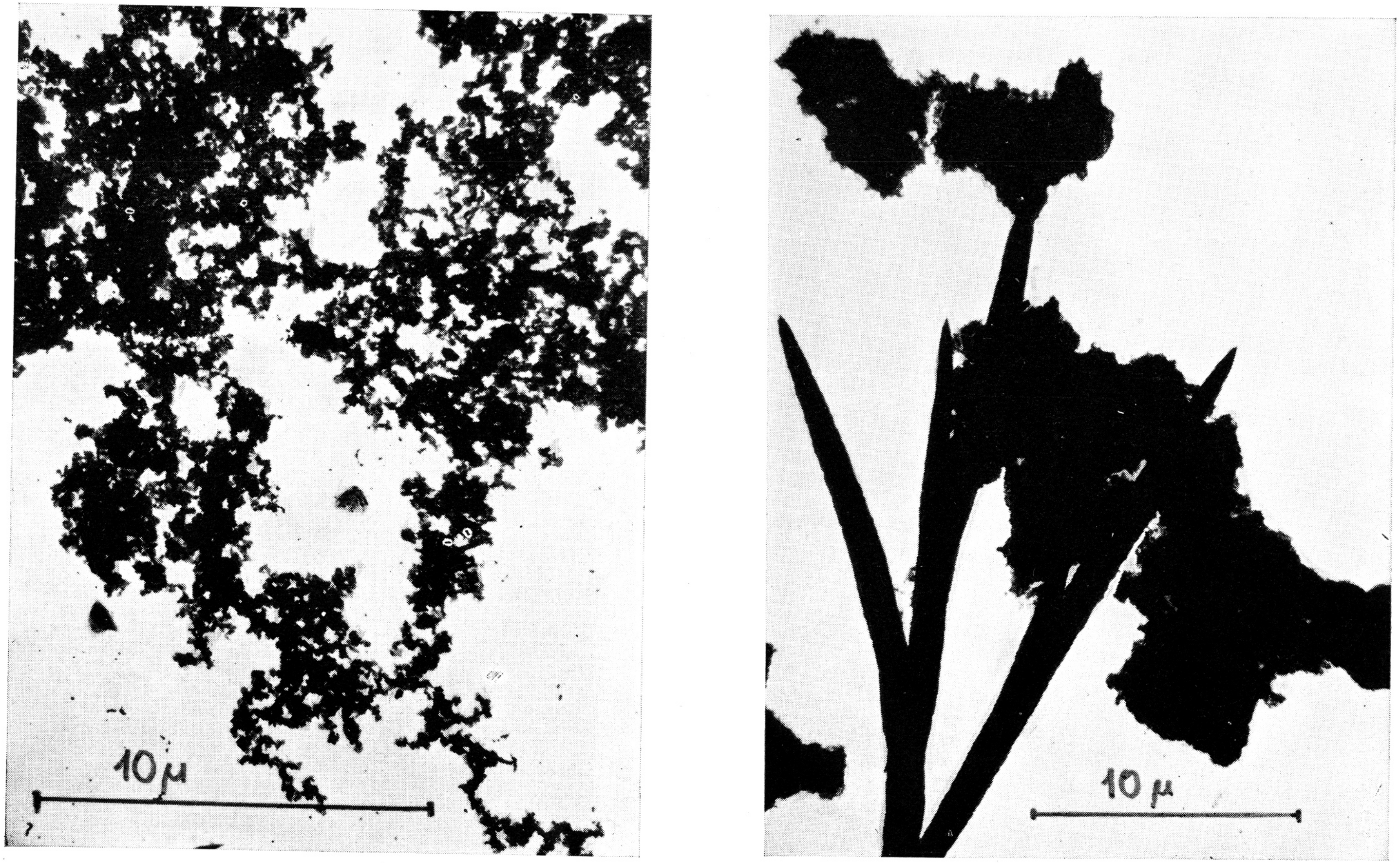


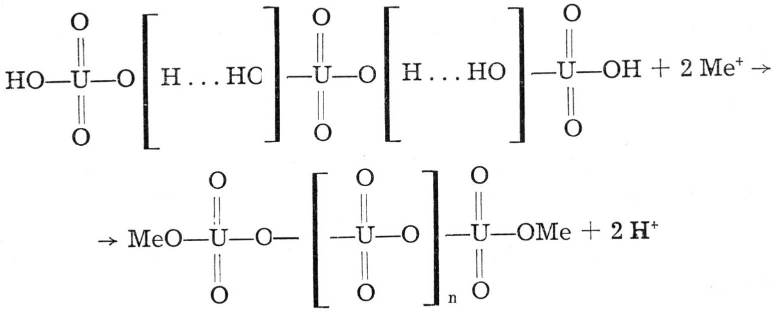
Fig. 9. Electron micrograms of strontium uranate formed from the solutions: —$10^{-3}M$ $UO_2(NO_3)_2$ — KOH — 4×10^{-3} M $Sr(NO_3)_2$, six weeks after mixing c) Z = 2.5 (left), d) Z = 10.0 (right). Room temperature

concentration of uranyl ion in the solution. According to this assumption, the precipitation of uranyl hydroxide should take place at Z from 1.4 to 2.0. He calculated the solubility product constant of uranyl hydroxide, although some other authors proved analytically that in these experimental conditions, only uranates are formed[9]. Our previous results have shown that in systems of highly hydrolysed uranium (VI) negative colloidal particles are formed. The cation of the hydroxide, as a constituent in the precipitate, plays an important role in the precipitation process. The transition from colloidal structures (negatively charged particles) to precipitate is made possible by the action of the cation simultaneously incorporated in the solid phase. A possible pattern of the precipitation process can be presented thus:

$$UO_2\,(OH)_{2n}\,OH^-_{colloid} + K^+ \rightarrow K\text{ — uranate} + H^+ \qquad (5)$$

After the begining of the precipitation process the release of protons causes a decrease of the pH value of the solution. According to some authors, uranates contain also hydroxide groups, the protons undergoing an exchange with the cations from the supernatant liquor[6]. Therefore uranates behave like cation exchangers, in the pH range from 4.5 to 11[6]. According to the conceptions of Baran *et al.*[2] and Deptula[7] the presence of hydroxide groups explains the formation of uranates. Baran distinguishes two kinds of hydroxide groups, only one of them possessing the possibility of ionic exchange of the proton. Chernyaew does not ascribe the property of proton exchange to uranates. He suggested that the cation is bounded in the precipitate causing the electroneutralization of the charged complex what results in the formation of neutral six coordinated uranyl complex[27]. This assumption seems very plausible but still more experiments should be done to prove it. Gutowski *et al.*[28] proved, by the NMR method, the existence of hydroxide groups in hydrates of uranium trioxide, the compound closely related to uranates.

The presence of various salts in the solution increases and accelerates the precipitation of highly hydrolyzed uranium(VI). The critical concentration precipitation values (CCP) for uni-, bi- and trivalent cations are not in accordance with the Schulze-Hardy rule[5]. The analysis proved the assumption that the cations of neutral electrolytes are included in the constitution of the precipitates. The differences in CCP for alkaline earth nitrates are likely to be correlated with the solubilities of the corresponding uranates. Assuming that negative coloidal particles of uranyl hydroxide are present in the solution, the following mechanism of precipitation by simultaneous condensation and substitution can be suggested:



$$HO\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}\!-\!O\left[H\ldots HC\right]\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}\!-\!O\left[H\ldots HO\right]\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}\!-\!OH + 2\,Me^+ \rightarrow$$

$$\rightarrow MeO\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}\!-\!O\!-\!\left[-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}\!-\!O\right]_n\!-\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{U}}\!-\!OMe + 2\,H^+ \qquad (6)$$

However, in this structure the presence of hydroxide groups is not pronounced. The structure containing hydroxide groups may result from the mechanism which includes the substitution reaction and oxygen bridging present in the postulated polynuclear complexes[16]:

$$\underset{\text{Colloid}}{\mathrm{HO[UO_2((OH)_2UO_2)_n]OH}} + \mathrm{Me^{2+}} + \underset{\text{Colloid}}{\mathrm{HO[UO_2((OH)_2UO_2)_n]OH}} \rightarrow$$

$$\rightarrow \mathrm{HO[UO_2((OH)_2UO_2)_n]O{-}Me{-}O[UO_2((OH)_2UO_2)_n]OH + 2\,H^+} \qquad (7)$$

When the Z value is further increased, the proton in the uranates may be substituted by the cation from the solution. Higher uranates are formed by this mechanism. This presentation is quite probable since it is in accordance with the coordination properties of hexavalent uranium[26,27]. The sensibility of this formation to the acidity of the supernatant is the cause of the ion exchange behaviour of uranates. It is therefore evident that washing of the formed precipitates with water or with other solvents (*e. g.* diethyl ether) is not desirable[9,12].

The presence of foreign cations influences the precipitation and the initial step of the hydrolytic process as well. Several studies on the hydrolysis of uranyl ion were performed in the constant ionic media of high concentration of salts, the results obtained being most probably influenced by neutral electrolytes[15,16,17].

The appearance of »heptauranates« at Z values from 2.0 to 2.5 (pH about 5 to 7) is in agreement with literature data[9]. The absence of heptauranate from the solutions with europium indicates another precipitation mechanism. The precipitation of europium hydroxide is not expected at less than pH 7[29]; it is likely that europium ion is partially hydrolysed, yielding two positively charged ions. A very slight difference in CCP for barium, yttrium and lanthanum nitrate indicates that yttrium and lanthanum behave as cations with two positive charges[5]. The same conclusion can be reached regarding to europium. This means that the hydrolyses of uranium and europium are two parallel processes. Once the colloidal particles of uranyl hydroxide are formed, the present hydrolysed europium ions perform the coagulation and incorporation into the structure of uranates. The high content of europium in uranates supports also that europium acts as a divalent cation. The very slight change of pH value observed when the Z value is increased is evidence for the simultaneous hydrolysis of europium. The presence of europium in the solution causes the buffer behaviour of the solution and once europium is precipitated completely, the pH increases rapidly. There are no data in the literature about the rare-earth uranates. Other tripositive cations are inconvenient for application because of their pronounced precipitation at lower pH.

The slight increase of potassium content in precipitates resulting from aging of systems can be attributed to equilibration of mixed uranates. This effect can be studied further by the application of various ratios of mixed neutral electrolytes.

The value of $\log K_{S0} = -23.5 \pm 0.4$ obtained for potassium heptauranate can be compared to the similar value of the corresponding sodium compound, obtained by Baran, $\log P_{0.14} = -23.92 \pm 0.03$, although the stoichiometric composition is different, probably due to the intensive washing of precipitates with water[2].

Uranates obtained by reactions of solids at high temperature have a crystalline structure, as known from earlier publications[9,26]. The observed phenomenon that by prolonged contact of precipitates with the mother liquor amorphous precipitates acquire a microcrystalline structure, can be used in further structural investigations of uranates. An investigation on the existence of hydroxide groups in uranates is in course.

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IZVOD

Taloženje i hidroliza urana (VI) u vodenim otopinama.V. Sastav taloga iz otopina: uranil-nitrat — kalium hidroksid — K-, Ca-, Sr-, Ba- i Eu-nitrat

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Pojava krute faze u taložnom sistemu: uranil-nitrat-kalium hidroksid ovisi o koncentraciji uranil-nitrata. Sniženjem koncentracije uranil-nitrata povećava se molarni odnos Z = [KOH] / [$UO_2(NO_3)_2$], kod kojega nastaje taloženje uranata. U uskom koncentracijskom području kalium hidroksida, primjećeno je smanjenje taloženja urana, što se može pripisati stvaranju negativno nabijenih koloidnih čestica.

Utjecaj različitih neutralnih elektrolita na taloženje urana u sistemu: 10^{-3} *M* uranil-nitrat — kalium hidroksid (varirane koncentracije) ima slijedeće zajedničke karakteristike:

— Taloženje započinje kod minimalnog odnosa $Z = 1,6$; prisutnost neutralnih elektrolita smanjuje stabilnost koloidnih sistema.

— Neutralni elektroliti ispoljavaju isto djelovanje kao i odgovarajući hidroksidi, što rezultira u stvaranju odgovarajućih uranata. Neutralni elektroliti istodobno pokazuju koagulacioni i konstitucioni efekt.

— Kod odnosa Z od 2 do 2,5 nastaju »heptauranati«. Izračunata je konstanta produkta topljivosti za kalium heptauranat:

$$\log K_{S_0} = -23,5 \pm 0,4$$

Daljim povećavanjem odnosa Z, povećava se odnos Me/U u talogu; konačni produkti su vjerojatno diuranati.

— Taloženje se povećava dužim stajanjem sistema; istovremeno raste i kiselost matične otopine. Stvoreni talozi imaju koloidalnu strukturu. Mikrokristalinične strukture zapažene su samo za odnose $2 < Z < 10$.

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ZAGREB

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