

Kinetics of uranyl ion polymerization in the presence of ammonium hydroxide

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Abstract Kinetics of the polymerization of UO_2^{2+} ion to $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ in the ammonia-uranyl nitrate system has been studied. The deepening of the color formed with the addition of ammonia made it possible to estimate spectrophotometrically the concentration of the formed $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ ions in the solution at 420.6 nm. The effects of pH, temperature as well as the concentration of uranyl ion have been investigated. The reaction rate equation for the polymerization reaction is presented. Linear dependencies of logarithm of the apparent reaction-rate constant on both pH and the reverse of temperature were observed.

Key words uranyl ion • hydrolysis • kinetics • polymerization

Introduction

The reaction between ammonia and uranyl nitrate has been the subject of intensive investigation for decades [3, 4, 7, 9, 12, 14]. The products of the reaction have been identified either as diuranate or polyuranate [2–5, 12–14]. Generally, these precipitated uranates are further processed to the final product, which is sinterable uranium dioxide [1, 5, 11]. The conditions of the precipitation reaction influence the properties of the produced powder and would, thereafter, affect the properties of nuclear fuel produced as well as its performance inside a nuclear reactor [1, 5, 10, 11].

Potentiometric studies showed that polymerization of the UO_2^{2+} ion is the first stage of the reaction between uranyl nitrate and ammonia. The product of the hydrolysis reaction may be in the form of $\text{UO}_2(\text{UO}_3)_n\text{OH}^+$ or $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ [2–4, 7]. Deptula [4] reported, that the $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ ion reacts with NH_4^+ ion to form ammonium uranate. Further course of the reaction depends on how the ammonia is added. When ammonia was added slowly and the reaction was allowed to reach equilibrium, an easily filterable precipitate of uranate was formed, of the hypothetical composition $[(\text{NH}_4)_2\text{O}]_3[\text{UO}_3\text{H}_2\text{O}]_{20} \cdot 13\text{H}_2\text{O}$ [4], which reacted further to form $[(\text{NH}_4)_2\text{O}]_5[\text{UO}_3\text{H}_2\text{O}]_{20} \cdot 7\text{H}_2\text{O}$ [4]. A fast addition of ammonia led to the formation of a poorly filterable precipitate of the composition $[(\text{NH}_4)_2\text{O}]_{2.5}[\text{UO}_3\text{H}_2\text{O}]_{20} \cdot 14\text{H}_2\text{O}$ [4], which easily undergone hydrolysis. This uranate, retaining its physical shape, reacted with excess of ammonia to form a compound, the composition of which corresponded approximately to $[(\text{NH}_4)_2\text{O}]_5[\text{UO}_3\text{H}_2\text{O}]_{20} \cdot 7\text{H}_2\text{O}$.

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Received: 20 May 2004
Accepted: 15 April 2005

Most of the potentiometric studies [3, 4, 7, 9, 14], showed that the pH increased as the $[\text{NH}_4\text{OH}]/[\text{UO}_2(\text{NO}_3)_2]$ mole ratio increased. As this ratio increased beyond 1.6:1, the pH increased rapidly. Further increase in this ratio would lead to the precipitation of the polyuranate. It was also reported [4] that, during the hydrolysis reaction, the color of the solution deepened due to the formation of the -U-O-U-bonds, which were formed during the hydrolysis of UO_2^{2+} ions in polynuclear complexes of the type $\text{UO}_2[(\text{OH})_2\text{UO}_2]_n^{2+}$. These complex ions are the intermediate stage for further reactions, which would lead to the formation of polyuranate.

The purpose of this work was to study the kinetics of the polymerization reaction and the effect of some process parameters as pH, temperature as well as the initial UO_2^{2+} concentration, in order to develop better scientific basis for determining the operating conditions associated with the precipitation of ammonium polyuranate.

Experimental

Ammonia (0.333 M) was added to 50 ml of 0.01–0.5 M aqueous solution of uranyl nitrate (Merck, Analar) using a peristaltic pump (Zalimp, type PP1B-05) with a rate of 1 ml/min at temperatures 22, 40 and 60°C.

The concentration of the $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ ion was determined using a Unicam spectrophotometer, UV4-100, and 10-mm glass cells. In the preliminary experiments, it was found that for all the solutions of molar ratio of $[\text{NH}_4\text{OH}]/[\text{UO}_2(\text{NO}_3)_2]$, ranged between 0 and 1.6, there is a single absorbance maximum at 420.6 nm. This wavelength was then used to construct calibration curves for $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ ion concentration. The absorbance value did not change when using water or ammonia as a reference sample, at least for 1 h.

Results and discussions

The absorbance increases linearly with the amount of NH_4OH added, therefore with the concentration of the $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ ions, C_{U_5} , as observed for 0.1 M uranyl nitrate solutions up to $C_{\text{U}_5} = 0.014$ M. At higher concentrations of $\text{UO}_2(\text{NO}_3)_2$, e.g. 0.5 M, such linear relation does not hold.

The dependence of the pH value on the concentration of the $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ ions, C_{U_5} , in the 0.1 M (initially) uranyl nitrate solution at different temperatures is plotted in Fig. 1. The figure presents an alternative way to present the potentiometric titration curves similar to those reported earlier [4, 9]. pH increases with the increase in C_{U_5} , for all temperatures studied. It should be mentioned that the titration curves reported earlier [9] were not affected by the ammonia addition rate, over the temperature range of 30–60°C, at least in the first part corresponding to $[\text{NH}_4\text{OH}]/[\text{UO}_2(\text{NO}_3)_2]$ mole ratios from 0.0 to 1.6. The pH was found to decrease linearly as the temperature increases.

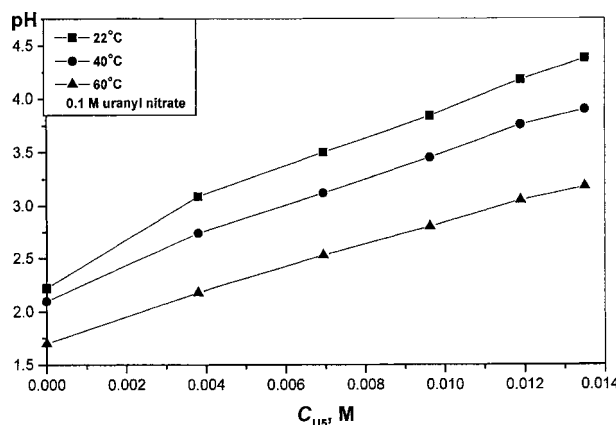
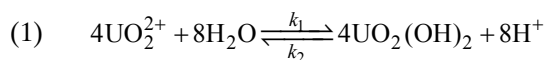


Fig. 1. pH change vs. polymerized ion concentration in 0.1 M uranyl nitrate solution at different temperatures.

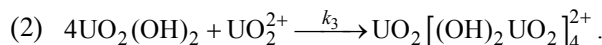
Development of the polymerization reaction kinetics

The scheme of the possible reactions which would lead to the formation of the complex ion $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ was assumed to be as follows:

1 – the uranyl ions hydrolyze according to the reaction,



2 – the uranyl hydroxide may further react with excess uranyl ion,



The rate of formation of intermediate compound $\text{UO}_2(\text{OH})_2$ may be expressed as

$$(3) \quad \frac{d[\text{UO}_2(\text{OH})_2]}{dt} = R^* = k_1[\text{UO}_2^{2+}]^4 - k_2[\text{UO}_2(\text{OH})_2]^4[\text{H}^+]^8 - k_3[\text{UO}_2(\text{OH})_2]^4[\text{UO}_2^{2+}].$$

Applying a steady-state approximation [6] and considering $\text{UO}_2(\text{OH})_2$ as an intermediate compound, we may assume that the rate of its change is equal to zero, $R^* = 0$. Hence,

$$(4) \quad [\text{UO}_2(\text{OH})_2]^4 = \frac{k_1[\text{UO}_2^{2+}]^4}{k_2[\text{H}^+]^8 + k_3[\text{UO}_2^{2+}]}.$$

The rate of formation of the complex ion $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ R_{U_5} , may be then expressed as

$$(5) \quad R_{\text{U}_5} = k_3[\text{UO}_2(\text{OH})_2]^4[\text{UO}_2^{2+}]$$

Table 1. Calculations result of the apparent reaction rate constant (k_3)

[NH ₄ OH]/ [UO ₂ (NO ₃) ₂], mole ratio	C_{U0} , M	C_{U5} , M	dC_{U5}/dt , mole/(L·min)	22°C		40°C		60°C	
				log k_3	pH	log k_3	pH	log k_3	pH
0.0	0.1	0.0	0.0	–	2.22	–	2.10	–	1.70
0.333	9.1E-02	0.0038	0.0035	–21.46	3.09	–18.69	2.74	–14.22	2.18
0.666	8.33E-02	0.00694	0.00288	–23.97	3.50	–20.91	3.12	–16.55	2.53
1.0	7.7E-02	0.00962	0.0025	–25.62	3.84	–22.76	3.45	–18.66	2.80
1.33	7.14E-02	0.0119	0.0022	–26.48	4.18	–23.33	3.76	–19.78	3.05
1.60	6.75E-02	0.0135	0.0	–	4.38	–	3.90	–	3.18

$$(6) \quad R_{U5} = \frac{k_3 k_1 [\text{UO}_2^{2+}]^5}{k_2 [\text{H}^+]^8 + k_3 [\text{UO}_2^{2+}]}$$

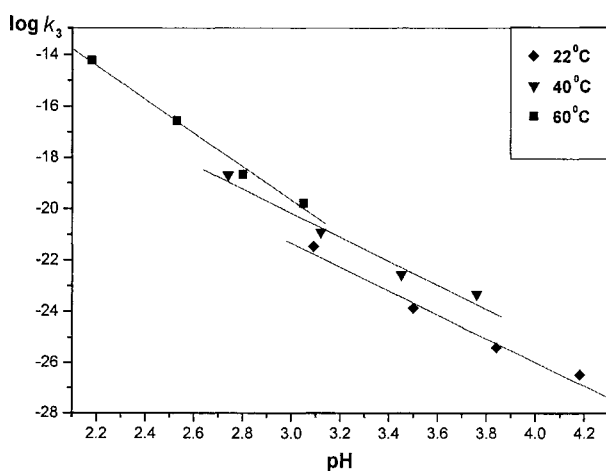
$$(7) \quad R_{U5} = \frac{k_3 k_1 k_2^{-1} [\text{UO}_2^{2+}]^5 [\text{H}^+]^{-8}}{1 + k_3 k_2^{-1} [\text{UO}_2^{2+}] [\text{H}^+]^{-8}}$$

At low pH values the considered molar ratio of [NH₄OH]/[UO₂(NO₃)₂] in the solutions ranged between 0 and 1.6, i.e. when the hydrogen ion concentration is extremely high, the additive term in the denominator of Eq. (7) may be neglected. Hence,

$$(8) \quad R_{U5} = \frac{k_3 k_1 [\text{UO}_2^{2+}]^5}{k_2 [\text{H}^+]^8}$$

Eq. (8) may be simplified by: (i) replacing the ratio k_1/k_2 by the equilibrium constant K of the hydrolysis reaction; (ii) expressing $[\text{H}^+]^8$ in terms of the pH of the medium and (iii) expressing $[\text{UO}_2^{2+}]$ in terms of the total uranium concentration, giving:

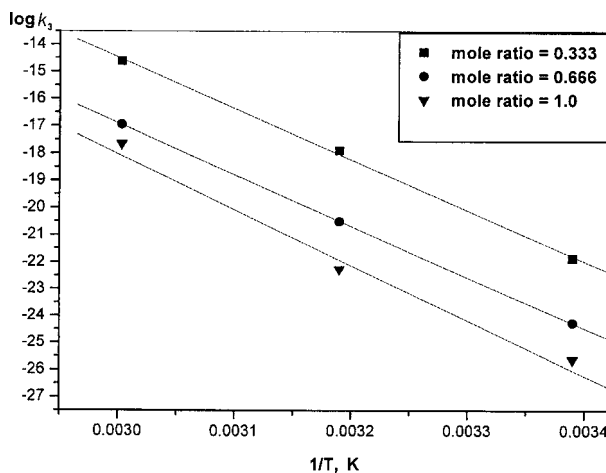
$$(9) \quad R_{U5} = k_3 K [C_{U0} - 5C_{U5}]^5 \cdot 10^{8\text{pH}}$$

**Fig. 2.** Change of reaction rate constant with pH in 0.1 M uranyl nitrate solution at different temperatures.

where: C_{U0} is the total uranium concentration in the solution and C_{U5} is the concentration of $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$. The value of K was reported [8] to range between $10^{-12\pm 1}$ at 22°C to $10^{-11\pm 1}$ at 60°C. An intermediate value of K at 40°C was assumed to be $2.5 \times 10^{-12\pm 1}$.

The concentration of $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ at each measurement step can be easily determined by measuring the absorbance and using the calibration curves. As the ammonia addition rate is constant all over the experiment for different cases, it is possible to calculate the apparent change of the complex ion concentration at any time (dC_{U5}/dt).

The dependence of the apparent reaction-rate constant, k_3 , on both pH and temperature would be evaluated from the experimental data. The results of the calculations are presented in Table 1. The variation of k_3 with pH at three different temperatures is plotted in Fig. 2, whereas the variation of k_3 with the temperature at three different mole ratios, [NH₄OH]/[UO₂(NO₃)₂], is depicted in Fig. 3. The reported data indicate that the apparent reaction-rate constant, k_3 , increases with temperature, but decreases with pH. In view of these findings, taking into account the variation of K with temperature, k_3 may be expressed, at least under the operating conditions used in this study, by the following form;

**Fig. 3.** Change of reaction rate constant with temperature in 0.1 M uranyl nitrate solution at different [NH₄OH]/[UO₂(NO₃)₂] mole ratios.

$$(10) \quad k_3 = 10^{(20.5 - 5.83\text{pH} - 7310./T)}.$$

Eqs. (9) and (10) may be combined to form the reaction rate equation,

$$(11) \quad R_{U5} = [C_{U0} - 5C_{U5}]^5 \cdot 10^{(20.5 + 2.174\text{pH} - 7310./T)}.$$

Conclusions

A scheme was suggested for the possible reactions which would lead to the polymerization of UO_2^{2+} ions to $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$, with uranyl hydroxide, $\text{UO}_2(\text{OH})_2$, as an intermediate compound. The reaction rate equation was derived, where the apparent reaction-rate constant was found to be influenced by both pH and temperature.

Nomenclature

- C_{U0} – total uranium concentration in the solution, mole/L
 C_{U5} – $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ polymerized ion concentration, mole/L
 K – hydrolysis reaction equilibrium constant (k_1/k_2)
 k_3 – apparent rate constant of polymerization reaction, liter⁴/(mole⁴·min)
 R^* – rate of formation of $\text{UO}_2(\text{OH})_2$ intermediate compound, mole/(L·min)
 R_{U5} – rate of formation of $\text{UO}_2[(\text{OH})_2\text{UO}_2]_4^{2+}$ polymerized ion, mole/(L·min)

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