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Original Scientific Paper

## Characterization of the Uranyl-mono-hydrogenperoxo Complex in Aqueous 0.7 mol dm<sup>-3</sup> LiClO<sub>4</sub> by Spectrophotometry

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UV spectra of uranyl solutions in the presence of hydrogen peroxide (in 0.7 mol dm $^{-3}$  LiClO $_4$ , at 3.0 < pH < 6.0) can be explained only by assuming the presence of uranyl-mono-hydrogenperoxo species. The apparent stability constant of this species determined spectrophotometrically amounts to  $K=(2.82\pm0.68)~{\rm x}~10^{11}~{\rm mol}^{-1}~{\rm dm}^3$ . By including this value into the programme for computing the distribution of uranyl species and by comparing the experimentally determined distribution to the calculated one, a good agreement was obtained.

#### INTRODUCTION

During the last decade, extensive systematic research on the presence and distribution of hydrogen peroxide in seawater has been carried out. Its concentration in oceans has been reported<sup>1–5</sup> to be about 10<sup>-7</sup> mol dm<sup>-3</sup>. The photochemical generation of hydrogen peroxide is very often encountered in the photic layer of the ocean<sup>3</sup> and, in specific areas, the concentration can be elevated<sup>6</sup> to 10<sup>-5</sup> mol dm<sup>-3</sup>.

Geochemical reactivity of dissolved uranium in seawater is partly related to the formation of uranyl-peroxo complexes. In seawater environment, the presence of  $\rm H_2O_2$  can have significant consequences on the speciation of uranyl species. Comprehensive understanding of uranyl peroxide equilibria pertaining to seawater environment is essential because of the high uranyl-ion affinity for complex formation with peroxide  $^{7,8}$  and because of the relatively high available concentration of hydrogen peroxide in the photic zone of seawater relative to uranium.

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Several classical papers are devoted to the effect of uranyl complexation with peroxide.  $^{9-15}$  Different uranyl peroxo complexes are formed depending on the molar  $H_2O_2: UO_2^{2+}$  ratio. The richest in peroxide is  $(UO_2(O)_2)_3)^{4-}$  which is predominant and stable  $^{13}$  at pH > 13. The most frequently cited and best defined sparingly soluble species is uranyl-monoperoxide  $(UO_2O_2\times n(H_2O);\ n=2\ \text{or}\ 4)$ , which is also formed as an intermediate in uranium purification procedure.  $^{13,14}$  From the solubility product of  $UO_2O_2\times 4H_2O$ , the formation constant of  $(UO_2O_2)^0$  complex has been calculated as  $K=1.1\times 10^{32}\ \text{mol}\ \text{dm}^{-3}$ .

In our previous study, <sup>16</sup> the apparent stability constant of uranyl-monoperoxo complex was determined as  $K_{\rm UO_2O_2}=(1.1\pm0.1)~10^{32}~{\rm mol~dm^{-3}}$ , from the pH-dependent apparent concentration stability constant  $K_{\rm UO_2O_2}=2\times10^5~{\rm mol~dm^{-3}}$ . These and all the other constants from the literature have been included into the program package, <sup>19,20</sup> which was developed to be used for the speciation of the uranium (VI) in natural waters.

During spectrophotometric measurements in the pH range from 4.0 to 5.2, discrepancies with the model have been observed, which make it necessary to postulate the existence of additional species  $(UO_2HO_2)^+$ , whose formation constant was evaluated. The hypothesis on the existence of this species is supported by the fact that, at constant total  $H_2O_2$  concentration and in the pH range 4–5, the concentration of free  $[HO_2]^-$  ligand is around  $10^{20}$  times higher than the concentration of  $[O_2]^{2-}$  form. Distinction of  $(UO_2HO_2)^+$  species and quantitative determination of its properties are the subject of this study.

### METHODOLOGY

Spectrophotometric measurements in the UV-region were performed on a Cary-219 spectrophotometer using a 5 cm optical path length cell. The pH of the solution was adjusted by varying the ratio of  $HClO_4$  and LiOH. The pH of the solutions was determined with the Iskra MA 5721 pH-meter each time before and after the spectrophotometric measurement.

The solutions were prepared from reagent-grade chemicals. The uranyl perchlorate stock solution was prepared from uranyl nitrate and gravimetrically standardized.  $^{17}$  For preparation of the solution of hydrogen peroxide, Suprapure 30% hydrogen peroxide (»Merck« Darmstadt) was used. In the starting solution, the content of  $\rm H_2O_2$  was standardized manganometrically.  $^{18}$ 

## Calculation of uranyl species distribution

Computer HP 9816 S interconnected to Printer HP 82906 A and Plotter HP 7475 A was used for distribution calculations based on the computational program described elsewhere. <sup>19,20</sup> The pH-dependent uranyl species distribution was derived taking into account complexation of uranyl with hydroxide and peroxide ligands.

The stability constants of uranyl-hydroxo and mono-, di-, tri- peroxo complexes used to calculate the uranium distribution at the ionic strength of 0.7 mol dm<sup>-3</sup> are reported in our previous papers. <sup>19,20</sup> The stability constant for uranyl mono-hydrogen-peroxo species derived in the present study was also included into the above computational program for metal species distribution and the two distribution sets were compared with the experimentally (spectrophotometrically) determined one.

#### RESULTS AND DISCUSSION

Speciation of a certain analytical concentration of uranyl-ions in the solution of  $0.7 \text{ mol dm}^{-3} \text{ LiClO}_4$  at a defined pH in the presence of  $H_2O_2$  is described by the following mass balance equations (charges omitted):

$$[UO_2]_{tot} = [UO_2]_{free} + [UO_2OH] + [UO_2O_2] + [UO_2HO_2]$$
 (1)

$$[H_2O_2]_{tot} = [H_2O_2] + [HO_2] + [O_2] + [UO_2O_2] + [UO_2HO_2]$$
 (2)

where  $[UO_2]_{free}$  represents the concentration of the hydrated uranyl-ions;  $[UO_2OH]$  the concentration of uranyl-mono-hydroxo complex;  $[UO_2O_2]$  and  $[UO_2HO_2]$  represent concentrations of the two types of uranyl-peroxo complexes *i.e.* the uranyl-monoperoxo and the uranyl-mono-hydrogen peroxo complex, respectively.

Partition of total uranyl concentration within two groups of uranyl species  $M_x$  and  $M_y$  is expressed by modifying Eq. (1) as follows:

$$[UO_2]_{tot} = [M_x] + [M_y]$$
 (3)

with

$$[M_x] = [UO_2]_{free} + [UO_2OH]$$
 (4)

$$[M_y] = [UO_2O_2] + [UO_2HO_2]$$
 (5)

The formation of  $M_y$  species can be followed spectrophotometrically from the increase of absorbance a at a defined wavelength after addition of  $H_2O_2$ . The absorption spectrum of  $3\times 10^{-5}$  mol dm<sup>-3</sup> (UO<sub>2</sub>)<sup>2+</sup>tot in 0.7 mol dm<sup>-3</sup> LiClO<sub>4</sub> and at pH 5 is presented as line 1 in Figure 1; the change of this spectrum, after adding  $[H_2O_2]_{tot}$ , is given by lines 2 to 12 in Figure 1. Obviously, for  $[H_2O_2]_{tot}$ , equal or higher than  $1.2\times 10^{-5}$  mol dm<sup>-3</sup>, a well pronounced absorption maximum develops at 230 nm, indicating complex formation according to the above equation.

Under the given experimental conditions, the overall absorbance a at 230 nm can be expressed as:

$$a = \varepsilon_{Mx} \times [M_x] + \varepsilon_{My} \times [M_y]$$
 (6)

where  $\varepsilon_{\rm Mx}$  and  $\varepsilon_{\rm My}$  correspond to the molar absorptivity of the respective group of uranyl species  $M_{\rm x}$  and  $M_{\rm y}$ . The unknown molar absorptivity of the group of uranyl species  $M_{\rm x}$  i.e.  $\varepsilon_{\rm Mx}$  is determined from the following set of experiments. In the range from  $1\times 10^{-5}$  to  $8\times 10^{-5}$  mol dm<sup>-3</sup> of uranyl concentration and at pH = 4.0, 4.4, 4.8 and 5.2, as presented in Figure 2, the absorbance at 230 nm has been measured. The molar absorptivity  $\varepsilon_{\rm Mx}$  has been determined from the slope of the linear relationship of the absorbance at 230 nm and the concentration of uranyl-ions at a given pH. The values of  $\varepsilon_{\rm Mx}$  determined at five pH values and their standard errors are presented in Table I. While the pH rises from 4.0 to 5.2, the  $\varepsilon_{\rm Mx}$  values increase from 1135 to 2843 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>, as noticeable from Table I. This can be explained by the fact that  $\varepsilon_{\rm Mx}$  comprises the individual molar absorptivities of uranyl species  $({\rm UO_2})^{2^+}_{\rm free}$  and  $({\rm UO_2OH})^+$ . By increasing the pH from 4.0 to 5,2, the partition of  $({\rm UO_2OH})^+$  increases,

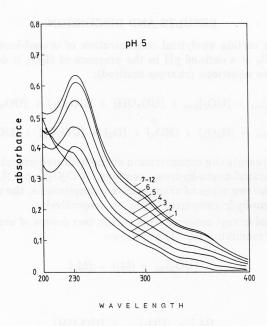


Figure 1. Absorption spectra of uranyl (3 × 10<sup>-5</sup> mol dm<sup>-3</sup>) in 0.7 mol dm<sup>-3</sup> LiClO<sub>4</sub> at constant pH 5 by varying the concentration of  $H_2O_2$ : (1) 0; (2) 6 × 10<sup>-6</sup>; (3) 1.2 × 10<sup>-5</sup>; (4) 1.8 × 10<sup>-5</sup>; (5) 2.4 × 10<sup>-5</sup>; (6) 3 × 10<sup>-5</sup>; (7) 3.6 × 10<sup>-5</sup>; (8) 4.2 × 10<sup>-5</sup>; (9) 4.8 × 10<sup>-5</sup>; (10) 5.4 × 10<sup>-5</sup>; (11) 6 × 10<sup>-5</sup>; (12) 1.2 × 10<sup>-4</sup> mol dm<sup>-3</sup>.

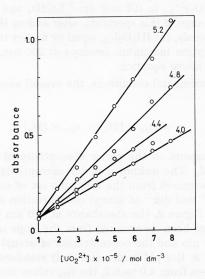


Figure 2. Dependence of the absorbance of  $M_x$  species (Eq. (3)) at 230 nm on the total uranyl concentration in 0.7 mol dm<sup>-3</sup> LiClO<sub>4</sub> solution and at four different pH's.

TABLE I

Molar absorptivity  $\varepsilon_{Mx}$  of  $M_x$  group of uranyl species (viz. Eqs. (4) and (6)) at different pH, and the standard error of the slope of the fitted straight line.

pH .	$rac{arepsilon_{ m Mx}}{ m cm^{-1}~mol^{-1}~dm^3}$	$\frac{\text{Standard error}}{\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3}$	
4.0	1135	26	
4.4	1370	68	
4.7	1730	72	
4.8	1962	75	
5.2	2843	69	

influencing the overall  $\varepsilon_{Mx}$ . The values of  $\varepsilon_{Mx}$  indicated in Table I were used to calculate the apparent stability constant of  $(UO_2HO_2)^+$ .

At pH 5 and for constant  $[UO_2]_{tot}$ , it has been previously determined that the absorbance of uranyl-peroxo complexes at 230 nm increases by increasing the  $[H_2O_2]_{tot}$ , until the equimolar ratio of  $H_2O_2$ :  $UO_2$  is attained. If the  $H_2O_2$  concentration increases above the equimolar one, the absorbance at 230 nm does not change any more, but attains a constant value (as one observes in Figure 1 lines 7–12). It can be concluded that the uranyl-peroxo-complex formation proceeds by the combination of one molecule of each uranyl and peroxide.

The molar absorptivity  $\varepsilon_{\rm My}$  (from Eq. (6)) has been determined from the slope of the absorbance at 230 nm of the solution containing an equimolar ratio of  $\rm H_2O_2$  and  $\rm UO_2$ . Figure 3 shows the absorbance a at 230 nm of 0.7 mol dm<sup>-3</sup> LiClO<sub>4</sub> pH 5 con-

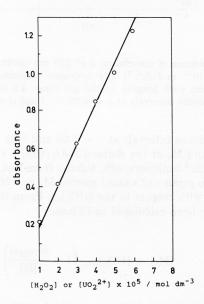


Figure 3. Absorbance a at 230 nm for the solutions of pH 5 having  $H_2O_2/UO_2^{2+} = 1:1$  in the concentration range of  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  mol dm<sup>-3</sup>.

taining the equimolar ratio  $H_2O_2: UO_2^{2+}$  in the range from  $1\times 10^{-5}$  to  $6\times 10^{-5}$  mol dm<sup>-3</sup>. By the least square method,  $\varepsilon_{My}$  is determined from the slope of the straight line as 4331 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>. This value of  $\varepsilon_{My}$  is in good agreement with 4160 cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup> determined previously<sup>16</sup> at the plateau of higher ligand-to-metal ratios, applying the mole-ratio method.

At a constant concentration of  $3\times 10^{-5}$  mol dm<sup>-3</sup> UO<sub>2</sub><sup>2+</sup> and  $6\times 10^{-5}$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>, the pH was varied in the range from 4 to 8 and the absorption was measured at 230 nm. Above pH 5, absorbance a approaches the constant value<sup>21</sup> of 0.66, as presented in Figure 4a. A linear relationship exists between the absorbance and the pH in the range from 4.0 to 5.0 if the H<sub>2</sub>O<sub>2</sub>/UO<sub>2</sub><sup>2+</sup> ratio is constant, as indicated in Figure 4a. The straight line defined by the least square method is indicated in Figure

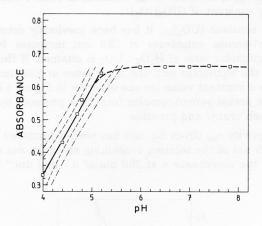


Figure 4a. The pH dependence of absorbance a at 230 nm (defined by Eq. (6)) of the solutions containing uranyl (3 × 10<sup>-5</sup> mol dm<sup>-3</sup>) and hydrogen peroxide (6 × 10<sup>-5</sup> mol dm<sup>-3</sup>) in 0.7 mol dm<sup>-3</sup> LoiClO<sub>4</sub> · (5 cm path length). In the pH range 4.0 to 5.0, a straight line has been fitted (——), with confidence intervals at  $\alpha = 0.05$  (– –) and  $\alpha = 0.01$  (– – –).

4a as well as its confidence intervals at  $\alpha=0.05$  and 0.01. The partition of the group of uranyl species  $M_x$  and  $M_y$  at the defined  $H_2O_2/UO_2^{2^+}$  ratio, in the pH range from 4.0 to 5.0 at 0.7 mol dm<sup>-3</sup> ionic strength, follows from Eqs. (6) and (3). The calculated distribution of the two groups of uranyl species  $M_x$  and  $M_y$  is presented in Figure 4b in molar percentages, with respect to the  $[UO_2]_{tot}$ . From the defined fraction  $M_x$  (Figure 4), the  $UO_{2free}$  has been calculated as follows:

$$[\mathbf{M}_{\mathbf{x}}] = [\mathbf{UO}_2]_{\text{free}} \left( 1 + \frac{K_{\mathbf{UO}_2\mathbf{OH}}}{[\mathbf{H}]} \right) \tag{7}$$

where  $K_{\rm UO_2OH}$  is the apparent stability constant of uranium-mono-hydroxo complex.<sup>23</sup> From the defined [M<sub>y</sub>] (Figure 4b), the unknown apparent stability constant  $K_{11}$  of the species  $({\rm UO_2HO_2})^+$  is calculated as follows:

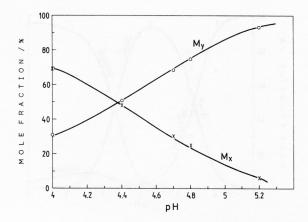


Figure 4b. The pH dependence of molar % of  $M_x$  and  $M_y$  species of the solution containing uranyl  $(3 \times 10^{-5} \text{ mol dm}^{-3})$  and hydrogen peroxide  $(6 \times 10^{-5} \text{ mol dm}^{-3})$  in 0.7 mol dm<sup>-3</sup> LiClO<sub>4</sub>.

$$[M_y] = [UO_2]_{free} (K_{11} \times [HO_2] + K_1 \times [O_2])$$
 (8)

where  $K_1$  is the stability constant of  $UO_2(O_2)^0$  species. 16

The obtained values of the apparent stability constant  $K_{11}$  of  $(UO_2HO_2)^+$  complex at four different pH values are presented in Table II. The mean value of  $K_{11}$  amounts to  $2.82 \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup>. For  $\alpha = 0.05$ , the confidence interval<sup>24</sup> of the mean value amounts to  $\pm 0.68 \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup>.

TABLE II

Concentration of  $(H_2O_2)_{tot}$   $(HO_2)^-$ ,  $(O_2)^{2-}$ ,  $(UO_2)^{2+}_{free}$  under equilibrium conditions. The apparent stability constant  $K_{11}$  for  $(UO_2HO_2)^+$  has been calculated at four pH values and at 0.7 mol  $dm^{-3}$  ionic strength.

pН	$\frac{[\mathrm{H_2O_2}]_{\mathrm{tot}}}{\mathrm{mol}\;\mathrm{dm}^{-3}}$	$\frac{[\mathrm{HO_2}]^-}{\mathrm{mol}\ \mathrm{dm}^{-3}}$	$\frac{[O_2]^{2-}}{\text{mol dm}^{-3}}$	$\frac{[\mathrm{UO_2}]_\mathrm{free}^{2+}}{\mathrm{mol}\;\mathrm{dm}^{-3}}$	$\frac{K_{11}}{10^{11} \text{ mol}^{-1} \text{ dm}^3}$
4.0	5.06E-5	1.13E-12	1.14E-33	1.87E-5	3.43
4.4	4.48E-5	2.52E-12	6.33E-33	1.19E-5	2.55
4.7	3.94E-5	4.42E-12	2.21E-32	6.22E-6	2.50
4.8	3.76E-5	5.31E-12	3.35E-32	4.64E-6	2.80

 $K_{11} = 2.82 \times 10^{11}$ 95% confidence interval:  $\pm 0.68 \times 10^{11}$ 

The uranyl hydrolysis and the complexation with peroxide are used to derive pH-dependent uranyl species distribution based on the apparent stability constants available in the literature. In Figure 5, the distribution of uranyl-species in the range of pH 3–9 and in the presence of  $H_2O_2$  is presented when the formation of uranyl-monohydrogenperoxo complex is not taken into account. Curve 1 presents a sum of free uranyl and hydrolyzed  $(UO_2OH)^+$  form (i.e.  $M_x$  according to Eq. (4)) while curve 2 presents  $(UO_2O_2)^0$  uranyl-monoperoxo complex.

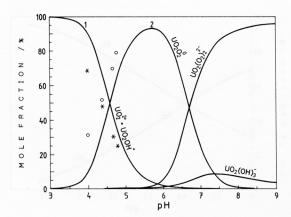


Figure 5. Calculated distribution of uranyl-hydroxo and -peroxo species as molar percentages of the total concentration of uranyl  $3\times 10^{-5}$  mol dm<sup>-3</sup> and of hydrogen peroxide  $6\times 10^{-5}$  mol dm<sup>-3</sup>. Curve 1 represents the sum of free uranyl and  $(UO_2OH)^+$  species and curve 2 represents  $(UO_2O_2)^0$  species. Spectrophotometric measurements of  $M_x$  (o) and  $M_y$  (\*) distribution are incorporated.

The spectrophotometric measurements of the distribution of the two groups of uranyl species  $M_x$  and  $M_y$  (viz. Figure 4b) are presented in Figure 5 using the following symbols: \* denotes the sum of free uranyl together with hydrolyzed (UO<sub>2</sub>OH)<sup>+</sup> form i.e.  $M_x$  fraction (Eq. 4) and  $\odot$  denotes uranyl bound to the peroxide. From Figure 5 it can be seen that, when the formation of uranyl-mono-hydrogenperoxo complex is not taken into account, the experimental and calculated distribution curves do not coincide in the pH range 4.0 to 5.2. Intersection of the two sets of distribution curves (at 50%) differs by 0.3 pH units. It indicates that not all relevant species have been taken into account in the speciation model. Therefore, the calculated apparent stability constant  $K_{11}$  (Table II) of uranyl-mono-hydrogenperoxo complex has to be included in the speciation model. The resulting distribution of uranyl- species presented in Figure 6 coincides with the experimentally determined distribution of the two groups of uranyl species i.e.  $M_x$  and  $M_y$  in the range 4.0 < pH < 5.2. In Figure 6, curve 1 is a sum of free and hydrolyzed forms i.e.  $[M_x]$  (Eq. (4), experimental data \*) and curve 2 is a sum of  $(UO_2O_2)^0$  and  $(UO_2HO_2)^+$  forms i.e.  $[M_y]$  (Eq. (5), experimental data o).

The distribution of  $UO_2$ -species in the range 3 < pH < 9 (viz. Figure 5), taking into account the existence of uranyl-mono-, di- and tri-peroxo complexes as well as uranyl-mono, -di and -tri hydroxo complexes, has been published already. <sup>16</sup> A more complete distribution of  $UO_2$ -species is obtained in the presence of  $H_2O_2$ , i.e. when, in addition to speciation from Figure 5, the formation of mono-hydrogen-peroxo complex is taken into the account (viz. Figure 6). These results indicate that the existence of  $(UO_2HO_2)^+$  does not influence the uranyl speciation at the pH of seawater.

According to the distribution of individual uranyl species in the pH range 3 to 6.5 as presented in Figure 7, the  $(UO_2HO_2)^+$  form has a significant influence on the uranyl-species distribution, but above pH 6 it is negligible. From the distribution curves of individual species (Figure 7), it can be noticed that around pH 4.5, the

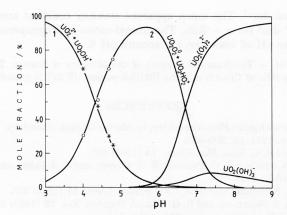


Figure 6. Calculated distribution of uranyl species under the same conditions as presented in Figure 5, including the apparent stability constant of  $(UO_2HO_2)^+$ . Curve 1 represents the sum of free uranyl and  $(UO_2HO)^+$  abd curve 2 represents the sum of  $(UO_2O_2)^0$  and  $(UO_2HO_2)^+$  species. Spectrophotometrix measurements of  $M_x$  (o) and  $M_v$  (\*) distribution are incorporated.

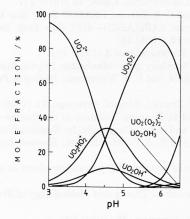


Figure 7. Calculated distribution of individual uranyl species under the conditions presented in Figure 6, but for the pH range 3-6.5.

 $[\mathrm{UO_2HO_2}]^+$  complex reaches its maximum at 35% with respect to the total uranyl concentration.

#### CONCLUSION

From spectrophotometric measurements, the apparent stability constant of uranyl-mono-hydrogenperoxo complex  $(UO_2HO_2)^+$  has been evaluated and reported for the first time. It has been determined that particularly the mono-form has a significant influence on the uranyl-species distribution in the pH range 3 to 6, at an ionic

strength of 0.7 mol dm<sup>-3</sup>. The mean apparent stability constant amounts to  $(2.82 \pm 0.68) \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> for  $\alpha = 0.05$ . The uranyl-mono-hydrogenperoxo species exerts no influence at the pH of seawater, *i.e.* around pH 8.

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#### SAŽETAK

# Spektrofotometrijska karakterizacija i monoperoksouranilne vrste u ${\rm LiCl_4}$ (0.7 mol $^{-1}$ dm $^{-3}$ )

R. Djogić, B. Raspor i M. Branica

Spektrofotometrijska svojstva otopine uranila u nazočnosti vodikova peroksida upućuju na postojanje i monoperoksouranilne vrste. Prividna koncentracijska konstanta stabilnosti te vrste, određena spektrofotometrijski, iznosi  $K=(2.82\pm0.68)\times10^{11}~\mathrm{mol^{-1}~dm^3}$ . Uključenjem te vrijednosti konstante stabilnosti u program za izračunavanje raspodjele uranskih vrsta u otopini LiClO<sub>4</sub> (0.7 mol dm<sup>-3</sup>), dobiveno je dobro slaganje eksperimentalne i izračunane raspodjele.