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Precipitation of Uranium(VI) Peroxide (UO_4) in Sodium Perchlorate Solution

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Precipitation diagrams were constructed using the data obtained in experiments with direct mixing of uranyl ion ($[UO_2]^{2+}$) and hydrogen peroxide. Three days after mixing the system, equilibrium was established in the $[H_2O_2]_{tot} > [UO_2]_{tot}$ concentration region, resulting in stability of the concentration boundary. From this boundary condition, the solubility product ($K_{sp} = [UO_2^{2+}] \times [O_2^{2-}]$) was defined. The mean value of the solubility product was $(1.32 \pm 0.02) \times 10^{-36}$ mol dm^{-3}.

From the solubility border, where equilibrium was established, *i.e.*, at $[UO_2^{2+}] = 1.4 \times 10^{-4}$ mol dm^{-3}, the heterogeneous distribution diagrams of uranyl species, including the solid phase, were calculated.

INTRODUCTION

The high level of dissolved uranyl, *i.e.*, 3.3 μg dm^{-3} in the ocean[1] is most probably due to its residence time[2] of about 3×10^6 years, which may be explained in terms of high uranyl solubility and generally conservative behaviour of this element[3] in the marine environment. This fact is supported, apart from carbonate species of dissolved uranyl in sea water,[4] also by the confirmed presence of uranyl peroxo species in seawater.[5] Namely, enhanced concentrations of hydrogen peroxide were found in the upper layer of the oceans, the euphotic zone.[6] The strong uranyl ion affinity for peroxide[7,8] prompted us to pursue this experimental verification.[5]

However, in freshwater and in more acidic media, where salinity and CO_3^{2-} are depleted, sparingly soluble compounds can be formed, resulting in a lower total uranyl ion concentration.[9] The high stability of peroxide (O_2^{2-}) species with uranyl ion (UO_2^{2+}) has been studied extensively.[10–12] Different uranyl-peroxo complexes in various $O_2^{2-} : UO_2^{2+}$ ratios are formed. The richest uranyl complex in peroxide is $UO_2(O_2)_3^{4-}$, which is stable at pH > 13.[13,14] From the solubility product of $UO_4 \cdot 4H_2O$, the formation constant of $UO_2O_2^\circ$ complex has been calculated[15] to be $K = 1.1 \times 10^{32}$. The exact composition of the complex has been confirmed spectrophotometrically (by the mole-ratio method), and the apparent concentration stability constant $K^*_{UO_2O_2} = 2 \times 10^5$ mol^{-1} dm^3 has been calculated.[16]

Mechanisms of the solubility of the uranium solid phase, such as schoepite $UO_3 \cdot 2H_2O$,[17,18] contribute to a better understanding of the behaviour of uranium in the environment. The effect of silica and phosphate on the transformation of schoepite into bequerelite $Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$ was examined as well.[19]

Used nuclear fuel, largely U(IV) oxide, is considered to be directly geologically disposed. Although re-

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ducing conditions generally prevail at disposal sites, conditions could become oxidizing through dissolution of oxygen trapped within the vault while sealing the containers. Therefore, oxidation and dissolution of nuclear fuel by the products of alpha radiolysis of water have been measured.[20]

The obtained results pertaining to the behaviour of solid U(IV) oxide surfaces in different aqueous media, which should be of relevance for the solubility characteristics of the nuclear fuel waste matrix in groundwater environments, led to different reaction mechanisms proposed.[21]

Counioux *et al.*[22] used pH measurements and isoplethic thermal analysis to obtain hydrated uranium(VI) peroxide ($UO_4 \cdot nH_2O$ with $n = 2, 4$) while working in nitric medium. This compound is formed as an intermediate in the uranium purification procedure and is the most frequently cited and the best-defined sparingly soluble species.

Moreover, with the aim to provide the knowledge needed for the potential development of some purification processes of nuclear materials,[23] it was interesting to study precipitation of UO_4. Because of poorly soluble UO_4 species, the precipitation diagram was constructed to determine the boundary of the homogeneous system.

EXPERIMENTAL

Solutions were prepared from reagent grade chemicals. The uranyl perchlorate stock solution was prepared from uranyl nitrate and was standardized gravimetrically.[24] Suprapur® 30 % hydrogen peroxide (Merck, Darmstadt, Germany) was used to prepare the hydrogen peroxide solution. Content of H_2O_2 (1 mol dm^{-3}) in the stock solution was standardized manganometrically.[25] All experiments were performed at 22±1 °C.

In all solutions, the initial pH was adjusted to 4.8 by addition of $HClO_4$ and was measured using the glass electrode connected to the ATI Orion PerpHecT Meter, model 320 (Cambridge, MA, USA). pH was also measured at the end of the experiment, when it decreased by about 0.2 pH units (to 4.6) due to hydrolysis and precipitation. All solutions were prepared in 0.7 mol dm^{-3} $LiClO_4$, so the ionic strength was constant, I = 0.7 mol dm^{-3}.

For the detection of the solid phase, a tyndallometer (Zeiss, Jena, Germany) in combination with a Pulfrich photometer (Zeiss) were used.

Structural properties of the precipitate were examined by X-ray diffraction, using a counter diffractometer with monochromatized Cu-Kα radiation [λ (α_1) = 1.54051 Å, λ (α_2) =1.54433 Å].

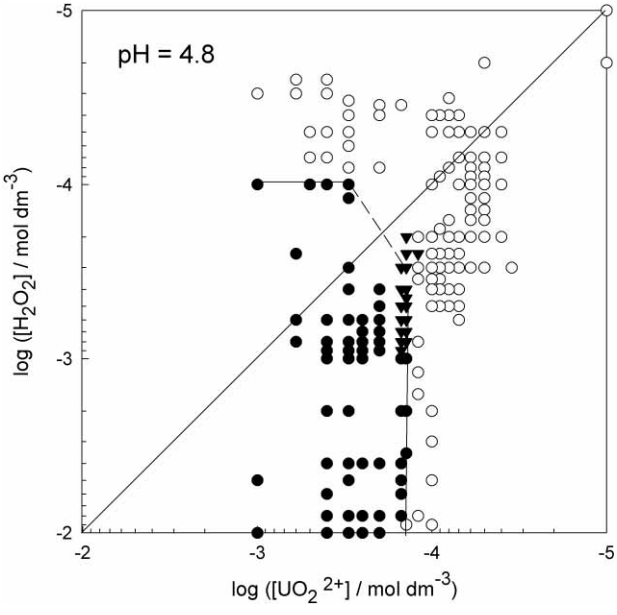

Figure 1. Precipitation diagram of UO_4 and the precipitation boundary 1 day after preparing the system: precipitate (●), metastable (▼) and clear (○) solutions.

RESULTS AND DISCUSSION

Precipitation Diagrams

Precipitation diagrams were constructed using the data from experiments with direct mixing (stirring) of uranyl perchlorate and hydrogen peroxide solutions. Cation component concentration varied in the range of total concentrations $10^{-5} < [UO_2^{2+}]_{tot} < 10^{-3}$ mol dm^{-3}, while total anionic concentrations varied in the range of $10^{-5} < [H_2O_2]_{tot} < 10^{-2}$ mol dm^{-3}.

Precipitation diagrams of this system, 1 and 3 days after mixing the solutions, are presented in Figures 1 and 2, respectively. In 10 systems, the precipitate was identified by X-ray diffraction analyses, but only two most informative are given (◘ in Figure 2). Based on diffraction data, as presented in Table No. 16 – 206,[26] it was confirmed that the solid phase is pure hydrated uranium(VI) peroxide ($UO_4 \cdot 4H_2O$), when dried at room temperature (Figure 3a). The X-ray diffraction pattern when the solid phase was dried at 85 °C for 1 hour is shown in Figure 3b, and is identified from the Table No. 16–207[26] as uranium(VI) peroxide dihydrate ($UO_4 \cdot 2H_2O$).

Precipitation boundary divides the system in which the solid phase appears from the system in which the precipitate was not observed (clear solutions). Thus, the precipitation boundary is actually the concentration boundary. $[UO_2^{2+}]_{tot}$ and $[H_2O_2]_{tot}$ at this boundary present the equilibrium concentrations at which supersaturations are identical to those in suspensions at which the solid/liquid equilibrium is achieved. Precipitation boundary in the concentration region where $[H_2O_2]_{tot} > [UO_2^{2+}]_{tot}$ shifts a little toward lower $[UO_2^{2+}]_{tot}$ during a period from 1 to 3 days. Due to this fact, we used the three days boundary after mixing the systems in further considerations. It was highly possible that the equilibrium was

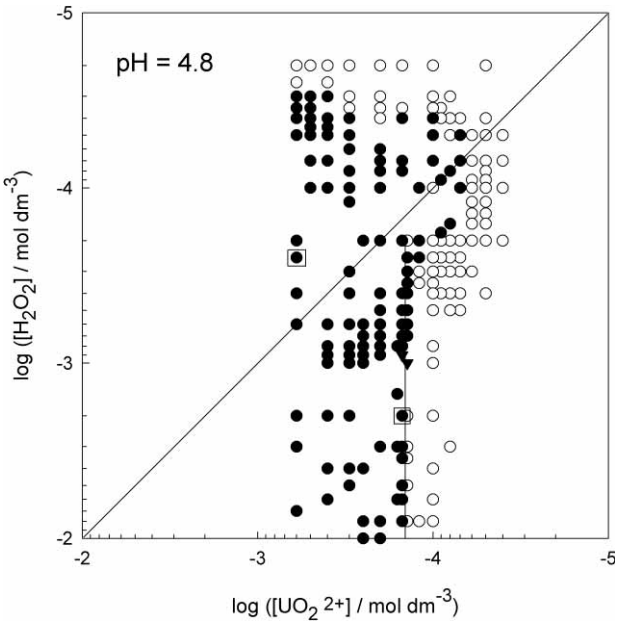

Figure 2. Precipitation diagram of UO_4 and the precipitation boundary 3 days after preparing the system: precipitate (●), metastable (▼) and clear (○) solutions. Precipitate taken for X-ray diffraction analyses (◙).

reached. Moreover, after 10 days this boundary was still stable. However, the boundary where $[H_2O_2]_{tot} < [UO_2^{2+}]_{tot}$ changed towards lower UO_2^{2+} concentrations with time. Among the anions that form stable complexes with the uranyl ion under the above mentioned conditions, peroxo and hydroxo ligands were taken into account. Thus, the total soluble uranyl concentration is equal to the sum of the following hydroxo and peroxo species concentrations:

$$[UO_2^{2+}]_{sol} = [UO_2^{2+}] + [UO_2OH^+] + [UO_2(OH)_2^0] + [UO_2(OH)_3^-] + [UO_2O_2^0] + [UO_2(O_2)_2^{2-}] + [UO_2(O_2)_3^{4-}] = [UO_2^{2+}] (1 + (K_{UO_2OH^-} [OH^-] + K_{UO_2(OH)_2^0} [OH^-]^2 + K_{UO_2(OH)_3^-} [OH^-]^3 + K_{UO_2O_2^0} [O_2^{2-}] + K_{UO_2(O_2)_2^{2-}} [O_2^{2-}]^2 + K_{UO_2(O_2)_3^{4-}} [O_2^{2-}]^3)) \quad (1)$$

and peroxide species under our experimental conditions are as follows:

$$[H_2O_2]_{sol} = [H_2O_2] + [HO_2^-] + [O_2^{2-}] + [UO_2O_2^0] + 2[UO_2(O_2)_2^{2-}] + 3[UO_2(O_2)_3^{4-}] \quad (2)$$

where K values have been taken from Table I.

At uranyl ions concentration of 1.4×10^{-4} mol dm^{-3} and pH of the system in the range from 4.8 to 4.6, polyhydroxo species are present in negligible concentrations (see Figure 4). To determine the solubility product (K_{sp}), the uranyl/peroxide concentration ratio was restricted to the higher concentrations of $[H_2O_2]_{tot}$ where

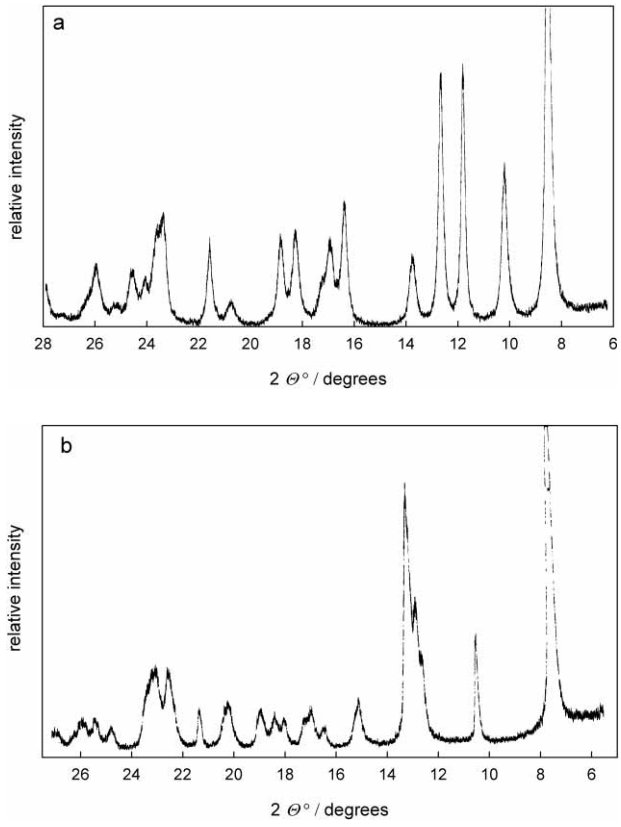

Figure 3. X-ray diffraction pattern of the precipitate taken from the sample (◙) (see Figure 2): a) after drying at room temperature and b) after drying at 85 °C.

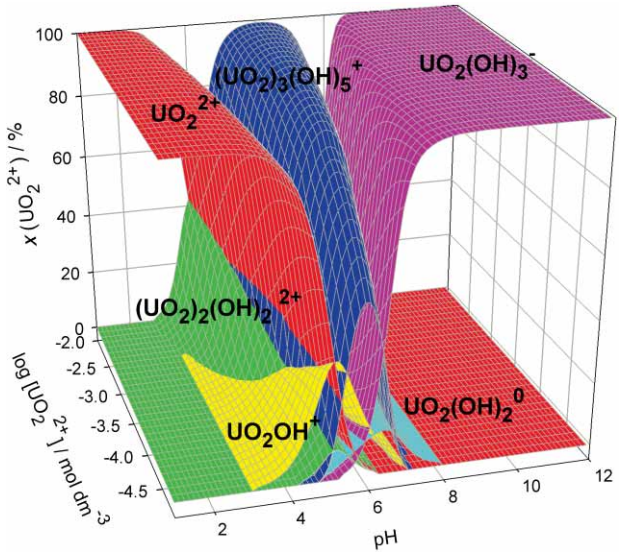

Figure 4. Distribution of UO_2^{2+} hydroxo species calculated by MINEQL$^+$ in dependence on pH values; x – mole fractions.

the solubility boundary coincides with that achieved after one and three days. At lower H_2O_2 concentrations (see Figures 1 and 2), the boundary shifts significantly with time towards lower $[UO_2^{2+}]_{tot}$. Therefore, this part of the solid/liquid boundary was not taken into account.

TABLE I. Stability constants of uranyl species used in this work

Species	Equilibrium formula	log K	Reference
UO_2OH^+	$UO_2^{2+} + H_2O \leftrightarrow UO_2OH^+ + H^+$	–5.0	27
$UO_2(OH)_2^0$	$UO_2^{2+} + 2H_2O \leftrightarrow UO_2(OH)_2^0 + 2H^+$	–11.2	27
$UO_2(OH)_3^-$	$UO_2^{2+} + 3H_2O \leftrightarrow UO_2(OH)_3^- + 3H^+$	–17.1	27
$UO_2(O_2)^0$	$UO_2(O_2)^0 \leftrightarrow UO_2^{2+} + O_2^{2-}$	32	15
$UO_2(O_2)_2^{2-}$	$UO_2(O_2)_2^{2-} \leftrightarrow UO_2^{2+} + 2O_2^{2-}$	60	15
$UO_2(O_2)_3^{4-}$	$UO_2(O_2)_3^{4-} \leftrightarrow UO_2^{2+} + 3O_2^{2-}$	72	15
H_2O_2	$H_2O_2 \leftrightarrow H^+ + HO_2^-$	–11.65	28
H_2O_2	$H_2O_2 \leftrightarrow 2H^+ + O_2^{2-}$	–36.65	28

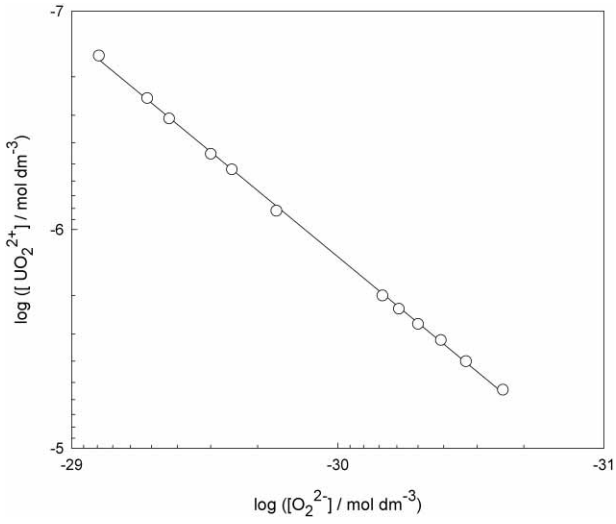

Figure 5. Dependence of –log([UO_2^{2+}]/mol dm^{-3}) on –log([O_2^{2-}]/mol dm^{-3}) constructed from the data presented in Table I.

In Table II, the $[UO_2^{2+}]_{tot}$ and $[H_2O_2]_{tot}$ from the precipitation boundary (shown in Figure 2) are given.

Applying equations 1 and 2 in the computation, the free concentrations of UO_2^{2+} and O_2^{2-} were obtained, which are given in subsequent columns of Table II and in the graphical presentation (Figure 5).

Solubility product is defined as the product of UO_2^{2+} and O_2^{2-} free concentrations:

$$K_{sp} = [UO_2^{2+}]_{free} \times [O_2^{2-}]_{free}. \quad (3)$$

The solubility product (K_{sp}) mean value was found to be (1.32±0.02) × 10^{-36} mol dm^{-3}.

Calculated Distribution Curves

Calculated distribution curves for the solubility boundary (1.4 × 10^{-4} mol dm^{-3} UO_2^{2+}) at different pH values and $10^{-2} > [H_2O_2] > 10^{-5}$ are presented in Figures 6a, 6b, and 6c. For this calculation, the commercial program MINEQL$^+$ was used.[29] The equilibrium constants for the calculations were taken from Table I, and those for polyhydroxo species $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^-$ from the cited paper.[4] The solubility product K_{sp} determined in this work was included into calculations. At lower peroxide concentrations, the distribution is affected by the polyhydroxo species (Figure 6a). However, at higher concentrations of H_2O_2, the peroxo species are predominant (Figure 6b) and the precipitate of UO_4(s) is formed (Figure 6c).

TABLE II. Equilibrium concentrations from the precipitation boundary

$[UO_2^{2+}]_{tot} \times 10^4$	$[H_2O_2]_{tot} \times 10^3$	$[UO_2^{2+}]_{free}^{(a)} \times 10^6$	$[O_2^{2-}]_{free}^{(a)} \times 10^{30}$	$K_{sp} \times 10^{36}$
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	
1.4	9.0	0.16	7.9	1.30
1.4	6.0	0.25	5.2	1.27
1.4	5.0	0.31	4.3	1.30
1.4	3.5	0.45	3.0	1.35
1.4	3.0	0.53	2.5	1.35
1.4	2.0	0.82	1.7	1.36
1.4	0.90	2.0	0.68	1.35
1.4	0.80	2.3	0.59	1.36
1.4	0.70	2.7	0.50	1.34
1.4	0.60	2.0	0.41	1.33
1.4	0.50	4.0	0.33	1.31
1.4	0.40	5.4	0.24	1.30

[(a)] Concentrations calculated by the MINEQL$^+$ computer program.[29]

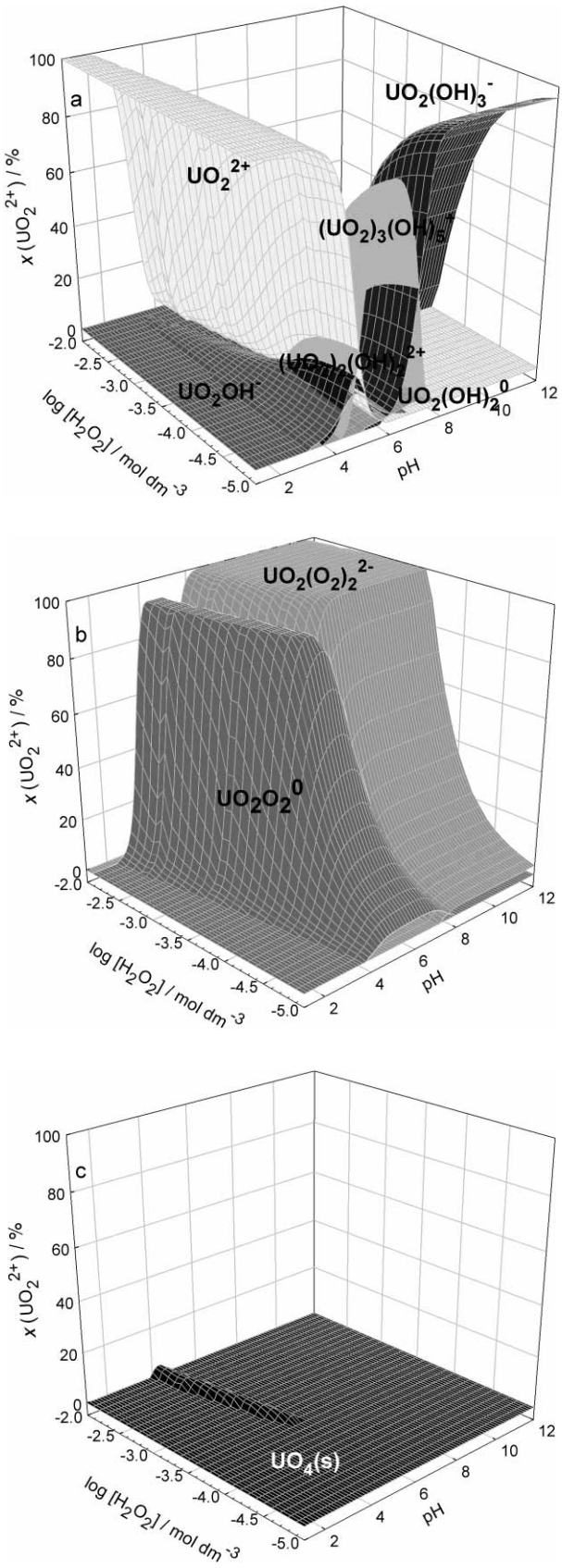

Figure 6. Distribution curves of 1.4×10^{-4} mol dm^{-3} UO_2^{2+} at different pH values and $10^{-2} > [H_2O_2]_{tot} > 10^{-5}$ calculated by MINEQL$^+$: a) only hydroxide species; b) only peroxide species, and c) mole fractions of UO_2^{2+} in solid phase UO_4(s).

DISCUSSION

Uranium(VI) peroxide is precipitated when the solutions containing uranyl ions are in contact with H_2O_2 in sufficiently high concentrations.[30] This mechanism is also known from a natural analogue in Africa where uranium peroxides formed the minerals studtite ($UO_4 \cdot 4H_2O$) and meta studtite ($UO_4 \cdot 2H_2O$) close to uranium ore bodies, obviously under highly oxidizing conditions.[31]

In the literature, only a few papers deal with the solubility product of $UO_4 \cdot 4H_2O$, so our results were compared with the values cited in the paper of Moskvin.[15] Although Gayer and Thompson[32] examined solubility of UO_2O_2 in acid and base media, their results are semiqualitative, because they determined only the total uranyl concentration. As the measurements were performed in the solutions at pH < 2 and pH > 12, they imply transformation of the precipitate $UO_2O_2 \cdot 4H_2O$ in $UO_3(OH)_2 \cdot H_2O$ or $UO_2(OH)_2 \cdot H_2O$, so that the solubility data of the initial compound were not given.

The value of K_{sp} determined by Moskvin[15] was found to be 1.8×10^{-39} mol dm^{-3}. That value is approximately three orders of magnitude lower than the value of K_{sp} determined in this work ($I = 0.7$ mol dm^{-3}). Moskvin determined the value of K_{sp} indirectly, without determining concentrations of the present $UO_2^{2+}{}_{free}$ and $O_2^{2-}{}_{free}$ at equilibrium concentrations. He defined K_{sp} as follows: $K_{sp} = K^0 K' K''$ where K' and K'' are the dissociation constants of hydrogen peroxide. One of the possible sources of this discrepancy is the fact that we determined the constant without empirical equations used for calculations of activity coefficients. In other words, the error in the values of K' and K'' can significantly change the value of K_{sp}.

In the region where $[UO_2^{2+}] > [H_2O_2]$, a significant shift in the solubility boundaries was observed. This means that in the period between 1 and 3 days there was a significant formation of the precipitate in mixed solutions. As the quantity of the precipitate was not sufficient for chemical analysis, we cannot claim that the precipitate is pure uranium(VI) peroxide ($UO_4 \cdot 4H_2O$). In this uranyl concentration range, the hydrolysis of uranyl ions is favoured. At 4 < pH < 6, polyhydroxo species predominates where uranyl ions concentrations are above 2×10^{-4} mol dm^{-3} (see Figure 6a). Microcrystalline $UO_2(OH)_2$ is often treated as an independent compound in the solubility database. Some uranyl oxide species most probably coprecipitate in this region. It is therefore quite likely that the precipitate was a mixture in the above mentioned concentration region. Due to this fact, we did not determine the value of K_{sp} from this boundary. If the shift of the boundary was only due to kinetic reasons, by determining that the precipitate is pure $UO_4 \cdot 4H_2O$, which defines all the equilibrium concentrations, it would be possible to determine the value of K_{sp} and compare it to the value obtained in this work. That would provide a definite evidence that there is exclusively precipitation of $UO_4 \cdot 4H_2O$ in the whole concentration region.

CONCLUSIONS

Precipitation diagrams were constructed by direct mixing of uranyl perchlorate and hydrogen peroxide solutions. The concentration boundary was stabilized three days after mixing the uranyl peroxide solutions.

From the newly established concentration boundary, the uranium(VI) peroxide solubility product was calculated:

$$K_{sp} = [UO_2^{2+}]_{free} \times [O_2^{2-}]_{free}.$$

The mean value of the solubility product (K_{sp}) was found to be $(1.32\pm0.02) \times 10^{-36}$ mol dm^{-3}.

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SAŽETAK

Taloženje uranijeva(VI) peroksida (UO_4) u otopini natrijeva perklorata

Renata Djogić, Vlado Cuculić i Marko Branica

Taložni sustavi priređeni su direktnim miješanjem otopina uranil iona i vodikova peroksida. Ravnoteža je uspostavljena 3 dana nakon miješanja sustava pri $[H_2O_2]_{tot} > [UO_2^{2+}]_{tot}$, gdje se granica taloženja stabilizirala. Dobivena je koncentracijska granica taloženja, iz koje je izračunan produkt topljivosti. Srednja vrijednost produkta topljivosti (K_{sp}) je $(1{,}32\pm0{,}02) \times 10^{-36}$ mol dm^{-3}.

Pomoću granice taloženja, gdje je uspostavljena ravnoteža, tj. pri $[UO_2^{2+}] = 1{,}4 \times 10^{-4}$ mol dm^{-3} izračunana je heterogena raspodjela uranijevih vrsta, koja uključuje i krutu fazu.