



Chemical stability of rare-earth elements' uranyl arsenates with general formula $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu) in aqueous solution

Oxana V. Nipruk¹ · Nikolay G. Chernorukov¹ · Kseniya A. Klinshova¹ · Maxim O. Bakhmetev¹ · Olga N. Tumaeva¹

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Abstract

The chemical stability of uranyl arsenates of rare-earth elements with the general formula $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu) in aqueous solutions has been studied in a wide range of acidity. The acid–base ranges of the existence of these compounds in aqueous solutions were established, the transformation products formed outside these ranges were identified, and the solubility of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ was determined. Based on the experimental data obtained, the solubility products, Gibbs free energies of the formation of the rare-earth elements uranyl arsenates were calculated, the solubility curves of the studied compounds were computed, and the speciation diagrams of uranium(VI), arsenic(V), and rare-earth elements in saturated aqueous solutions and equilibrium solid phases were constructed.

Keywords Uranyl arsenates · Rare-earth elements · Solubility · Aqueous solution · Solubility product · Heterogeneous equilibria · Speciation diagram

Introduction

This study focuses on rare-earth elements (REE) uranyl arsenates, that belong to a large family of uranium(VI) compounds with a general formula $M^k(AsUO_6)_k \cdot nH_2O$, where M^k represents a wide array of chemical elements in different oxidation states k . A number of mineral species of this family, such as abernathyite $KAsUO_6 \cdot 4H_2O$, novacekite $Mg(AsUO_6)_2 \cdot 12H_2O$, uranospinite $Ca(AsUO_6)_2 \cdot 10H_2O$, heinrichite $Ba(AsUO_6)_2 \cdot 10H_2O$, kahlerite $Fe(AsUO_6)_2 \cdot (10–12)H_2O$, zeunerite $Cu(AsUO_6)_2 \cdot (10–16)H_2O$, lodevite $Zn(AsUO_6)_2 \cdot 10H_2O$, are found in nature. A range of compounds $M^k(AsUO_6)_k \cdot nH_2O$, where M^k represents chemical elements in oxidation states of +1, +2 and +3 was synthesized in laboratory conditions [1–16].

All $M^k(AsUO_6)_k \cdot nH_2O$ compounds have a similar layered structure, where negatively charged layers $[AsUO_6]_{2\infty}^{\delta-}$ are comprised of uranium square bipyramids

and arsenic tetrahedra [1–3, 11–13, 16]. Cations M^{k+} and H_2O molecules occupy the interlayer space, link uranium–arsenic layers and determine their arrangement. Molecular water in the structure of uranyl arsenates serves the role of ligand deficiency compensator for interlayer cations hence its amount is determined by the coordination number of interlayer atoms and the hydration energy of their ions. REE uranyl arsenates contain the largest amount of molecular water in the $M^k(AsUO_6)_k \cdot nH_2O$ family of compounds. Similar characteristics of REE allow of the same number of water molecules $n = 16$ in the composition of all studied compounds $M^{III}(AsUO_6)_k \cdot nH_2O$ (M^{III} –La–Lu).

Any way of usage of uranium compounds requires data on their chemical stability and speciation in aqueous media. Despite the successes in gas and melt technologies in the nuclear industry, most stages of the nuclear fuel cycle are conducted in aqueous solutions. Research into chemical stability and solubility of uranyl arsenates is crucial to solving many technological and ecological tasks. Despite all of this, there are few scientific papers devoted to the solubility of uranyl arsenates of alkaline [17, 18], alkaline earth [19] and transition elements in aqueous solutions [11–13, 19, 20].

REE uranyl arsenates are the least studied among $M^k(AsUO_6)_k \cdot nH_2O$ compounds and there are no publications devoted to their solubility and chemical stability in aqueous

✉ Oxana V. Nipruk
nipruk@yandex.ru

¹ Chemical Department, Lobachevsky State University of Nizhni Novgorod, Gagarin Avenue, 23, Nizhni Novgorod, Russian Federation 603950

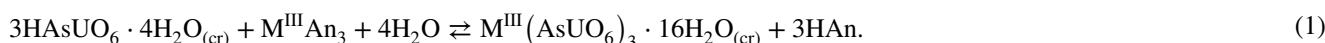
solutions. At the same time, data on their chemical stability is of scientific and technological importance due to REE predominantly forming during the fission of uranium nuclei and their close contact with uranium species during post-reactor stages of the nuclear fuel cycle [21]. Interaction of uranium compounds with rare-earth elements is also possible in natural conditions and the environment [22, 23].

Therefore this paper presents the results of a comprehensive study of the state of REE uranyl arsenates in water and aqueous solutions of perchloric acid and sodium hydroxide at 25 °C.

Experimental

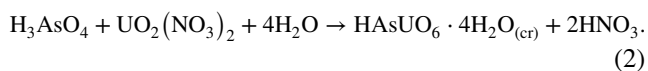
Synthesis of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu) compounds

REE uranyl arsenates were obtained via an ion-exchange reaction between crystalline $HAsUO_6 \cdot 4H_2O$ and 0.1 mol/l solutions of $M^{III}An_3$ ($An=Cl^-, NO_3^-$) [14]:



To push the equilibrium point towards the increased formation of the product, the REE salt solution that was in contact with the precipitate was refreshed multiple times. The increase in temperature led to a similar effect. The completeness of the ionic exchange was determined through the measurement of pH of the mother liquor. The synthesis was considered to be complete if the pH value was the same for 0.5–1 h and was equal to the pH value of 0.1 mol/l solution of $M^{III}An_3$. The precipitates were rinsed with distilled water and air-dried.

Uranyl arsenic acid $HAsUO_6 \cdot 4H_2O$, that was used in the uranyl arsenates synthesis, was obtained via precipitation [4]:



The temperature conditions of the reaction and the acidity of the mother liquor were under close consideration. Only acidic medium and boiling facilitate sufficiently pure product. The synthesis of $HAsUO_6 \cdot 4H_2O$ was conducted in a round-bottom flask with a volume of 0.5 l. 100 ml of 0.15 mol/l solution of H_3AsO_4 was put into the flask and stirred while 60 ml of 0.25 mol/l solution of $UO_2(NO_3)_2$ was added drop by drop. Then the flask containing the working solution was connected to a reflux condenser and heated on sandbath for three days. The precipitate $HAsUO_6 \cdot 4H_2O$ was separated from solution via centrifugation, rinsed with distilled water and air-dried at 18–25 °C.

Phase individuality of synthesized compounds and absence of crystalline impurity were established via X-ray powder diffraction. The resulting diffraction patterns were compared to reported data [14]. The mass fraction of H_2O was found gravimetrically by calcining the samples at a temperature of 600 °C for five hours. Contents of uranium, arsenic and REE were determined via X-ray fluorescence analysis, using the fundamental parameter method with correction sensitivity coefficients calculated with data from standard samples. The standard samples were prepared by mixing UO_3 , As_2O_5 and $M^{III}_2O_3$ in molar ratios of 3:1.5:0.5 and homogenising the mix. The oxides were calcined tentatively to remove excess moisture. The found amounts of the elements in the solid phase have coincided with theoretical values within a margin of 0.5% (Table 1).

Study of the $M^{III}(AsUO_6)_3 \cdot nH_2O$ (M^{III} –La–Lu) state in aqueous solution

In order to investigate the state of REE uranyl arsenates in aqueous solutions, sample weights (~ 100 mg) were placed

into 100 ml of solutions of $HClO_4$ or $NaOH$ (with molar concentration of 0.1, 0.01, 0.001 and 0.0001 mol/l) or distilled water. The experiments were conducted in plastic isolated containers with the minimal free volume of air (less than 1–2 ml) to minimize contact between solutions and CO_2 . The solutions with precipitates were shaken periodically and pH values were measured for several months. After the constant pH values were reached, the precipitate was separated from the solution, rinsed with distilled water, air-dried at room temperature and studied via X-ray fluorescence and powder diffraction analysis. The saturated aqueous solutions were analyzed via spectrophotometry to determine total concentrations of uranium(VI), arsenic(V) and REE(III). Nephelometry and turbidimetry were used to demonstrate the absence of suspended and colloidal particles in the studied solutions.

Spectrophotometric study of aqueous solutions

Arsenic(V) concentration in aqueous solution was determined via spectrophotometric method using the absorption of the reduced form of arsenic-molybdenum heteropolyacid ($\lambda_{max} = 900$ nm, reducing agent–ascorbic acid) [24]. The stock solution of arsenic(V) was prepared by dissolving NaH_2AsO_4 in distilled water. The uranium(VI) concentration was determined using the absorption of its adduct with Arsenazo III ($\lambda_{max} = 650$ nm, pH 3 for uranium concentration

Table 1 Analytical results for $M^{III}(AsUO_6)_3 \cdot 16H_2O$ ($0.5M^{II} \cdot \frac{1}{2}O_3 \cdot 3UO_3 \cdot 1.5As_2O_5 \cdot 16H_2O$) composition

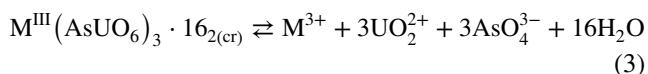
M^{III}	$M^{III}_2O_3$, wt %		As_2O_5 , wt %		UO_3 , wt %		H_2O , wt %	
	Found	Theory	Found	Theory	Found	Theory	Found	Theory
La	9.8(1)	9.84	20.7(2)	20.84	51.8(5)	51.88	17.4(1)	17.43
Ce	9.8(1)	9.92	20.8(2)	20.82	51.7(5)	51.84	17.4(1)	17.41
Pr	9.9(1)	9.96	20.7(2)	20.82	51.7(5)	51.82	17.4(1)	17.41
Nd	10.1(1)	10.14	20.7(2)	20.78	51.7(5)	51.71	17.3(1)	17.37
Sm	10.4(1)	10.47	20.6(2)	20.70	51.5(5)	51.52	17.3(1)	17.31
Eu	10.5(1)	10.56	20.6(2)	20.68	51.3(5)	51.47	17.3(1)	17.29
Gd	10.8(1)	10.84	20.5(2)	20.62	51.3(5)	51.31	17.2(1)	17.24
Tb	10.9(1)	10.93	20.5(2)	20.59	51.2(5)	51.26	17.2(1)	17.22
Dy	11.1(1)	11.11	20.5(2)	20.55	51.1(5)	51.15	17.1(1)	17.18
Ho	11.2(1)	11.25	20.4(2)	20.52	50.9(5)	51.08	17.1(1)	17.16
Er	11.3(1)	11.37	20.4(2)	20.49	50.9(5)	51.0	17.1(1)	17.13
Tm	11.4(1)	11.45	20.4(2)	20.47	50.8(5)	50.95	17.1(1)	17.12
Yb	11.6(1)	11.67	20.3(2)	20.42	50.7(5)	50.83	17.0(1)	17.07
Lu	11.7(1)	11.77	20.3(2)	20.40	50.6(5)	50.77	17.0(1)	17.06

more than 10^{-4} mol/l and $\lambda_{max} = 675$ nm, using concentrated HCl after reduction of U(VI) to U(IV) with metallic zinc for uranium concentration less than 10^{-5} mol/l [25]. The stock solution of uranium(VI) was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in distilled water. REE concentrations in aqueous solutions were determined via a spectrophotometric titration with 10^{-3} mol/l solution of disodium EDTA in the presence of xylenol orange ($\lambda_{max} = 570$ nm, pH 5.5, detection limit is $1 \cdot 10^{-6}$ mol/l) [26]. The equivalence point was determined as the point of intersection of linear sections of spectrophotometric curves.

Calculation

Solubility products calculation

The solubility products were calculated on the basis of solubility data for REE uranyl arsenates in $1 \cdot 10^{-3}$ mol/l $HClO_4$. The following equation represents the heterogeneous reaction:



The equilibrium constant K_{SP} of this reaction is called solubility product and is represented by the following equation:

$$K_{SP}(M^{III}(AsUO_6)_3 \cdot 16H_2O) = a(M^{3+}) \times a(UO_2^{2+})^3 \times a(AsO_4^{3-})^3 \quad (4)$$

To calculate ionic activities for Eq. (4), uranium(VI), arsenic(V) and M(III) were assumed to exist in aqueous solutions as a collection of species, presented in Table 2 [27–29]. The activity coefficients of ions were calculated using Debye–Huckel equation which considered the theory of specific ionic interaction [29]:

$$\lg \gamma_z = -0.5090 z^2 I^{0.5} / [1 + 1.5 I^{0.5}] + \sum \varepsilon_{(z \pm, m, l)} C_m \quad (5)$$

I —ionic strength of an aqueous solution, $\varepsilon_{(z \pm, m, l)}$ —coefficient of ionic interaction of $z \pm$ ion with counterions [29], C_m —molar concentration of ion m .

The values of M^{3+} , UO_2^{2+} , AsO_4^{3-} activity coefficients in $1 \cdot 10^{-3}$ mol/l $HClO_4$ solutions used for the calculations of solubility products are shown in Table 3.

The activity coefficients of molecular species were assumed to be equal to 1.0.

Solubility curves and speciation diagrams calculation

To simulate the behaviour of REE uranyl arsenates in aqueous solutions, the formation of various secondary solids was assumed in studied heterogeneous systems. With that in mind, the following system of equations was devised.

$$K_{SP}(HAsUO_6 \cdot 4H_2O) = a(H^+) \times a(UO_2^{2+}) \times a(AsO_4^{3-}) \quad (6)$$

$$K_{SP}((UO_2)_3(AsO_4)_2 \cdot 12H_2O) = a(UO_2^{2+})^3 \times a(AsO_4^{3-})^2 \quad (7)$$

Table 2 The equilibrium constants of reactions of U(VI), As(V) and M(III) in aqueous solutions [27–29]

Equation	Equilibrium constant	
	Mark	Value
Homogeneous equilibria		
General reaction equation $i\text{UO}_2^{2+} + j\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_i(\text{OH})_j^{(2i-j)} + j\text{H}^+$		
Equilibrium constant K_{ij}		
$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}^+ + \text{H}^+$	K_{11}	5.62×10^{-6}
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2^0 + 2\text{H}^+$	K_{12}	7.08×10^{-13}
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_3^- + 3\text{H}^+$	K_{13}	5.62×10^{-21}
$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$	K_{14}	3.98×10^{-33}
$2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+$	K_{21}	2.00×10^{-3}
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	K_{22}	2.40×10^{-6}
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	K_{35}	2.82×10^{-16}
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	K_{37}	6.31×10^{-33}
$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	K_{47}	1.26×10^{-22}
General reaction equation $\text{AsO}_4^{3-} + \text{hH}^+ \rightleftharpoons \text{H}_h\text{AsO}_4^{h-3}$		
Equilibrium constant K_h		
$\text{AsO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{HAsO}_4^{2-}$	K_1	3.98×10^{11}
$\text{AsO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{AsO}_4^-$	K_2	2.29×10^{18}
$\text{AsO}_4^{3-} + 3\text{H}^+ \rightleftharpoons \text{H}_3\text{AsO}_4^0$	K_3	3.98×10^{20}
General reaction equation $\text{UO}_2^{2+} + \text{mAsO}_4^{3-} + \text{mhH}^+ \rightleftharpoons \text{UO}_2(\text{H}_h\text{AsO}_4)_m^{(h-3)m+2}$		
Equilibrium constant k_{hm}		
$\text{UO}_2^{2+} + \text{AsO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{UO}_2\text{HAsO}_4^0$	k_{11}	5.78×10^{18}
$\text{UO}_2^{2+} + \text{AsO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{UO}_2\text{H}_2\text{AsO}_4^+$	k_{21}	9.12×10^{21}
$\text{UO}_2^{2+} + 2\text{AsO}_4^{3-} + 4\text{H}^+ \rightleftharpoons \text{UO}_2(\text{H}_2\text{AsO}_4)_2^0$	k_{22}	3.40×10^{41}
General reaction equation $\text{M}^{3+} + j\text{H}_2\text{O} \rightleftharpoons \text{M}^{\text{III}}(\text{OH})_j^{(3-j)} + j\text{H}^+$		
Equilibrium constant K_{Mj}		
$\text{La}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{LaOH}^{2+} + \text{H}^+$	K_{M1}	2.53×10^{-10}
$\text{La}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{La}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Ce}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{CeOH}^{2+} + \text{H}^+$	K_{M1}	3.53×10^{-10}
$\text{Ce}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ce}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Pr}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{PrOH}^{2+} + \text{H}^+$	K_{M1}	7.54×10^{-10}
$\text{Pr}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Pr}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Nd}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{NdOH}^{2+} + \text{H}^+$	K_{M1}	9.66×10^{-10}
$\text{Nd}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Nd}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Sm}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{SmOH}^{2+} + \text{H}^+$	K_{M1}	1.24×10^{-9}
$\text{Sm}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Sm}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{EuOH}^{2+} + \text{H}^+$	K_{M1}	1.39×10^{-9}
$\text{Eu}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Gd}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{GdOH}^{2+} + \text{H}^+$	K_{M1}	1.16×10^{-9}
$\text{Gd}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Gd}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Tb}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{TbOH}^{2+} + \text{H}^+$	K_{M1}	1.80×10^{-9}
$\text{Tb}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Tb}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Dy}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{DyOH}^{2+} + \text{H}^+$	K_{M1}	2.09×10^{-9}
$\text{Dy}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Dy}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Ho}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{HoOH}^{2+} + \text{H}^+$	K_{M1}	2.40×10^{-9}
$\text{Ho}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ho}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Er}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{ErOH}^{2+} + \text{H}^+$	K_{M1}	2.50×10^{-9}
$\text{Er}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Er}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Tm}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{TmOH}^{2+} + \text{H}^+$	K_{M1}	2.98×10^{-9}
$\text{Tm}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Tm}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}
$\text{Yb}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{YbOH}^{2+} + \text{H}^+$	K_{M1}	2.65×10^{-9}
$\text{Yb}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Yb}(\text{OH})_3^0 + 3\text{H}^+$	K_{M3}	1.11×10^{-42}

Table 2 (continued)

Equation	Equilibrium constant	
	Mark	Value
Heterogeneous equilibria		
Equilibrium constant K_{SP}		
$(\text{UO}_2)_3(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}_{(s)} \rightleftharpoons 3\text{UO}_2^{2+} + 2\text{AsO}_4^{3-} + 12\text{H}_2\text{O}$		4.77×10^{-46}
$\text{UO}_3 \cdot 2.25\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{UO}_2^{2+} + 2\text{OH}^- + 1.25\text{H}_2\text{O}$		1.91×10^{-22}
$\text{Na}_2\text{U}_2\text{O}_7_{(s)} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Na}^+ + 2\text{UO}_2^{2+} + 6\text{OH}^-$		1.26×10^{-59}
$\text{La}(\text{OH})_{3(s)} \rightleftharpoons \text{La}^{3+} + 3\text{OH}^-$		1.40×10^{-23}
$\text{Ce}(\text{OH})_{3(s)} \rightleftharpoons \text{Ce}^{3+} + 3\text{OH}^-$		4.00×10^{-25}
$\text{Pr}(\text{OH})_{3(s)} \rightleftharpoons \text{Pr}^{3+} + 3\text{OH}^-$		2.93×10^{-24}
$\text{Nd}(\text{OH})_{3(s)} \rightleftharpoons \text{Nd}^{3+} + 3\text{OH}^-$		1.81×10^{-19}
$\text{Sm}(\text{OH})_{3(s)} \rightleftharpoons \text{Sm}^{3+} + 3\text{OH}^-$		7.46×10^{-25}
$\text{Eu}(\text{OH})_{3(s)} \rightleftharpoons \text{Eu}^{3+} + 3\text{OH}^-$		2.60×10^{-27}
$\text{Gd}(\text{OH})_{3(s)} \rightleftharpoons \text{Gd}^{3+} + 3\text{OH}^-$		1.19×10^{-27}
$\text{Tb}(\text{OH})_{3(s)} \rightleftharpoons \text{Tb}^{3+} + 3\text{OH}^-$		4.30×10^{-27}
$\text{Dy}(\text{OH})_{3(s)} \rightleftharpoons \text{Dy}^{3+} + 3\text{OH}^-$		1.11×10^{-26}
$\text{Ho}(\text{OH})_{3(s)} \rightleftharpoons \text{Ho}^{3+} + 3\text{OH}^-$		2.38×10^{-27}
$\text{Er}(\text{OH})_{3(s)} \rightleftharpoons \text{Er}^{3+} + 3\text{OH}^-$		2.39×10^{-27}
$\text{Tm}(\text{OH})_{3(s)} \rightleftharpoons \text{Tm}^{3+} + 3\text{OH}^-$		2.39×10^{-27}
$\text{Yb}(\text{OH})_{3(s)} \rightleftharpoons \text{Yb}^{3+} + 3\text{OH}^-$		1.92×10^{-27}
$\text{Lu}(\text{OH})_{3(s)} \rightleftharpoons \text{Lu}^{3+} + 3\text{OH}^-$		9.69×10^{-28}

$$K_{SP}(\text{UO}_3 \cdot 2.25\text{H}_2\text{O}) = a(\text{UO}_2^{2+}) \times a(\text{OH}^-)^2 = a(\text{UO}_2^{2+}) \times K_W^2 \times a(\text{H}^+)^{-2} \quad (8)$$

$$K_{SP}(\text{Na}_2\text{U}_2\text{O}_7) = a(\text{Na}^+)^2 \times a(\text{UO}_2^{2+})^2 \times a(\text{OH}^-)^6 = a(\text{M}^+)^2 \times a(\text{UO}_2^{2+})^2 \times K_W^6 \times a(\text{H}^+)^{-6} \quad (9)$$

$$K_{SP}(\text{M}^{\text{III}}(\text{OH})_3) = a(\text{M}^{3+}) \times a(\text{OH}^-)^3 = a(\text{M}^{3+}) \times K_W^3 \times a(\text{H}^+)^{-3} \quad (10)$$

$$C_U = a(\text{UO}_2^{2+})/\gamma_2 + \sum I \times K_{ij} \times a(\text{UO}_2^{2+})^i \times a(\text{H}^+)^{-j}/\gamma_{(2i-j)\pm} + \sum k_{hm} \times a(\text{UO}_2^{2+}) \times a(\text{AsO}_4^{3-})^m \times a(\text{H}^+)^{mh}/\gamma_{[(h-3)m+2]} \quad (11)$$

$$C_{As} = a(\text{AsO}_4^{3-})/\gamma_3 + SK_h \times a(\text{AsO}_4^{3-}) \times a(\text{H}^+)^h/\gamma_{(h-3)\pm} + \sum m \times k_{hm} \times a(\text{UO}_2^{2+}) \times a(\text{AsO}_4^{3-})^m \times a(\text{H}^+)^{mh}/\gamma_{[(h-3)m+2]} \quad (12)$$

$$C_M = a(\text{M}^{3+})/\gamma_3 + K_{Mj} \times a(\text{M}^+)/a(\text{H}^+)^j/\gamma_{(3-j)\pm} \quad (13)$$

$$3 \cdot m^0(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \times 16\text{H}_2\text{O})/M(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \times 16\text{H}_2\text{O}) = C_U V + \sum m_L \omega_{U,L}/M(U) \quad (14)$$

$$3 \cdot m^0(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \times 16\text{H}_2\text{O})/M(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \times 16\text{H}_2\text{O}) = C_{As} V + \sum m_L \omega_{As,L}/M(As) \quad (15)$$

$$m^0(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \times 16\text{H}_2\text{O})/M(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \times 16\text{H}_2\text{O}) = C_M V + \sum m_L \omega_{M,L}/M(M) \quad (16)$$

$m^0(\text{M}^{\text{III}}(\text{AsUO}_6)_3 \cdot 16\text{H}_2\text{O})$ —the mass of the primary REE uranyl arsenate phase; V—the volume of the primary solution of HClO_4 , NaOH or water; M—molar mass; m_L —the mass of the forming solid phase component; L— $\text{M}^{\text{III}}(\text{AsUO}_6)_3 \cdot 16\text{H}_2\text{O}$, $\text{HAsUO}_6 \cdot 4\text{H}_2\text{O}$, $(\text{UO}_2)_3(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{UO}_3 \cdot 2.25\text{H}_2\text{O}$, $\text{M}^{\text{III}}(\text{OH})_3$, $\text{Na}_2\text{U}_2\text{O}_7$;

Table 3 The ions activity coefficients in $1 \cdot 10^{-3}$ mol/l HClO_4 solutions

M(III)	activity coefficient		
	M^{3+}	UO_2^{2+}	AsO_4^{3-}
La	0.754	0.883	0.754
Ce	0.772	0.892	0.772
Pr	0.766	0.889	0.766
Nd	0.769	0.891	0.769
Sm	0.771	0.892	0.771
Eu	0.768	0.890	0.768
Gd	0.768	0.890	0.768
Tb	0.767	0.890	0.767
Dy	0.764	0.888	0.764
Ho	0.760	0.886	0.760
Er	0.756	0.884	0.756
Tm	0.756	0.884	0.756
Yb	0.752	0.882	0.752
Lu	0.746	0.879	0.746

$\omega_{As,L}$, $\omega_{U,L}$, $\omega_{M,L}$ —the mass fraction of arsenic(V), uranium(VI) and REE(III) in L; K_w —ionic product of water.

The system of combined Eqs. (4, 6–16) allows us to simulate not only the existence of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ in the solid phase, but also the formation of several known secondary solids, such as $HAsUO_6 \cdot 4H_2O$, $((UO_2)_3(AsO_4)_2 \cdot 12H_2O)$, $UO_3 \cdot 2.25H_2O$, $M^{III}(OH)_3$, $Na_2U_2O_7$ and a few others. In the system above, Eqs. (4, 6–10) denote the equilibrium constants for heterogeneous reactions between primary and secondary compounds in the solid phase and equilibrium solutions. Equations (11–13) consider homogeneous equilibria between different species of uranium(VI), arsenic(V) and REE(III) in aqueous solutions, and Eqs. (14–16) correspond to the total amounts of U(VI), As(V) and M(III) in the solid phase and solution. Overall, the proposed system of Eqs. (4, 6–16) allows us to simulate and predict different parameters of studied heterogeneous systems « $M^{III}(AsUO_6)_3 \cdot 16H_2O_{(cr)}$ —aqueous solution» in a wide interval of solution acidity. Thus, ionic activities $a(UO_2^{2+})$, $a(AsO_4^{3-})$, $a(M^{3+})$, total concentrations C_U , C_{As} , C_M , primary and secondary solids mass $m(M^{III}(AsUO_6)_3 \cdot 16H_2O)$, $m(HAsUO_6 \cdot 4H_2O)$, $m((UO_2)_3(AsO_4)_2 \cdot 12H_2O)$, $m(UO_3 \cdot 2.25H_2O)$, $m(M^{III}(OH)_3)$, $m(Na_2U_2O_7)$ were calculated based on set equilibrium pH values, the initial volume V and the mass of primary REE uranyl arsenate in the solid phase. The secondary solids mass were used to plot speciation diagrams and determine pH ranges of the existence of the solid phase components. Calculated concentrations were used to plot solubility curves. Ionic activities were used to calculate speciation diagrams of U(VI), As(V), M(III) in saturated aqueous solutions.

The calculation of Gibbs energies of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ formation

Obtained solubility product values were used to calculate standard Gibbs free energies of formation of studied compounds. The following equations were used:

$$\Delta G_r(298) = -RT \ln K_{SP}, \quad (17)$$

$$\Delta G_f(M^{III}(AsUO_6)_3 \times 16H_2O) = \Delta G_f(M^{3+}) + 3\Delta G_f(UO_2^{2+}) + 3\Delta G_f(AsO_4^{3-}) + 16\Delta G_f(H_2O) - \Delta G_r(298). \quad (18)$$

ΔG_f —Gibbs energy (298 K) of formation of ions or molecules [27–29]; $\Delta G_r(298)$ —Gibbs energy (298 K) of reaction (3).

Calculated ΔG_f of REE uranyl arsenates and known ΔG_f of secondary compounds [27–29] were used for thermodynamic evaluation of the possibility of transformation

Table 4 pH ranges of REE uranyl arsenates $M^{III}(AsUO_6)_3 \cdot 16H_2O$ existence in saturated aqueous solutions

Compound	pH range	
	boundary	width
La(AsUO ₆) ₃ ·16H ₂ O	1.8–9.2	7.4
Ce(AsUO ₆) ₃ ·16H ₂ O	1.8–8.8	7.0
Pr(AsUO ₆) ₃ ·16H ₂ O	1.8–9.0	7.2
Nd(AsUO ₆) ₃ ·16H ₂ O	1.8–9.0	7.2
Sm(AsUO ₆) ₃ ·16H ₂ O	2.0–8.6	6.6
Eu(AsUO ₆) ₃ ·16H ₂ O	2.0–8.4	6.4
Gd(AsUO ₆) ₃ ·16H ₂ O	2.0–9.0	7.0
Tb(AsUO ₆) ₃ ·16H ₂ O	1.8–8.6	6.8
Dy(AsUO ₆) ₃ ·16H ₂ O	1.8–8.6	6.8
Ho(AsUO ₆) ₃ ·16H ₂ O	1.8–8.6	6.8
Er(AsUO ₆) ₃ ·16H ₂ O	1.8–8.6	6.8
Tm(AsUO ₆) ₃ ·16H ₂ O	1.8–8.6	6.8
Yb(AsUO ₆) ₃ ·16H ₂ O	1.8–8.6	6.8
Lu(AsUO ₆) ₃ ·16H ₂ O	1.8–8.9	7.1

reactions in studied heterogeneous aqueous-salt systems at 298 K. The following equation was used for the calculation:

$$\Delta G_r(298) = \sum q \Delta G_f(\text{products}) - \sum r \Delta G_f(\text{reagents}) \quad (19)$$

q and r —stoichiometric numbers.

Equipment and reagents

Diffraction patterns were recorded with a Shimadzu XRD-6000 diffractometer at the $CuK\alpha$ line. The elemental composition of the samples was determined using Shimadzu EDX-900 HS energy dispersive X-ray fluorescence spectrometer. The spectrophotometric measurements were performed using Shimadzu UV-1650 spectrophotometer. Scattered radiation intensity was measured using NPM (Russia) nephelometer. The solid phases and saturated solutions were separated using CLN-2 centrifuge (Russia) at 10,000 rpm. The pH values were measured with a pH-meter pH-410 Aquilon

and a glass electrode (ESK-10601/7). Distilled water free of CO_2 was used in all experiments [26, 27]. The sodium hydroxide solutions free of CO_2 were prepared as described in [27]. All reagents were of the “chemically pure” grade. Mathematical simulation of the heterogeneous system and the prediction of its state were performed using Mathcad 8.0.

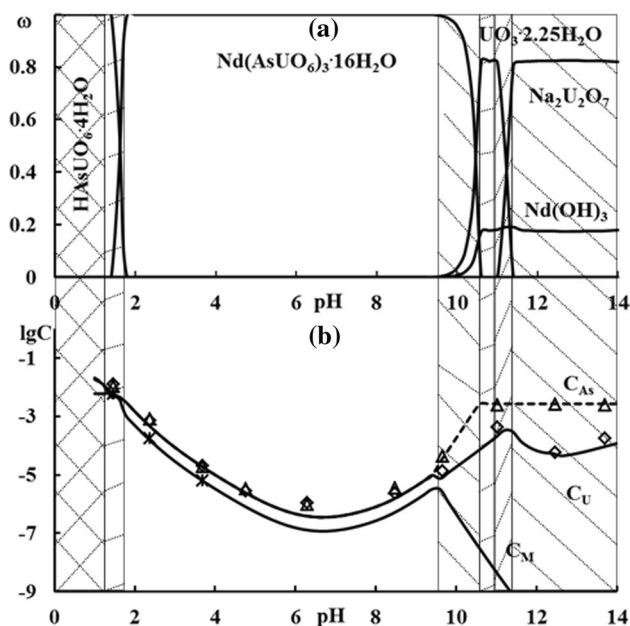


Fig. 1 State of heterogeneous systems «Nd(AsUO₆)₃·16H₂O_(cr)—aqueous solution». Lines represent calculated curves, dots represent experimental data. **a** The dependence of solid phase components' mass fraction ω on the acidity; **b** the U(VI) (◇), As(V) (Δ) and M(III) (*) concentration dependence on the acidity.

Results and discussion

Acid–base ranges of REE uranyl arsenates existence and transformation of $\text{M}^{\text{III}}(\text{AsUO}_6)_3 \cdot 16\text{H}_2\text{O}$ (M^{III} —La–Lu) into other compounds

The behaviour of all REE uranyl arsenates in aqueous solutions obeys a general pattern. The acidity of the medium has the biggest impact on the state of studied heterogeneous aqueous-salt systems. The pH value of the equilibrium solution largely determines the composition and structure of solid compounds, solubility of uranyl arsenates and their transformation products, the dominant species of uranium(VI), arsenic(V) and REE in aqueous solution. Uranyl arsenates retain their composition and structure upon contact with solutions in a certain acidity range from pH of 1.8–2.0 to pH of 8.4–9.8 (Table 4). The width of this acid–base range changes slightly in the series of REE uranyl arsenates due to the analogous structure of the studied compounds and similar properties of interlayer atoms M^{III} .

Solid-phase speciation diagrams for all REE uranyl arsenates in equilibrium heterogeneous systems are almost identical. The dependence of the mass fraction of solid compounds on pH values for neodymium uranyl arsenate is presented in Fig. 1 as an example. Shaded regions denote the formation of various secondary compounds in the solid phase. The acidity range of studied uranyl arsenate existence, presented in Table 2, is the range of pH in which the

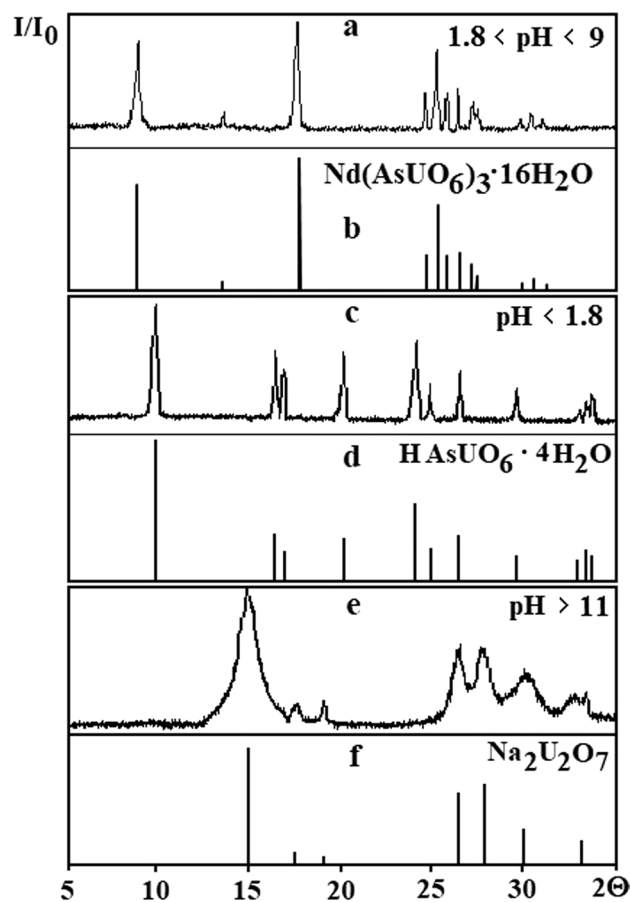
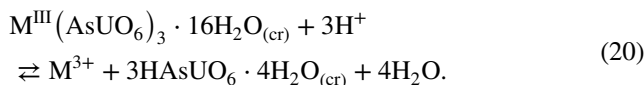


Fig. 2 X-ray patterns of the solids in the system «Nd(AsUO₆)₃·16H₂O_(cr)—aqueous solution» at different pH values (a, c, e present the experimental data; b, d, f—literary data) [4, 14, 43]

solid phase contains more than 97%_w of crystalline compound $\text{M}^{\text{III}}(\text{AsUO}_6)_3 \cdot 16\text{H}_2\text{O}$. This is confirmed by powder diffraction analysis of equilibrium solid phases (Fig. 2a, b).

Outside the given existence pH ranges the structure of REE uranyl arsenates in aqueous solutions deteriorates. The nature of transformation products is also determined by the acidity. Solid-phase REE uranyl arsenates transform into uranyl arsenic acid in acidic medium:



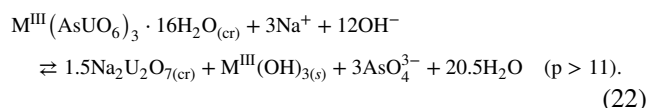
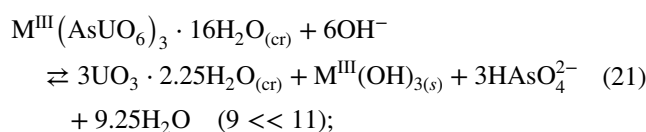
This transformation causes changes in solid-phase diffraction patterns—the reflections of corresponding REE uranyl arsenates are replaced by the reflections of crystalline $\text{HAsUO}_6 \cdot 4\text{H}_2\text{O}$ (Fig. 2 (c, d)). Intensive band $\delta(\text{H}_3\text{O}^+)$ at 1737 cm^{-1} in IR-spectra of solids convincingly indicates the formation of $\text{HAsUO}_6 \cdot 4\text{H}_2\text{O}$. X-ray fluorescent analysis confirms the lack of rare-earth elements in precipitate under these conditions. Described transformation is facilitated by

both analogous layered structure of studied compounds $M^{III}(AsUO_6)_3 \cdot 16H_2O$ and forming acid $HAsUO_6 \cdot 4H_2O$ and a large concentration of hydrogen ions in the aqueous solution. In terms of equilibrium thermodynamics, the ion-exchange reaction between the solid phase and the solution (20) is spontaneous and can happen in studied systems under standard conditions, which is proven by negative values of standard Gibbs free energies of these reactions for all compounds from $M^{III}(AsUO_6)_3 \cdot 16H_2O$ series. The values of standard Gibbs free energies of the transformation reaction are presented in Table 5.

REE uranyl arsenates are less stable in alkaline solutions than reported earlier [18] alkaline elements derivatives. Their structure starts deteriorating at pH values large than 8–9 and new solid phases, that are rich with uranium and M^{III} element, begin to form. In all likelihood, it is caused by a greater hydrolysis affinity of rare earth element ions, which leads to the formation of stable hydroxy-complexes in aqueous solutions and their precipitation in the form of insoluble compounds. The low crystallinity of the solid-phase transformation products at pH 9–11 and the limited information on uranium compounds with REE in the literature [32–35] do not allow their reliable identification. Thermodynamic simulation shows that the formation of uranyl oxide hydrate phases is possible in this pH range such as $UO_3 \cdot 2.25H_2O$ (schoepite), its dehydrated forms and products of interaction with REE [36–43]. The formation of largely crystalline $Na_2U_2O_7$ and REE hydroxides with various degree of crystallinity $M^{III}(OH)_3$ occurs for all REE uranyl arsenates in highly alkaline media with $C(NaOH) > 0.1 \text{ mol/l}$ (Fig. 2e, f) [44]. The transformation process of REE uranyl arsenates can be presented as the following equations in accordance with obtained data:

Table 5 Gibbs energies of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu) transformation into corresponding products ($T=298 \text{ K}$)

Compound	$\Delta_r G(298), \text{ kJ/mol}$		
	(20)	(21)	(22)
La($AsUO_6$) ₃ ·16H ₂ O	–11.415(9)	–39.34(1)	–176.00(1)
Ce($AsUO_6$) ₃ ·16H ₂ O	–10.274(9)	–101.82(1)	–238.4(1)
Pr($AsUO_6$) ₃ ·16H ₂ O	–9.703(9)	–96.31(1)	–232.97(1)
Nd($AsUO_6$) ₃ ·16H ₂ O	–9.703(9)	–68.97(1)	–205.63(1)
Sm($AsUO_6$) ₃ ·16H ₂ O	–9.70(1)	–99.70(1)	–236.36(1)
Eu($AsUO_6$) ₃ ·16H ₂ O	–10.84(1)	–114.87(1)	–251.53(1)
Gd($AsUO_6$) ₃ ·16H ₂ O	–12.557(8)	–118.52(1)	–255.18(1)
Tb($AsUO_6$) ₃ ·16H ₂ O	–10.845(9)	–113.62(1)	–250.28(1)
Dy($AsUO_6$) ₃ ·16H ₂ O	–9.70(2)	–65.32(1)	–201.98(1)
Ho($AsUO_6$) ₃ ·16H ₂ O	–9.132(9)	–113.38(1)	–250.04(1)
Er($AsUO_6$) ₃ ·16H ₂ O	–8.562(9)	–112.79(1)	–249.45(1)
Tm($AsUO_6$) ₃ ·16H ₂ O	–7.991(9)	–112.23(1)	–248.89(1)
Yb($AsUO_6$) ₃ ·16H ₂ O	–7.99(1)	–112.77(1)	–249.43(1)
Lu($AsUO_6$) ₃ ·16H ₂ O	–8.56(2)	–115.03(1)	–251.69(1)



Spontaneousness of these reactions in heterogeneous aqueous-salt systems for studied REE uranyl arsenates is also confirmed by the thermodynamic calculations. Table 5 demonstrates that the Gibbs energies of the transformation of all studied REE compounds are sufficiently large negative values at the temperature 298 K.

Solubility of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu) compounds in aqueous solutions

Concentrations of uranium(VI) C_U , arsenic(V) C_{As} and rare-earth elements C_M in saturated aqueous solutions of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ are presented in Table 6. The analysis of presented data leads to the conclusion that the aqueous solution acidity has the most influence of the concentration of uranium(VI) and other structure-forming elements in heterogeneous aqueous-salt systems of studied compounds. Not only the absolute values of C_U , C_{As} and C_M change depending on the pH, but their ratio changes as well, which correlates well with supposed uranyl arsenates transformation process. In the wide range of pH values from 1.8–2.0 to 8.4–9.8, wherein studied compounds retain their structure, uranium and arsenic concentrations are equal within the experimental error margins. Under the same conditions, rare earth element concentration is approximately three times smaller than C_U and C_{As} . These ratios are consistent with stoichiometry of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ compounds and are evidence of congruent dissolution of uranyl arsenates and, consequently, an equivalent transition of uranium(VI), arsenic(V) and M(III) into the solution. In acidic medium, wherein the transformation of the studied compound into uranyl arsenic acid takes place, hydrogen ions fully replace M^{III} in the solid phase and C_M becomes constant. Under these conditions, uranium(VI) and arsenic(V) concentrations are the same and are determined by the solubility of the forming $HAsUO_6 \cdot 4H_2O$. In the alkaline media determined C_U and C_{As} differ by a factor of 10 and more, which is explained by the deterioration of uranyl arsenates structure and the formation of secondary solids, rich in uranium and rare earth element. The solubility of these solids determines the concentrations of U(VI) and M(III) in the solution in that case. Arsenic(V) is not retained in the solid phase under these conditions and is leached into the solution. All described patterns are similar to the ones exhibited

Table 6 U(VI), As(V) and M(III) concentrations (mol/l) in the saturated aqueous solutions of $M^{III}(As_2O_6)_3 \cdot 16H_2O$ compounds (25 °C)

solAsent	Data	M^{III}													
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1×10^{-1} M HClO ₄	pH	1.32	1.41	1.44	1.47	1.45	1.43	1.38	1.40	1.28	1.32	1.25	1.23	1.20	1.22
	$C_U \times 10^2$	1.15(2)	1.32(2)	1.35(2)	1.29(2)	1.38(2)	1.41(2)	1.12(2)	1.17(2)	1.35(2)	1.25(2)	1.07(2)	1.17(2)	1.29(2)	1.58(2)
	$C_{As} \times 10^2$	1.05(2)	1.15(2)	1.12(2)	1.07(2)	1.35(2)	1.55(2)	1.02(2)	1.05(2)	1.20(2)	1.29(2)	1.45(2)	1.38(2)	1.45(2)	1.45(2)
	$C_M \times 10^2$	0.59(2)	0.60(2)	0.58(1)	0.61(2)	0.58(2)	0.59(2)	0.58(2)	0.59(2)	0.59(2)	0.60(2)	0.61(2)	0.58(2)	0.58(2)	0.62(2)
1×10^{-2} M HClO ₄	pH	2.20	2.18	2.20	2.37	2.32	2.01	2.15	2.08	2.03	2.05	2.10	2.04	2.05	2.01
	$C_U \times 10^3$	1.10(3)	1.45(3)	1.15(3)	0.74(3)	1.07(3)	1.55(3)	1.82(5)	1.78(5)	1.91(5)	1.29(3)	1.41(3)	1.78(4)	1.29(3)	1.29(3)
	$C_{As} \times 10^3$	1.45(2)	0.85(4)	0.89(4)	0.85(4)	0.85(4)	1.32(2)	1.38(3)	1.35(3)	2.14(7)	1.05(2)	1.10(2)	1.48(3)	1.17(2)	1.51(3)
	$C_M \times 10^3$	0.32(1)	0.35(1)	0.22(1)	0.182(7)	0.22(1)	0.46(2)	0.41(1)	0.41(1)	0.43(2)	0.35(2)	0.32(2)	0.48(2)	0.36(2)	0.42(2)
1×10^{-3} M HClO ₄	pH	3.47	3.74	3.63	3.68	3.71	3.68	3.68	3.66	3.59	3.51	3.46	3.45	3.42	3.35
	$C_U \times 10^5$	3.31(9)	1.75(8)	2.29(9)	2.08(8)	1.94(8)	2.27(8)	2.29(9)	2.37(8)	2.24(8)	2.62(9)	3.19(8)	2.89(8)	3.09(9)	3.53(9)
	$C_{As} \times 10^5$	3.47(9)	1.86(9)	2.09(8)	1.94(9)	1.81(8)	2.08(9)	2.63(9)	2.12(9)	2.53(9)	2.85(9)	2.95(9)	3.03(9)	3.14(9)	3.72(9)
	$C_M \times 10^5$	1.2(1)	0.61(6)	0.72(6)	0.64(6)	0.56(5)	0.66(6)	0.66(6)	0.70(6)	0.71(6)	0.76(7)	0.66(6)	0.89(7)	1.01(4)	1.23(4)
1×10^{-4} M HClO ₄	pH	5.10	4.87	4.71	4.75	4.82	4.96	4.97	4.86	4.75	4.77	4.82	4.69	4.79	4.85
	$C_U \times 10^6$	2.8(2)	3.0(2)	2.9(2)	2.9(2)	2.3(2)	2.9(2)	2.6(2)	3.3(2)	3.4(2)	3.7(2)	3.6(2)	3.9(2)	2.5(2)	2.5(2)
	$C_{As} \times 10^6$	3.3(2)	3.5(2)	3.5(2)	3.5(2)	2.8(2)	2.3(2)	2.8(2)	2.9(2)	4.6(4)	4.3(3)	3.1(2)	4.0(3)	3.0(2)	2.8(2)
	$C_M \times 10^6$	6.36	6.21	6.25	6.28	6.23	6.32	6.36	6.38	6.40	6.40	6.50	6.35	6.56	6.63
1×10^{-4} M NaOH	$C_U \times 10^7$	11(1)	8.3(8)	7.8(8)	11.0(8)	7.8(8)	7.8(8)	9.1(8)	7.8(8)	8.7(8)	7.8(8)	7.8(8)	5.9(6)	5.9(6)	5.9(6)
	$C_{As} \times 10^7$	17(1)	9.1(9)	9.3(9)	9.8(8)	9.4(9)	7.6(8)	9.8(9)	10(1)	12(1)	17(1)	11(1)	6.8(7)	8.7(7)	7.1(7)
	pH	7.69	7.76	7.79	8.47	7.75	7.95	8.20	7.97	8.00	8.08	8.14	8.03	8.23	8.48
	$C_U \times 10^6$	1.5(2)	1.4(1)	1.4(1)	2.4(2)	1.3(1)	1.5(1)	1.6(1)	1.3(1)	2.0(1)	1.3(1)	1.1(1)	1.3(1)	1.5(1)	1.8(1)
1×10^{-3} M NaOH	$C_{As} \times 10^6$	2.1(2)	1.8(2)	2.0(2)	3.6(2)	2.3(2)	1.5(2)	9.6(6)	5.0(3)	2.9(2)	7.9(4)	7.6(4)	5.0(3)	5.9(3)	8.9(5)
	pH	9.07	9.10	9.30	9.66	9.40	9.45	9.55	9.59	9.62	9.74	9.78	9.74	9.77	9.82
	$C_U \times 10^5$	0.51(3)	0.47(3)	0.77(3)	1.35(6)	1.58(6)	1.62(6)	1.35(6)	1.91(9)	4.1(2)	3.0(1)	2.9(1)	2.1(1)	2.4(1)	3.4(2)
	$C_{As} \times 10^5$	2.5(1)	7.1(3)	13.8(6)	4.4(2)	11.5(6)	15.8(6)	3.0(1)	28(1)	6.2(3)	27(1)	20(1)	37(2)	56(3)	51(3)
1×10^{-2} M NaOH	pH	10.80	10.18	11.18	11.01	11.10	11.28	11.29	11.39	11.41	11.31	11.25	11.28	11.26	11.31
	$C_U \times 10^4$	0.53(2)	5.6(2)	6.5(2)	4.4(2)	6.5(3)	3.9(2)	6.9(3)	5.5(2)	4.4(2)	2.5(1)	3.2(1)	3.6(1)	3.6(1)	3.8(1)
	$C_{As} \times 10^3$	2.6(1)	2.5(1)	2.7(1)	2.5(1)	2.5(7)	2.6(1)	2.5(1)	2.58(9)	2.54(9)	2.6(1)	2.5(1)	2.6(1)	2.7(1)	2.6(1)
	pH	12.02	12.35	12.39	12.46	12.35	12.42	12.59	12.72	12.72	12.68	12.63	12.80	12.70	12.78
1×10^{-1} M NaOH	$C_U \times 10^5$	3.7(1)	3.1(1)	5.9(3)	5.9(3)	6.6(3)	3.7(1)	6.3(3)	5.0(2)	6.3(3)	9.3(4)	9.3(4)	9.3(4)	9.3(4)	8.7(4)
	$C_{As} \times 10^3$	2.52(9)	2.65(8)	2.55(9)	2.6(1)	2.51(8)	2.6(1)	2.5(1)	2.52(8)	2.6(1)	2.7(1)	2.5(1)	2.6(1)	2.6(1)	2.5(1)
	pH	13.64	13.70	13.68	13.70	13.73	13.80	13.79	13.80	13.82	13.84	13.77	13.73	13.77	13.74
	$C_U \times 10^4$	2.6(1)	1.86(8)	1.95(8)	1.86(7)	1.87(6)	1.86(7)	1.86(7)	1.89(7)	3.0(1)	3.0(1)	2.3(1)	2.0(1)	2.0(1)	2.1(1)
1×10^{-3} M NaOH	$C_{As} \times 10^3$	2.6(1)	2.5(9)	2.6(1)	2.5(1)	2.58(9)	2.6(1)	2.6(1)	2.56(8)	2.6(1)	2.7(1)	2.6(1)	2.7(1)	2.6(1)	2.7(1)

by alkaline elements uranyl arsenates and consistent with theoretical assumptions about the composition and structure of $M^k(AsUO_6)_k \cdot nH_2O$ compounds [18].

The REE uranyl arsenates solubility can only be discussed in the range of pH values from 1.8–2.0 to 8.4–9.8, wherein the compounds retain their composition and structure. Solubility of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ compounds is related to concentrations of structure-forming elements in saturated aqueous solutions by the following ratio $S = C_M = C_U / 3 = C_{As} / 3$. The dependence of uranyl arsenates solubility on pH in the range of their chemical stability is parabolic with the minimum in the neutral solutions, wherein S is equal to 10^{-7} – 10^{-6} mol/l (Fig. 2). The concentration of various species in saturated solutions increases correspondingly with increases in acidity or alkalinity and reaches 10^{-4} – 10^{-2} mol/l at the boundaries of the pH range of existence. At the same pH values, the solubility changes very little depending on the interlayer atom and varies in the range $(1.1$ – $1.5) \cdot 10^{-7}$ mol/l at pH 7.

Solubility products of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu)

Solubility products of studied uranyl arsenates were calculated using experimental data on the solubility of the compounds and the results are presented in Table 7.

General structural likeness of REE uranyl arsenates and similarity in properties of rare-earth elements explain the insignificant influence of the nature of interlayer element on solubility and chemical resistance of all $M^{III}(AsUO_6)_3 \cdot 16H_2O$ compounds.

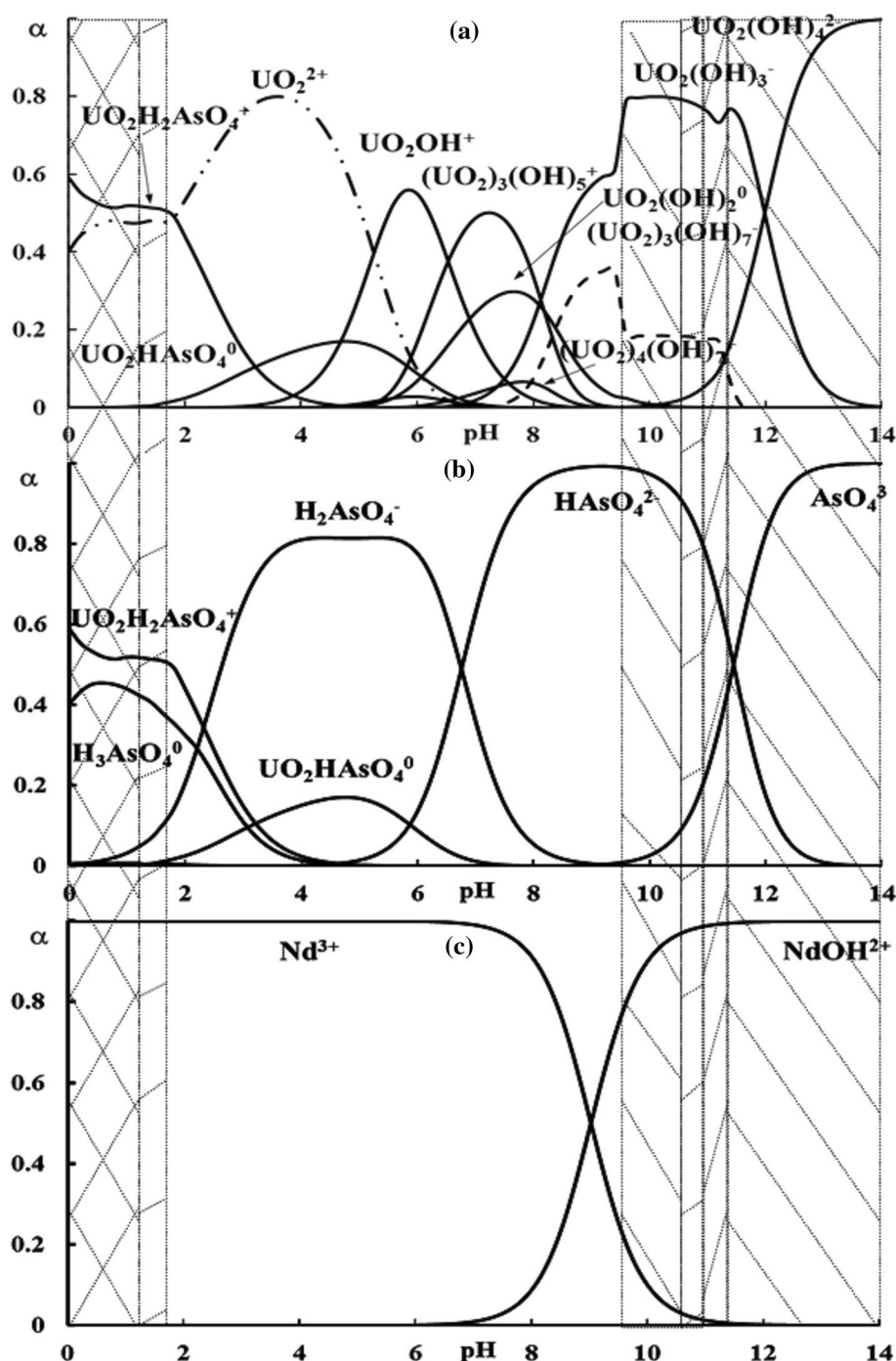
Ionic-molecular composition of saturated aqueous solutions in the system « $M^{III}(AsUO_6)_3 \cdot 16H_2O_{(cr)}$ –aqueous solution»

Ionic-molecular composition of saturated aqueous solutions of studied uranyl arsenate systems correlates well with processes of transformation and dissolution of crystalline compounds. Heterogeneous reactions in the system « $M^{III}(AsUO_6)_3 \cdot 16H_2O_{(cr)}$ –aqueous solution» are a consequence of complex ionic-molecular interactions between various species of uranium(VI), arsenic(V) and rare earth element M(III) in liquid phase. Those reactions cause the deterioration of the structure of studied uranyl arsenates, their transformation into compounds with different composition and structure, and changes in solubility of uranium compounds. Thus, to gain insight into the dissolution process, composition of aqueous solutions in the studied heterogeneous systems is closely examined. Speciation diagrams for uranium(VI), arsenic(V) and rare earth element in saturated solutions of $Nd(AsUO_6)_3 \cdot 16H_2O_{(cr)}$ as an example are presented in Fig. 3. They facilitate the evaluation of the state of structure-forming elements in aqueous solutions, the fraction of different dominant species at different pH values and their influence on general state of the heterogeneous system and indicate a rather complex composition of saturated aqueous solutions of uranyl arsenates. Cationic species of rare-earth elements M^{3+} and uranium(VI) with arsenic(V) $UO_2H_2AsO_4^+$ and are dominant in the solution in acidic media. The latter, in all likelihood, facilitates the formation of $HAsUO_6 \cdot 4H_2O$ acid. High chemical resistance of uranyl arsenic layer allows for the preservation of anionic layer $[AsUO_6]_{\infty}^{6-}$ and the existence of solid with given composition despite highly acidic medium usually causing the

Table 7 Solubility products of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} –La–Lu) compounds and standard Gibbs free energies

Compound	$-lgK_{SP}$	$\Delta_r G(298)$, kJ/mol	$-\Delta_f G(298)$, kJ/mol
La($AsUO_6$) ₃ ·16H ₂ O	67.0 ± 0.5	382 ± 12	9662 ± 55
Ce($AsUO_6$) ₃ ·16H ₂ O	67.2 ± 0.5	384 ± 12	9656 ± 55
Pr($AsUO_6$) ₃ ·16H ₂ O	67.3 ± 0.5	384 ± 12	9659 ± 55
Nd($AsUO_6$) ₃ ·16H ₂ O	67.3 ± 0.5	384 ± 12	9651 ± 55
Sm($AsUO_6$) ₃ ·16H ₂ O	67.3 ± 0.5	384 ± 12	9642 ± 55
Eu($AsUO_6$) ₃ ·16H ₂ O	67.1 ± 0.5	383 ± 12	9658 ± 55
Gd($AsUO_6$) ₃ ·16H ₂ O	66.8 ± 0.5	381 ± 12	9538 ± 55
Tb($AsUO_6$) ₃ ·16H ₂ O	67.1 ± 0.5	383 ± 12	9644 ± 55
Dy($AsUO_6$) ₃ ·16H ₂ O	67.3 ± 0.5	384 ± 12	9642 ± 55
Ho($AsUO_6$) ₃ ·16H ₂ O	67.4 ± 0.5	385 ± 12	9668 ± 55
Er($AsUO_6$) ₃ ·16H ₂ O	67.5 ± 0.5	385 ± 12	9653 ± 55
Tm($AsUO_6$) ₃ ·16H ₂ O	67.6 ± 0.5	386 ± 12	9653 ± 55
Yb($AsUO_6$) ₃ ·16H ₂ O	67.6 ± 0.5	386 ± 12	9627 ± 55
Lu($AsUO_6$) ₃ ·16H ₂ O	67.5 ± 0.5	385 ± 12	9613 ± 55

Fig. 3 Speciation diagrams for U(VI) (a), As(V) (b) and Nd(III) (c) in saturated aqueous solutions of $\text{Nd}(\text{AsUO}_6)_3 \cdot 16\text{H}_2\text{O}$



deterioration of the structure of many uranium compounds [38, 45–47].

Slightly acidic media facilitate the hydrolysis of uranyl ions, leading to the formation of stable uranyl hydroxy-complexes of various composition, that are the dominant species in neutral and alkaline solutions. Under these conditions, the described hydroxy-complexes are the reason for the formation of insoluble uranyl oxide hydrate phases of complex

composition and structure. However, the formation of ionic-molecular species of uranium(VI) with a high degree of condensation, leading to the formation of colloidal particles, is not observed in the studied systems, which can be proven via nephelometry and turbidimetry. In highly alkaline media non-condensed products of uranyl ions hydrolysis, containing a large amount of OH^- per each UO_2^{2+} moiety, are dominant, which leads to the formation of a crystalline uranate of constant composition in the solid phase.

The minimal solubility of uranyl arsenates is observed in neutral media, which correlates well with ionic-molecular composition of saturated aqueous solutions. Under these conditions, the least charged species of uranium(VI), arsenic(V) and element M(III) are dominant in the solution, which facilitates the least influence of electrostatic forces on the polar structure of crystalline solids. In acidic and alkaline solutions more charged species of structure-forming elements are dominant, which, as well as the presence of H^+ and OH^- ions, leads to an increase in solubility of studied compounds.

Conclusion

The chemical stability of uranyl arsenates of rare-earth elements with the general formula $M^{III}(AsUO_6)_3 \cdot 16H_2O$ (M^{III} —La—Lu) in aqueous solutions has been studied in a wide range of acidity. Rare-earth elements uranyl arsenates retain their composition and structure upon the contact with aqueous solutions in the range of pH values from 1.8–2.0 to 8.4–9.8. Outside this range, they transform into compounds with different composition and structure, such as $HAsUO_6 \cdot 4H_2O$, $UO_3 \cdot nH_2O$, $M^{III}(OH)_3$, $Na_2U_2O_7$. The solubility of $M^{III}(AsUO_6)_3 \cdot 16H_2O$ compounds has the least value (10^{-7} mol/l) in neutral solutions and increases up to 10^{-4} – 10^{-2} mol/l in acidic or alkaline solutions. Ionic-molecular composition of saturated aqueous solutions of studied uranyl arsenate systems correlates well with processes of transformation and dissolution of crystalline compounds. The dependence of solubility product logarithm lgK_{SP} on interlayer atom ionic radius $r(M^{3+})$ is typical for REE compounds and displays the characteristic gadolinium break. However, general structural likeness of studied compounds and similarity in properties of interlayer atoms M^{III} lead to a small spread of lgK_{SP} values and analogous influence of different factors on all $M^{III}(AsUO_6)_3 \cdot 16H_2O$ compounds chemical resistance in aqueous solutions.

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