Precipitation and Hydrolysis of Uranium(VI) in Aqueous Solutions: Uranyl Nitrate-Potassium Hydroxide-Neutral Electrolyte*

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The precipitation and hydrolysis of uranium (VI) in aqueous solutions of uranyl nitrate — potassium hydroxide — neutral electrolyte, was investigated. Clear and stable systems of uranyl nitrate and potassium hydroxide, were studied, in equivalent concentration of $2 \times 10^{-3} N$. The pH value, of the mentioned system was between 5 and 6. By addition of neutral electrolytes (potassium, calcium, strontium, barium, yttrium, and lantanium nitrate) the precipitation process was initiated and up to 70% of the uranium present was precipitated.

The experimental results showed, that the precipitation of uranium (VI), in the observed system, was accomplished by several mechanisms, *i.e.* hydrolysis, coagulation, and formation of mixed uranates.

INTRODUCTION

The aqueous solution of uranyl nitrate is acid due to the hydrolysis of uranyl ions[1-9]. The addition of hydroxides augments the hydrolysis and above a critical concentration the precipitation of uranium[10-20] begins. The precipitation of uranyl ions is sensitive to changes of the concentration[14-16] of uranyl ions. Some results on precipitation and coprecipitation of uranyl ions were given elsewhere[14,21].

Uranium (VI) is precipitated from hydroxide solutions (pH values above 9) even from very low concentrations of uranyl nitrate. In absence of neutral electrolytes, and concentrations below $5 \times 10^{-3} N$ no precipitation of uranium (VI) has been observed at pH 5—6. Therefore, in this work special attention has been paid to precipitation, hydrolysis and coagulation phenomena in systems having a pH 5—6. The concentration of uranyl nitrate was, in general, kept constant at $2 \times 10^{-3} N$. At given conditions the solutions were optically clear, but by addition of neutral electrolytes, uranium (VI) was precipitated.

EXEPERIMENTAL

Solutions have been prepared by dissolving analytically pure chemicals in triple distilled water. The concentration of uranyl nitrate has been determined

by the precipitation of uranium with ammonium hydroxide or, alternatively, with 8-oxiquinoline, and weighing as U_3O_8[22]. The neutral electrolyte concentration was determined by ion exchange (Dowex-50 X-8, 50/100 mesh) technique[26]. Standardized stock solutions were diluted to the required concentrations with water.

The changes in turbidity were determined at 530 mμ using a Zeiss tyndallometer, conneceted with a Pulfrich photometer. The glass cells with solutions were kept at 20 ± 0.1^0C in a constant temperature water bath. The same bath was also used for keeping a constant temperature in the cell compartment of the photometer. The acidity was determined 24 hours after mixing of the components with a PYE - Master pH meter with a cup formed micro glass electrode. For each measurement only 1—2 ml of the solution was needed; the sign of charge of the solid phase particles was determined by the ultramicroscopic electrophoresis technique.

The concentration of uranium in the mother liquor was determined polarographically using the Cambridge Instrument Co. Pen-Recording Polarograph. Aliquots were taken after 24 hours from clear mother liquors. Systems in which the mother liquors were turbid, even after 24 hours, were centrifuged in a Serwall SS-4 centrifuge, (rotor SM-24) in polypropylene tubes during 10 min. at 16.000 r. p. m. After addition of a few drops of concentrated perchloric or sulphuric acid, the samples were evaporated using an IR lamp and the residue dissolved in a supporting electrolyte consisting of 1.6 g. of salicylic acid, 4 ml. of concentrated sulphuric acid and 90 mg. of tymol per liter. To prevent the loss of uranium by coprecipitation with barium sulphate, before dissolution a few drops of a saturated solution of salicylic acid were added to samples containing barium ions.

All the precipitation systems were prepared by mixing the content of the corresponding pairs of glass tubes, each containing 5 ml. of the solutions of the precipitating components. The concentration is always given for the whole volume *i.e.* for 10 ml. at 20^0C. After mixing the turbidities were determined at regular time intervals.

<div align="center">RESULTS</div>

The titration curves of uranyl nitrate with potassium hydroxide show two inflection points at characteristic UO_2^{2+}/OH^- ratio. The colour of the light yellow solution is intensified by increasing of the pH above 3.5. Titration of uranyl nitrate of a concentration lower than $2 \times 10^{-3} N$ yields no precipitate. At higher concentrations turbidity is observed and a precipitate is obtained before the second inflection point. In presence of potassium nitrate ($5 \times 10^{-3} N$) at lower concentrations of uranyl nitrate ($1 \times 10^{-3} N$) a precipitate was also obtained. Table I shows the characteristic hydroxide *vs.* uranyl ion ratio at the first and second inflection points.

<div align="center">TABLE I</div>

UO$_2$(NO$_3$)$_2$ (N)	KNO$_3$ (N)	1st inflexion point		2nd inflexion point	
		pH	OH$^-$/UO$_2^{2+}$	pH	OH$^-$/UO$_2^{2+}$
2×10^{-2}	—	4.7	1.52	8.0	2.4
2×10^{-3}	—	4.5	1.62	7.1	2.35
1×10^{-3}	5×10^{-3}	4.85	1.58	7.0	2.7

It was observed that some minimum pH value of the systems was required to initiate the precipitation process. Visually, there are two different precipitates. The first, a yellow green, is obtained at pH values (about 5) and at higher uranyl nitrate concentrations ($2 \times 10^{-3} N$). At higher pH the

formation of a yellow-orange precipitate begins. Above pH 9.5 only the later kind of precipitate is formed. For the formation of the orange-yellow precipitate at low uranyl nitrate concentrations a much higher hydroxide to uranyl ratio is required. The precipitate is obtained at potassium hydroxide concentrations of $2 \times 10^{-2} N$ in $2 \times 10^{-4} N$ uranyl nitrate solutions, while $1 \times 10^{-4} N$ solutions in uranyl remain clear.

TABLE II

$UO_2(NO_3)_2$ (N)	OH^-/UO_2^{2+} ratio, for the appearence of the first precipitate	pH values for the system 24 hours after mixing	Colour of the precipitate
1.0×10^{-3}	4	9.8	orange-yellow
2×10^{-3}	2.3	9.5	orange-yellow
3×10^{-3}	1.2	6.8	yellow
5×10^{-3}	0.8	4.8	green-yellow
7.5×10^{-3}	0.75	4.4	green-yellow

Table II shows potasisum hydroxide to uranyl nitrate ratio, at which the first precipitate is formed, in dependence of uranyl nitrate concentration. The pH values and the colour of the formed precipitates are also given. These data have been obtained 24 hours after mixing the systems. The specific effect of potassium ions cannot be studied at uranyl nitrate concentrations higher than $2 \times 10^{-3} N$. In such a case the required potassium hydroxide concentration for the hydrolysis process would be higher than $6 \times 10^{-3} N$, thus exceeding the critical potasisum ion concentration.

Fig. 1. shows turbidity (tyndallometric value) and pH values in dependence of the potassium hydroxide concentrations. The uranyl nitrate concentration is constant, $5 \times 10^{-3} N$. Fig. 2. represents the same dependence, but for a lower
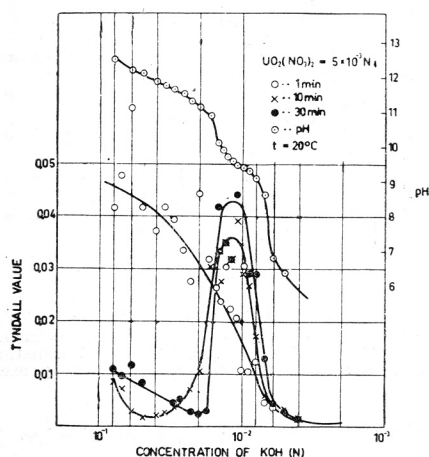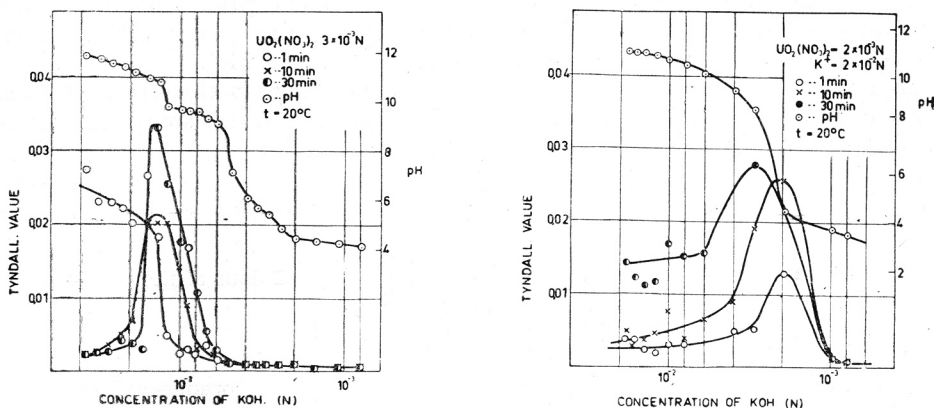

Fig. 1. Concentration tyndallograms of the system: uranyl nitrate ($5 \times 10^{-3} N$)- potassium hydroxide (varying concentrations) at 1, 10, and 30 minutes. The upper curve denotes the pH values measured 24 hours after mixing.

Fig. 2. Concentration tyndallograms of the system: uranyl nitrate (3×10^{-3} N)- potassium hydroxide (varying concentrations) at 1, 10, ad 30 minutes. The upper curve denotes the pH values measured 24 hours after mixing.

Fig. 3. Concentration tyndallograms of the system: uranyl nitrate (2×10^{-3} N)- potassium hydroxide — potassium nitrate (varying concentrations) at 1, 10, and 30 minutes. The concentration of the potassium ion was kept constant (2×10^{-2} N). The upper curve denotes the pH values measured 24 hours after mixing.

uranyl nitrate concentration (3×10^{-3} N). Similar curves have been obtained for other uranyl nitrate concentrations. A minimum potassium concentration of about 6×10^{-3} N is required for the formation of the solid phase independent of the uranyl nitrate concentration, (Figs. 1. and 2.) which indicates that the potassium ions play an important role in the precipitation process in this system. Therefore a constant uranyl nitrate concentration of 2×10^{-3} N was chosen for further studies.
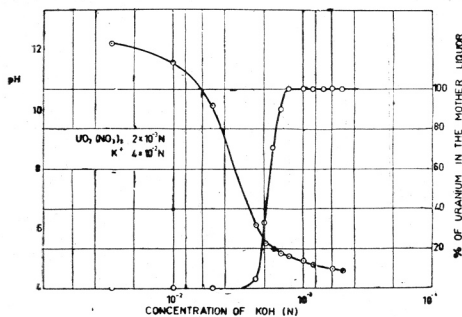

Fig. 4. The percentage of uranium (VI) in mother liquor of the system: uranyl nitrate (2×10^{-3} N)- potassium hydroxide-potassium nitrate (varying concentrations) 24 hours after mixing. The concentration of the potassium ion was kept constant, (4×10^{-2} N). pH Values measured 24 hours after mixing are also presented.

Fig. 3. shows the influence of potassium hydroxide concentration on turbidity and pH. By adding potassium nitrate the concentration of potassium ions in solution was kept constant at 2×10^{-2} N. In Fig. 4. the percentage of uranium in the mother liquor, and the pH is given for various potassium

hydroxide concentrations at constant potassium ion concentrations of $4 \times 10^{-2}\, N$. The curves in Figs. 3. and 4. indicate that for $2 \times 10^{-3}\, N$ uranyl nitrate, a critical potassium hydroxide concentration of $2 \times 10^{-3}\, N$ is required in order to precipitate about 60% of the initial uranium content. Therefore, potassium hydroxide concentration was also kept constant at $2 \times 10^{-3}\, N$ in all experiments where the influence of other neutral electrolytes on the formation of preci-
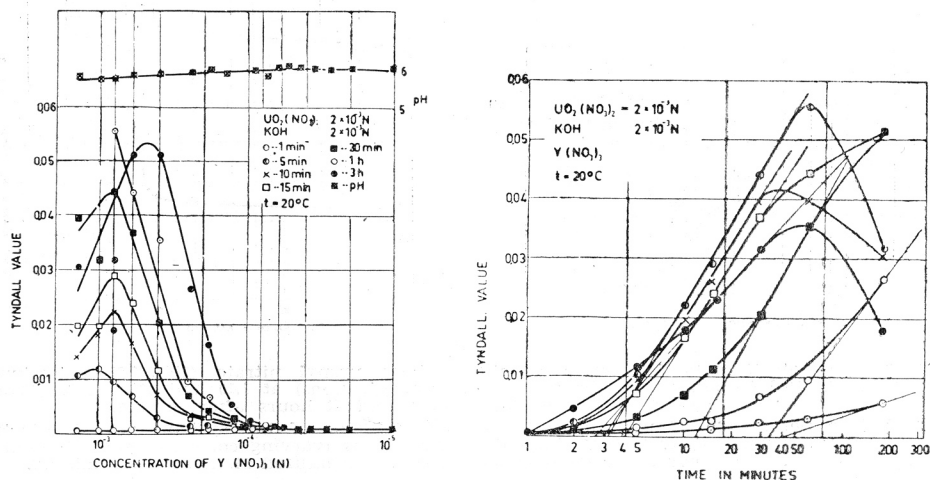

Fig. 5. Concentration tyndallograms of the system: uranyl nitrate $(2 \times 10^{-3}\, N)$- potassium hydroxide $(2 \times 10^{-3}\, N)$- yttrium nitrate (varying concentrations) at 1, 5, 15, 30 minutes and 1 and 3 hours. The upper curve denotes pH values measured 24 hours after mixing.

Fig. 6. Time tyndallograms of the system: uranyl nitrate $(2 \times 10^{-3}\, N)$- potassium hydroxide $(2 \times 10^{-3}\, N)$- yttrium nitrate (varying concentrations). The intersections of tangents on time tyndallograms with the abscissa gives the critical time of the coagulation for $Y(NO_3)_3$ concentrations of: ⊙ $1.8 \times 10^{-4}\, N$,
◦ $2.5 \times 10^{-4}\, N$,   ▨ $4.0 \times 10^{-4}\, N$,   ☐ $6.0 \times 10^{-4}\, N$
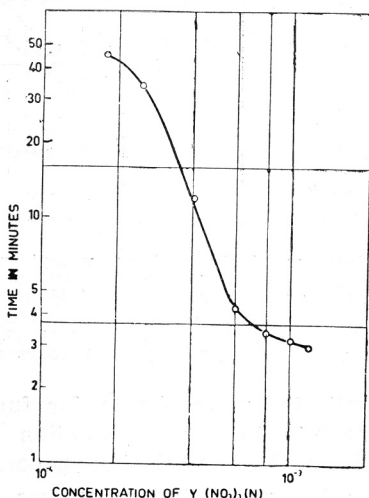× $8.0 \times 10^{-4}\, N$,   ◑ $1.0 \times 10^{-3}\, N$,   ◍ $1.2 \times 10^{-3}\, N$.

Fig. 7. Dependence of the critical time for the precipitation of uranium (VI) on the concentration of yttrium nitrate for the system: uranyl nitrate $(2 \times 10^{-3}\, N)$- potassium hydroxide $(2 \times 10^{-3}\, N)$.

pitates was studied. The pH of these systems was always between 5 and 6. The hydrolysis of uranyl nitrate in the pH range from 5—6 leads to formation of colloids with a negative charge. This was shown by the electrophoretic measurements. Neutral electrolytes: potassium, calcium, strontium, barium,
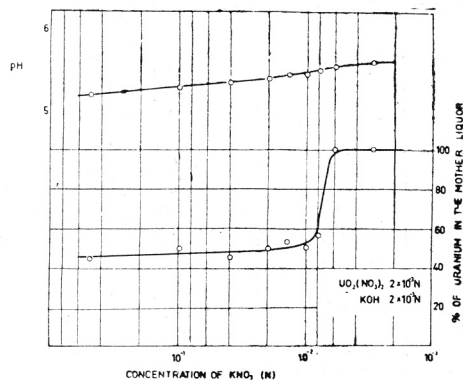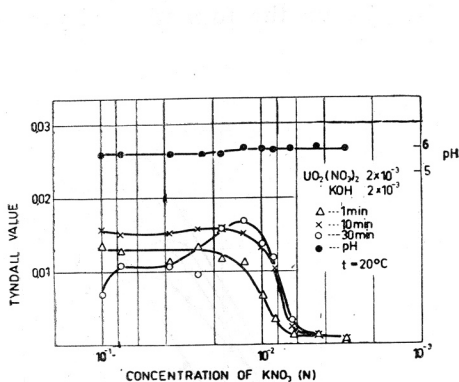

Fig. 8. Concentration tyndallograms of the system: uranyl nitrate (2×10⁻³ N)- potassium hydroxide (2×10⁻³ N)- potassium nitrate (varying concentrations) at 1,10 and 30 minutes. The upper curve denotes the pH values measured 24 hours after mixing.

Fig. 9. The percentage of uranium (VI) in mother liquor of the system: uranyl nitrate (2×10⁻³ N)- potassium hydroxide (2×10⁻³ N)- potassium nitrate (varying concentrations), 24 hours after mixing. The upper curve denotes the pH values measured 24 hours after mixing.
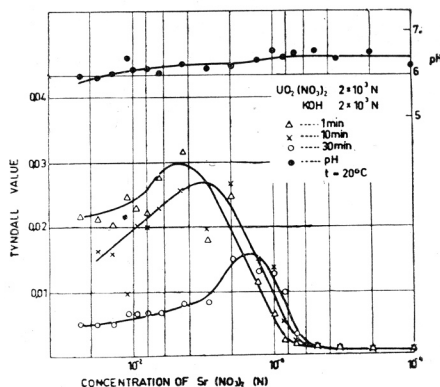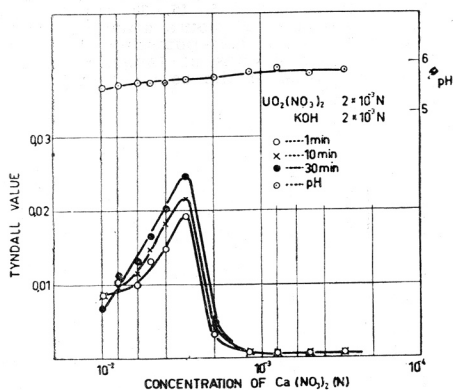

Fig. 10. Concentration tyndallograms of the system: uranyl nitrate (2×10⁻³ N)- potassium hydroxide (2×10⁻³ N)- calcium nitrate (varying concentrations) at 1, 10, and 30 minutes. The upper curve denotes the pH values measured 24 hours after mixing.

Fig. 11. Concentration tyndallograms of the system: uranyl nitrate (2×10⁻³ N)- potassium hydroxide (2×10⁻³ N)- strontium nitrate (varying concentrations) at 1, 10, and 30 minutes. The upper curve denotes the pH values measured 24 hours after mixing.

yttrium and lantanum nitrate, were chosen for further experiments. The addition of neutral electrolyte to a clear solution of uranyl nitrate and potassium hydroxide initiates the precipitation process.

The critical time for the precipitation process was determined using tyndallometric techniques. The results obtained are illustrated on the example of the influence of yttrium nitrate. The turbidity — concentration curves are

discontinuous, but are well defined with respect to the concentration of the neutral electrolyte, at which precipitation is initiated.

Fig. 8. shows the influence of the various potassium nitrate concentrations on the turbidity of the mentioned systems. The curves in Fig. 9. show the percentage of uranium in the mother liquor and the pH of the systems in dependence of various potassium nitrate concentrations. In both cases the lowest concentration of potassium nitrate, at which the precipitation of uranium begins, is about $6 \times 10^{-3} N$.
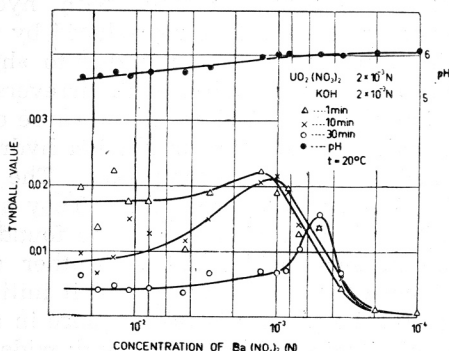

Fig. 12. Concentration tyndallograms of the system: uranyl nitrate $(2 \times 10^{-3} N)$- barium nitrate (varying concentrations) at 1, 10, and 30 minutes. The upper curve denotes the pH values measured 24 hours after mixing.
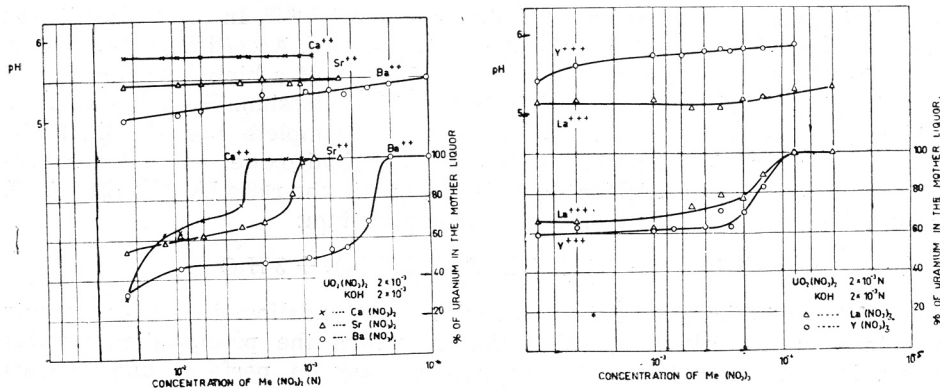

Fig. 13. The percentage of uranium (VI) in mother liquor of the system: uranyl nitrate $(2 \times 10^{-3} N)$- potassium hydroxide $(2 \times 10^{-3} N)$- calcium, strontium or barium nitrate (varying concentrations) 24 hours after mixing. The upper curve denotes the pH value measured 24 hours after mixing.

Fig. 14. The percentage of uranium (VI) in mother liquors of the system: uranyl nitrate $(2 \times 10^{-3} N)$- potassium hydroxide $(2 \times 10^{-3} N)$- lanthanum or yttrium nitrate (varying concentrations) 24 hours after mixing. The upper curve denotes the pH values measured 24 hours after mixing.

The curves in Figs. 10., 11., and 12 show the turbidity and the pH values for the same systems to which the various concentrations of calcium, strontium and barium nitrate are different.

The curves in Fig. 13. indicate the percentage of uranium in the mother liquor, and the pH values for various concentrations of calcium, strontium and barium nitrate. There is no direct correlation between the tyndallometric

maximum shown in Figs. 10., 11., and 12 and the percentage of uranium in the mother liquor. In spite of the smaller turbidity at high neutral electrolyte concentrations, these systems show equal, or even higher percentage of uranium precipitated.

The influence of the trivalent yttrium, and lantanum cations on the percentage of uranium left in the mother liquor is shown in Fig. 14.

<div style="text-align:center">DISCUSSION</div>

The titration curves of uranyl nitrate with hydroxides show two inflection points. The curves could not be reproduced by titrating an alkaline system with perchloric or nitric acid. This is due to »hysteresys«, observed already by Kraus and Nelson[5], which indicates the irreversibility of the uranyl hydrolysis. The formation of the solid phase is the cause of the irreversibility. In the course of hydroxide addition the uranyl ion hydrolyzes over a series of consecutive polynuclear hydroxy - complexes. The first and second complex have pK values 6.1 and 5.8 respectively. They exist in acid solution at pH lower than $4^{8,9}$. No colloid particles could be found in the optical field of the ultramicroscope in such acid systems. Neither did the addition of neutral electrolyte influence the turbidity, nor did it initiate the precipitation process. This indicates that the process is taking place in a real ionic solution.

At more basic uranyl nitrate and potassium hydroxide solutions (pH above 4), the solid phase could be formed, either at high concentrations of both precipitation components, or by addition of neutral electrolytes at lower concentrations. There is disagreement in literature with respect to the composition of the formed precipitates and the mechanism of their formation[10,11,12,20]. In most cases it was suggested that either $Na_2U_2O_7$ or $Na_2U_7O_{22}$ are formed. According to the results shown in Fig. 4., it is probable that in the presence of a high concentration of potassium ions (4×10^{-2} N) the precipitate might be potassium diuranate, $K_2U_2O_7$. This conclusion follows from the fact that a complete uranyl (2×10^{-3} N) precipitation is achieved at 3×10^{-3} N potassium hydroxide, while the supernatant solution is neutral (pH is about 7). We obtain the ratio $UO_2^{2+}/OH^- = 1:3$, i.e. and the reaction corresponds to the equilibrium:

$$2\,UO_2^{+2} + 6\,OH^- + 2\,K^+ \rightleftharpoons K_2U_2O_7 + 3\,H_2O$$
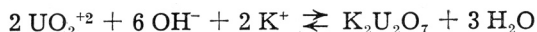
With reference to the given data, it is obvious that tyndallometric measurements indicate only the critical concentration at which the precipitation process begins. But the measurements are simple, easy to perform and copious experimental data can be obtained in a short time. The composition of the formed precipitates and hydrolyzates, can be determined only by using quantitative analytical techniques, which are more elaborate and, above all, more time consuming. Combining both methods a rapid and good review of the precipitation phenomena is achieved.

The precipitation of uranium from uranyl nitrate solutions at concentrations higher than 5×10^{-3} N was also observed in acid media, in absence of neutral electrolyte. At lower uranyl nitrate concentrations the precipitates appear only at the pH above 9 (see e.g. Figs. 1. and 2., Table II).

Further investigations have shown that it is possible to precipitate uranium (VI) from clear solutions consisting of uranyl nitrate (2×10^{-3} N) and potassium hydroxide, at pH values below 7, when the potassium ions are in excess. This

is illustrated in figures 4. and 3. The pH values of solutions containing equivalent quantities of uranyl nitrate and potassium hydroxide (2×10^{-3} N), is about 6.

The turbidity of the systems is time dependent and was successfully measured (Figs. 5., 6., and 7.). Figures 9 to 14 represent the precipitation of uranium (VI) vs. neutral electrolyte concentrations. They show that precipitation of uranium (VI) is accompanied by a simultaneous decrease of pH. It was suposed that the hydroxyl ions from the solution are bound to uranyl ion in the precipitation process. Because of the dissolution of the precipitate at pH below 5 the system becomes self-buffering and there is little change in pH. For this reason in the system of the given composition, a maximum of 70% of uranium (VI) is precipitated.
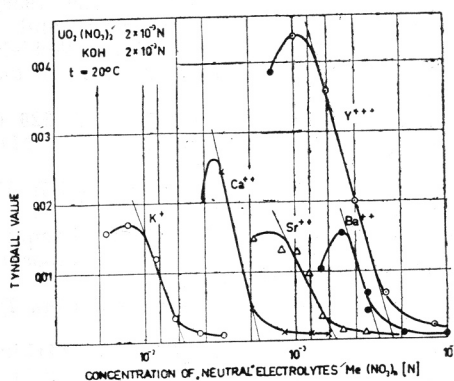

Fig. 15. Concentration tyndallograms of the system: uranyl nitrate (2×10^{-3} N)- potassium hydroxide (2×10^{-3} N)- neutral electrolytes (varying concentrations) at 30 minutes.

A survey of »coagulation« values i.e. of the lowest concentrations of neutral electrolytes, necessary for the initiation of the precipitation in the same system is given in Fig. 15. The values for uni-, bi-, und trivalent cations are not in accordance with the Schulze-Hardy rule. The specific action is best shown for the bivalent cations (calcium, strontium and barium). Such behaviour cannot be attributed to the differences of their ionic radia, or solvation behaviour. This is probably a specific influence due to the building-in and formation of the corresponding uranates.

The obtained results indicate that neutral electrolytes influence the precipitation of uranium through several mechanisms including coagulation, salting out and formation of mixed uranates.

Further investigations of the quantitative determination of the composition of the precipitates, as well as the influence of the neutral electrolyte, and pH on the precipitation of uranium (VI), are in progress.

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IZVOD

Taloženje i hidroliza urana(VI) u vodenim otopinama: uranil nitrat-kalijev hidroksid-neutralni elektrolit

B. Tomažič, M. Branica i B. Težak

Istraživani su uvjeti taloženja i hidrolize urana (VI) u vodenoj otopini: uranil nitrata - kalijeva hidroksida - neutralnog elektrolita. Osobito su bili proučavani (stabilni i bistri) sistemi uranil nitrata i kalijeva hidroksida u ekvivalentnoj koncentraciji od 2×10^{-3} N. Takvi sistemi imaju pH vrijednost od 5 do 6. Taložni proces počinje dodatkom neutralnog elektrolita (kalij, kalcij, stroncij, barij, itrij i lantan nitrat), te se maksimalno istaloži do 70% prisutnog urana. Eksperimentalni rezultati pokazuju, da je taloženje urana (VI), u promatranome sistemu, posljedica nekoliko mehanizama, kao što su: hidroliza, koagulacija i stvaranje miješanih uranata.

Taloženja su praćena tindalometrijski i pH-metrijski, dok je postotak urana u matičnici određivan polarografski.

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