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Uranium(VI) in Aqueous Solutions at 25°C and a Pressure of 1 bar: Insight from Experiments and Calculations

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Abstract—The behavior of the 0.1 mNaCl + 0.002 mHCl + 1.9×10^{-5} mUO$_2$(NO$_3$)$_2$ solution was studied at pH from 2.7 to 11.0, 25°C, and 1 bar in an argon atmosphere. The curve of variations in U concentration exhibits two minima at pH = 6.6 ± 0.7 and 10.0 ± 0.5. These minima are related to the precipitation of schoepite and clarkeite, respectively. The experimental data were used to refine the stability constants of U(VI) (hydroxo) complexes. For the polymer species of U(VI) with charges from +2 to –1, the method of additivity of thermochemical increments was used, and increments of the linear relation were determined for the calculation of the Gibbs free energies of formation ($\Delta_f G^0_{298.15}$) of respective homologue series. The proposed method was applied to calculate the $\Delta_f G^0_{298.15}$ of formation of U(VI) (hydroxo)complexes containing from one to five uranium atoms.

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INTRODUCTION

Uranium is the most important element in the nuclear industry, and its chemical properties have attracted much attention for more than 50 years. The interest in uranium is considerable, despite the fact that its chemical [1–4] and thermodynamic properties [5–12] have been extensively studied. The demand for uranium, as an alternative energy source, will be high for many decades [13]. The technique of underground mining and treatment of spent nuclear fuel will be improved, while the requirements for the methods and strategy of disposal of radioactive wastes and environmental protection (also in the areas of uranium mining) will increase. Natural uranium is a weakly radioactive element and does not pose a significant radiation hazard, but many U(VI) compounds show toxic properties and can be accumulated in plants and human organs. Hence, the permissible concentrations of uranium in aqueous solutions must be very low and are prescribed by respective statutes [14].

During the past 10–20 years, the investigations of uranium sorption on mineral surfaces have significantly intensified. Sorption is usually carried out from dilute solutions undersaturated with respect to U(VI)-bearing solid phases in order to exclude coprecipitation on mineral surfaces. In other cases, uranium coprecipitation on the surface is considered. Tetravalent uranium is not very interesting as a sorbate, because of the very low solubility of U(IV) compounds in natural waters [15–17]. The concept of surface complexation has been widely and fruitfully used to describe adsorption by mineral surfaces [18]. It implies that surface adsorption is similar to a reversible chemical reaction between a water-soluble species and a reactive surface. The thermodynamic description of sorption equilibria relies heavily on the reliability of thermodynamic data for the species participating in these reactions. As for U(VI), such data still need to be refined.

It was previously noted [19, 20] that pure-water solutions containing 10^{-3} mU(VI) were weakly acidic (pH = 4.08). We did not observe solid particles and colloids in the analyzed solutions, although they were oversaturated with respect to schoepite, $UO_3 \times 2H_2O$, which is thermodynamically stable under ambient conditions. Precipitates were formed in these solutions during prolonged storage (7 days), and the solutions became neutral. Potentiometric investigations showed that, at uranium concentrations from 10^{-3} to 3×10^{-7} mol/kg H$_2$O, anionic forms of U(VI) hydroxide complexes were more abundant in the solution or other acidifying elements were present in the solution.

Thermodynamic calculations on the basis of data from [5, 8, 21] indicated weakly alkaline or neutral pH for such solutions. According to the data of Sutton [21], the neutral hydroxide complex $U_3O_8(OH)_2^0$ must be predominant in aqueous solutions with U contents from 10^{-5} to 10^{-3} mol/kg H$_2$O, whereas other authors [11, 22] argued that the most important complexes are $(UO_2)_3(OH)_7^-$ ($U_3O_8(OH)_3^-$ or $HU_3O_{10}^-$) and

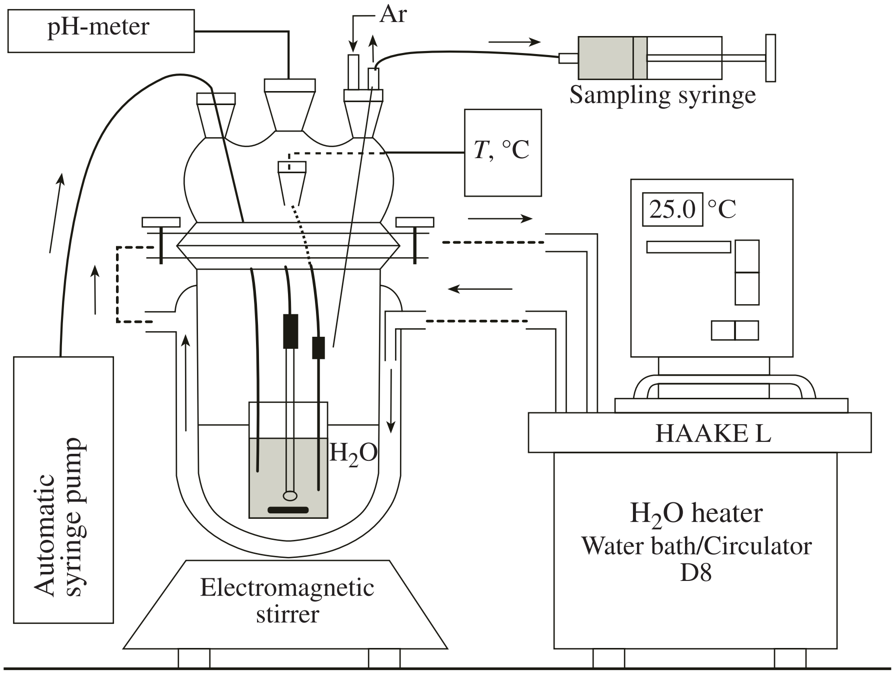

Fig. 1. Experimental setup for potentiometric titration, modified after [24].

$(UO_2)_3$ (or $U_3O_8OH^+$). Calculations show that the fraction of uranyl in aqueous solutions containing even 10^{-3} mol U(VI) per one kilogram H_2O is small (neutral solutions) and close to 1%. Only the data of Palmer and Nguyen-Trung [23], who refined the constants of formation of $(UO_2)_3(OH)_7^-$ and introduced two new species, $(UO_2)_3(OH)_8^{2-}$ and $(UO_2)_3(OH)_{10}^{4-}$, suggested that the 0.001 *m* solutions of U(VI) are weakly acidic (pH = 5.9).

Attempts to reconcile the calculations with the results of potentiometric titration showed that the thermodynamic properties of negatively charged polymeric complexes of U(VI), $HU_3O_{10}^-$ and $HU_2O_7^-$, had to be significantly revised. Aqueous solutions containing 0.001 *m*U(VI) must be unstable during prolonged storage, and the colloidal suspensions of U(VI) that may precipitate from these solutions are potential sorbents of hydroxyl ions leading to changes in the pH value of the suspension. Therefore, it is of interest to explore the behavior of homogeneous solutions over a wide range of acidity.

EXPERIMENTAL TECHNIQUES AND METHODS

The behavior of U(VI) in chloride solutions was investigated by potentiometric titration, which was carried out in a thermostatted cell at 25 ± 0.1°C in an Ar atmosphere. The initial solution of 0.1 *m*NaCl + 0.002 *m*HCl + 1.9 × 10^{-5} *m*U(VI) was prepared from deionized water (DI), NaCl (S271-3, Fisher Chemical), 1 N HCl solution (SA48-1, Fisher Chemical), and 10 mg/l solution of $UO_2(NO_3)_2$ in 4% HNO_3 (plasma grade standard PLU2-2Y, Fisher Chemical). The 0.1 *m*NaOH titrant solution was prepared from 50% NaOH (SS254-4, Fisher Chemical) filtered through a 0.2 μm filter (Whatman Puradisc 25 mm Syringe filters) and DI water. This solution contained no more than 2×10^{-4} *m*Na_2CO_3, which was confirmed by potentiometric titration. The general scheme of the experimental set-up for potentiometric titration is shown in Fig. 1. In contrast to [24], the solution (50 ml) was loaded into an 80-ml beaker, in which the titration was carried out. The initial acidic solution of uranyl was kept for two hours under continuous intense electromagnetic stirring in an argon atmosphere, which flowed through the vessel for the complete removal of CO_2. Argon from a cylinder was first passed through Ascarite and, then, through a 25% NaOH solution, after which it flowed into the reaction vessel. The volume of 0.1 *m*NaOH used for titration from pH = 3 to 11 was 2 ml; thus, the *m*CO_2 of the final solution was no higher than 10^{-5} mol/kg H_2O. The titrant was introduced into the reaction chamber through a capillary with an automatic syringe pump (KD Scientific, model 210). The solution was kept for 10–30 min to attain steady-state conditions, i. e. when pH varied by less than 0.002 in 5 min. The pH value ($\equiv -\log aH^+$, where aH^+ is the activity of proton, equal to the product of H^+ molar concentration and its activity coefficient in the solution) was monitored using a combination glass electrode (Accu · pHast) connected to a pHmeter (Radiometer Copenhagen model PHM84) with a sensitivity of ±0.001 pH units. The accuracy of pH measurement was ±0.005. The electrode was preliminarily calibrated using three standard solutions (pH = 4.00 ± 0.01, red; pH = 7.00 ± 0.01, yellow; and pH = 10.00 ± 0.02, blue; all Fisher Chemical) and three specially prepared solutions of 0.1 *m*NaCl containing 0.01, 0.001, and 0.0003 *m*HCl, respectively. This calibration was used to estimate the liquid junction potential (LJP), which appeared to vary as $LJP = 4.7 \times 10^{-3} - 5.1 \times 10^{-5} V$, where V is the measured electrode potential in millivolts. The solution from the reaction chamber was sampled using a polyethylene syringe with a plastic capillary. The mass of the collected solution was determined on an electronic balance with a precision of ±0.0001 g. Then, the solution was rapidly (1–10 s) vacuum filtered through a 0.02 μm filter (Whatman Anodisc filter) into a plastic tube. An aliquot of the filtered solution was acidified with HNO_3, brought to 10 ml, and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) on a Hewlett Packard 4500 instrument. The error of the ICP-MS analysis with the use of internal standards (^{89}Y, ^{115}In, and ^{187}Re) was no higher than 2%.

Table 1. Influence of pH on *m*U(VI) in true (filtered) solution for the initial system 0.1 *m* NaCl + 0.002 *m* HCl + 1.9×10^{-5} $mUO_2(NO_3)_2$, at $T = 25 \pm 0.1$°C and $P = 1$ bar Ar

pH exp	log*m*U	Dilution during filtering
2.72	–4.72	Starting solution
2.72	–4.73	1.000
3.00	–4.73	0.991
3.51	–4.73	0.985
4.02	–4.76	0.982
4.61	–4.88	0.982
5.06	–5.04	0.981
5.69	–5.39	0.981
7.47	–5.41	0.981
8.65	–5.04	0.981
9.46	–5.21	0.981
10.00	–5.38	0.980
10.52	–5.09	0.978
11.04	–5.10	0.970

RESULTS AND DISCUSSION

In spite of the low bulk concentration of uranium (1.9×10^{-5} mol/kg H_2O) in the initial solution, the uranium concentration in the solution showed considerable variations over a pH range from 5 to 10.5 (Table 1), and two concentration minima were observed at pH = 6.6 ± 0.7 and 10.0 ± 0.5. The formation of colloids or other suspensions were never visually detected in the solution. There are no grounds for supposing that such significant amounts of uranium could be sorbed on the inner surfaces of the inert plastic tubes and the glass (Pyrex) beaker. Therefore, the variations in *m*U in the solution were related to the precipitation of unidentified solid phases of unknown crystallinity. It is known that two phases are thermodynamically stable in the solution within the pH range 5–10: schoepite, $UO_3 \cdot 2H_2O$, and clarkeite, $Na_2U_2O_7 \times nH_2O$. According to the data of [11], equilibrium of schoepite with clarkeite in 0.1 *m*NaCl occurs at pH = 6.8. This value depends on the degree of crystallinity and the size of particles of newly formed solid phases, which affects their solubility and stability.

The treatment of the experimental data (Table 1) was based on the thermodynamic properties of the following U(VI) species: UO_2^{2+}, UO_2OH^+, $UO_2(OH)_2^0$ (or UO_3^0aq), HUO_4^-, UO_4^{2-}, $(UO_2)_2OH^{3+}$, $(UO_2)_2(OH)_2^{2+}$, $U_3O_6(OH)_4^{2+}$, $U_3O_6(OH)_5^+$, $U_3O_6(OH)_7^-$, $U_4O_8(OH)_7^+$, UO_2Cl^+, and $UO_2Cl_2^0aq$ [11, 25]. In order to support the future use of the thermodynamic data at high temperatures, the data of [25] were accepted for the uranyl ion and U(VI) hydroxide complexes, whose HKF parameters are key data in the UNITHERM database [26]. The Gibbs free energies of these species are practically identical to the data of [11]. When data were missing in [25], the data of [11] at 25°C were used in calculations. The calculations were carried out by the method of Gibbs free energy minimization using the software package HCh [26]. The activity coefficients of aqueous species were calculated by the third-approximation Debye–Huckel equation adjusted for NaCl solutions [27]. The calculations resulted in unsatisfactory agreement with the experimental results, which suggested that the thermodynamic properties of a number of dissolved species and solid phases had to be revised.

According to the calculations, the predominant uranium species in acidic (pH ≤ 3) and alkaline (pH ≥ 10.5) solutions with low U(VI) concentrations are depolymerized UO_2^{2+} and UO_4^{2-}, respectively. The uranyl ion UO_2^{2+} is a basis species for all U(VI) compounds, and the constants of formation of other U(VI) species and reaction of dissolution of uranium phases will be considered therefore in relation with UO_2^{2+} and other simple ions.

Our investigations showed that the obsurved pH–*m*U dependence (Table 1) can be adequately described by the reactions presented in Table 2. The dissolution constant of schoepite (S1) was adjusted to agree with the pH–*m*U data for acidic solutions. Assuming that pH = 8.65 corresponds to the two-mineral schoepite–clarkeite assemblage in 0.1 *m*NaCl, we calculated the dissolution constants of clarkeite (S2 and S3) and $\Delta_f G^0_{298.15}$ ($Na_2U_2O_7$ (s)) = –3005.500 ± 0.3 kJ/mol. The

Table 2. Logarithms of equilibrium constants of uranyl hydrolysis reactions, formation of carbonate complexes, and dissolution of some solid phases at 25°C and 1 bar

No.	Reaction	[11]	This study	[40]	[8]
11	$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$	–5.200	–5.209	–5.070	–5.754
12	$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2^0 + 2H^+$	–10.301	–10.049	–12.303	–11.91
13	$UO_2^{2+} + 2H_2O \rightleftharpoons HUO_4^- + 3H^+$	–19.201	–18.541	–	–
14	$UO_2^{2+} + 2H_2O \rightleftharpoons UO_4^{2-} + 4H^+$	–33.001*	–29.310	–	–
21	$2UO_2^{2+} + H_2O \rightleftharpoons (UO_2)_2OH^{3+} + H^+$	–2.626	–2.648*	–	–
22	$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$	–5.62	–5.652	–5.712	–5.551
23	$2UO_2^{2+} + 3H_2O \rightleftharpoons (UO_2)_2(OH)_3^+ + 3H^+$	–	–10.498	–	–
24	$2UO_2^{2+} + 3H_2O \rightleftharpoons H_2U_2O_7^0 + 4H^+$	–	–15.072	–	–
25	$2UO_2^{2+} + 3H_2O \rightleftharpoons HU_2O_7^- + 5H^+$	–	–23.243	–	–
34	$3UO_2^{2+} + 4H_2O \rightleftharpoons U_3O_6(OH)_4^{2+} + 4H^+$	–11.901	–11.307	–	–
35	$3UO_2^{2+} + 5H_2O \rightleftharpoons U_3O_6(OH)_5^+ + 5H^+$	–15.551	–15.787	–	–15.558
36	$3UO_2^{2+} + 4H_2O \rightleftharpoons H_2U_3O_{10}^0 + 6H^+$	–	–20.094	–	–
37	$3UO_2^{2+} + 4H_2O \rightleftharpoons HU_3O_{10}^- + 7H^+$	–31.002	–28.145	–	–30.675
47	$4UO_2^{2+} + 7H_2O \rightleftharpoons U_4O_8(OH)_7^+ + 7H^+$	–21.901	–21.077	–	–
C1	$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3^0$	9.666	10.122	11.465	10.042
C2	$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2^{2-}$	16.912	16.681	18.289	17.052
C3	$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$	21.557	21.326	22.972	21.435
C4	$3UO_2^{2+} + 6CO_3^{2-} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-}$	53.91	53.88*	–	–
S1	$UO_3 \times 2H_2O(s) + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O$	4.812	4.304	5.532	5.628
S2	$0.5Na_2U_2O_7(s) + 1.5H_2O \rightleftharpoons Na^+ + UO_2^{2+} + 3OH^-$	–30.69**	–30.165	–	–
S3	$0.5Na_2U_2O_7(s) + H^+ + 1.5H_2O \rightleftharpoons Na^+ + UO_3 \times 2H_2O(s)$	6.474	7.514	6.550	–
S4	$UO_2CO_3(s) \rightleftharpoons UO_2^{2+} + CO_3^{2-}$	–14.456	–14.445*	–15.863	–14.071
S5	$UO_2CO_3(s) + 2H_2O \rightleftharpoons UO_3 \times 2H_2O(s) + CO_2(g)$	–1.13	–0.61	–2.09***	–1.56
S6	$CaH_2(UO_2)_2(SiO_4)_2 \times 5H_2O(s) + 6H^+ \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 9H_2O + 2SiO_2aq$	11.7	12.23	–	–

Notes: * Based on the data of [11, 25].

** $\log K(S2) = -30.10 \pm 0.1$, refined after [12].

*** Data for schoepite are after [5].

constants of formation of UO_4^{2-}, $H_2U_2O_7^0$, $HU_2O_7^-$, $H_2U_3O_{10}^0$, and $HU_3O_{10}^-$ were adjusted in such a way as to best describe the pH–*m*U curve in alkaline solutions and provide an approximately linear relationship between the free energy of formation of polymer species of a particular homologue series (identical charges but different numbers of UO_3 units) and the number of UO_3 units in the chain.

Investigations at a fixed ionic strength of solution are insufficient to estimate the relations of all of the U(VI) species given in Table 2. Quantitative relations between ions with charges of +2, +1, 0, and –1 can be obtained by applying the methods of equilibrium thermodynamics. The proportions of monomeric and polymeric U(VI) species can be determined by spectral methods. Unfortunately, even spectral methods (UV, IR, Raman, and other techniques) cannot provide unambiguous information on the charge of a polymeric species, and, in such a case, the main argument is the experience gained in previous investigations, which was summarized and critically evaluated by Grenthe et al. [11]. The following 11 species are considered as predominant U(VI) (hydroxo) complexes [11]: UO_2^{2+}, UO_2OH^+, $UO_2(OH)_2^0$ (or UO_3^0aq), $UO_2(OH)_4^{2-}$ (or UO_4^{2-}), HUO_4^-, $(UO_2)_2OH^{3+}$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$, and $(UO_2)_4(OH)_7^+$. Earlier handbook data [5] ignored all polymeric hydroxide complexes, except for $(UO_2)_2(OH)_2^{2+}$, although they were known [21, 28]. The question arises why several species with charges from +2 to –1 are missing in the list of polymeric complexes. Much experience has been gained in chemical thermodynamics on the estimation of the thermodynamic properties of polymeric species of a particular homologue series [29] using the method of the additivity of thermochemical increments. Relevant studies have shown that the free energy of formation of such compounds (species) can be described with sufficient accuracy by a linear function of the number of units in the chain:

$$\Delta_f G_T^0(AC_n) = b_i + nG_i, \qquad (1)$$

where b_i and G_i are the increments, which are constant for the given homologue series AC_n under given *T* and *P*, and *n* corresponds to the number of C units in the chain. In the case of U(VI) polymeric complexes, the UO_3 group is such a unit. The contribution of this group to complex species with different charges must be different owing to the difference in their hydration. For uncharged species (Z = 0), the main reactions were

$$UO_3 \times 2H_2O(s) \rightleftharpoons UO_2(OH)_{2aq}^0 + H_2O, \qquad (2)$$

and

$$nUO_2(OH)_{2aq}^0 \rightleftharpoons H_2U_nO_{3n+1}^0 + (n-1)H_2O. \qquad (3)$$

The bulk concentration of hydroxide complexes with Z = 0 (mU_{T-0}) was calculated by the expression:

$$mU_{T-0} = \sum_{n=1}^{5} n(mUO_2(OH)_2^0)^n \times 10^{a_0(n-1)}, \qquad (4)$$

where $mUO_2(OH)_2^0$ is the molal concentration of the monomeric hydroxide complex, *n* is the number of U atoms in the hydroxide complex (between 1 and 5), and a_0 is the negative logarithm of the constant of reaction (3) of formation of dimer (biuranyl hydroxide), which is calculated as

$$a_0 = (\Delta_f G_T^0(H_2O) - b_0)/2.303RT.$$

The solution must satisfy the condition of symmetric variations in $\Delta_f G_T^0(H_2U_nO_{3n+1}^0)$ as a function of a_0.

The following reactions were used for charged hydroxide complexes:

$$nHUO_4^- \rightleftharpoons HU_nO_{3n+1}^- + (n-1)OH^-, \qquad (5)$$

$$nUO_2OH^+ \rightleftharpoons U_nO_{3n}H^+ + (n-1)H^+, \qquad (6)$$

and

$$nUO_2^{2+} + (n-1)H_2O \rightleftharpoons U_nO_{3n-1}^{2+} + 2(n-1)H^+. \qquad (7)$$

Correspondingly, the total concentrations of U(VI) hydroxide complexes with charges of –1, +1, and +2 were calculated by the folloing expressions:

$$mU_{T-1} = \sum_{n=1}^{5} n(mHUO_4^-)^n(mOH^-)^{(1-n)} \times 10^{a_1(n-1)}, \qquad (8)$$

$$mU_{T+1} = \sum_{n=1}^{5} n(mUO_2(OH)^+)^n(mH^+)^{(1-n)} \times 10^{a_2(n-1)}, \qquad (9)$$

and

$$mU_{T+2} = \sum_{n=1}^{5} n(mUO_2^{2+})^n\gamma_{2+}^{(n-1)}(mH^+\gamma_+)^{2(1-n)} \times 10^{a_3(n-1)}. \qquad (10)$$

The constants of reactions, a_1, a_2, and a_3, in Eqs. (8), (9), and (10) are given by

$$a_1 = (\Delta_f G_T^0(OH^-) - b_1)/2.303RT,$$

$$a_2 = (-b_2)/2.303RT,$$

Table 3. Parameters of the linear extrapolation $G^0_{298.15}$ $(i, Z, n) = b_i + n \times G_i$ of the thermodynamic properties of various homologue series of U(VI) hydroxide complexes and constants of formation of dimers, a_i, at 25°C and 1 bar

Charge, Z	Homologue series	b_i, kJ/mol	G_i, kJ/mol	a_i,
–1	$HU_nO^-_{3n+1}$	–158.718	–1162.345	–0.255
0	$(UO_2)_n(OH)^0_2$	–208.454	–1161.083	5.0259
+1	$(UO_3)_nH^+$	–0.460	–1159.563	–0.281
+2	$U_nO^{2+}_{3n-1}$	204.839	–1157.474	–5.659

and

$$a_3 = (-\Delta_f G^0_T(H_2O) - b_3)/2.303RT.$$

Equations (4), (8), (9), and (10) are valid for any n, but our estimates for noncritically oversaturated solutions indicated that hydroxide complexes with $n > 5$ can be ignored.

Using this method, we calculated the approximation increments and free energies of formation of U(VI) complexes with charges between –1 and +2 containing up to five uranium atoms. The results are shown in Tables 3–7. The error of the $\Delta_f G^0_{298.15}$ values for the formation of complexes was estimated for the case when the accuracy of a_i is ±0.3, which corresponds to an error in the constant of formation of biuranyl (or in the concentration of this species) by a factor of 2. The real error for a_i is probably not higher than the error in the calculations of the bulk solubility of schoepite, i.e., ±(0.1–0.2).

The introduction of corrections into the $\Delta_f G^0_{298.15}$ values of U(VI) species and the addition of polymeric U(VI) hydroxide complexes to the list of species changes the relations of predominant U(VI) species compared with the data of [11] (Figs. V4, V5, and V6 in [11]). Figure 2 presents the results of model calculations for the UO_3–H_2O–HCl–NaOH system in 0.1 mNaCl. According to these calculations, the contribution of the $(UO_2)_2OH^{3+}$ and $(UO_2)_2(OH)^{2+}_2$ species in equilibrium with schoepite is no higher than 8% relative at pH < 5; that of $(UO_2)_2(OH)^+_3$ and UO_2Cl^+ is ≤ 4%; and $U_3O_6(OH)^{2+}_4$, $U_3O_6(OH)^+_5$, $U_4O_8(OH)^+_7$, and $UO_2Cl^0_2$ account for no more than 1%. The main contribution to the solubility of schoepite (at pH < 8.64) is related to the species UO^{2+}_2, UO_2OH^+ (the contribution of the latter is ≤15% at pH = 5.1), $UO_2(OH)^0_2$ (63% at pH = 6.5), $H_2U_2O^0_7$ (24%), $H_2U_3O^0_{10}$ (7%), HUO^-_4, $HU_2O^-_7$, and $HU_3O^-_{10}$ at pH from 8.0 to 8.6. Within the pH range 5.5–8.0, the uncharged hydroxide complexes $UO_2(OH)^0_2$ and $H_2U_2O^0_7$ are predominant. The solubility of clarkeite at pH > 8.6 is controlled by the species HUO^-_4, UO^{2-}_4, $HU_2O^-_7$, and $HU_3O^-_{10}$ (≤11%). The main contribution at pH > 10.5 is due to depolymerized UO^{2-}_4 species. Such solutions can be in equilibrium with sodium metauranate, Na_2UO_4(s), or its hydrates, the solubility of which at pH > 10.5 must be only slightly dependent on the pH of solution:

$$Na_2UO_4(s) \times nH_2O = 2Na^+ + UO^{2-}_4 + nH_2O.$$

This fact is probably responsible for the invariance of uranium concentration (8×10^{-6} mU) in the experiments at pH of 10.5 and 11.0. Note that in the case of the complete dissolution of solid phases, the concentration of uranium at pH = 11.0 must be 1.8×10^{-5} mU, i.e., higher by a factor of 2.2 than that in the filtered solution. We argue that adsorption on the walls of the glass reactor

Table 4. Free energies of formation of U(VI) hydroxide complexes with $Z = 0$ at 25°C; numbers in parentheses show the contribution (%) of the given complex to the bulk concentration of neutral U(VI) hydroxide complexes, mU_{T-0}

Species	$\Delta_f G^0_{298.15}$, kJ/mol (fraction in mU_{T-0})	Species	$\Delta_f G^0_{298.15}$, kJ/mol
H_2O	–237.141	–	–
$UO_2(OH)^0_2$	–1369.537 ± 0.53 (65.29%)	$UO_2(OH)^0_2$	–1369.537 ± 0.53
$H_2U_2O^0_7$	–2530.620 ± 0.65 (25.14%)	$U_2O_4(OH)^0_4$	–2767.761 ± 0.65
$H_2U_3O^0_{10}$	–3691.703 ± 1.8 (7.26%)	$U_3O_6(OH)^0_6$	–4165.985 ± 1.8
$H_2U_4O^0_{13}$	–4852.786 ± 3.0 (1.86%)	$U_4O_8(OH)^0_8$	–5564.209 ± 3.0
$H_2U_5O^0_{16}$	–6013.869 ± 4.2 (0.45%)	$U_5O_{10}(OH)^0_{10}$	–6962.433 ± 4.2

Table 5. Free energies of formation of U(VI) hydroxide complexes with $Z = -1$

Species	$\Delta_f G^0_{298.15}$, kJ/mol (fraction in mU_{T-1})	Species	$\Delta_f G^0_{298.15}$, kJ/mol
OH^-	–157.262	–	–
HUO_4^-	–1321.063 ± 0.8 (46.94%)	$UO_2(OH)_3^-$	–1558.204 ± 0.8
$HU_2O_7^-$	–2483.408 ± 0.2 (30.04%)	$(UO_2)_2(OH)_5^-$	–2957.690 ± 0.2
$HU_3O_{10}^-$	–3645.752 ± 1.1 (14.42%)	$(UO_2)_3(OH)_7^-$	–4357.175 ± 1.1
$HU_4O_{13}^-$	–4808.097 ± 2.1 (6.15%)	$(UO_2)_4(OH)_9^-$	–5756.661 ± 2.1
$HU_5O_{16}^-$	–5970.442 ± 3.0 (2.45%)	$(UO_2)_5(OH)_{11}^-$	–7156.147 ± 3.0

Table 6. Free energies of formation of U(VI) hydroxide complexes with $Z = +1$

Species	$\Delta_f G^0_{298.15}$, kJ/mol (fraction in mU_{T+1})	Species	$\Delta_f G^0_{298.15}$, kJ/mol
H^+	0	–	–
UO_3H^+	–1160.023 ± 0.2 (80.33%)	UO_2OH^+	–1160.023 ± 0.2
$U_2O_6H^+$	–2319.586 ± 1.3 (16.67%)	$(UO_2)_2(OH)_3^+$	–2556.727 ± 1.3
$U_3O_9H^+$	–3479.149 ± 2.8 (2.60%)	$(UO_2)_3(OH)_5^+$	–3953.431 ± 2.8
$U_4O_{12}H^+$	–4638.711 ± 4.3 (0.35%)	$(UO_2)_4(OH)_7^+$	–5350.134 ± 4.3
$U_5O_{15}H^+$	–5798.274 ± 5.8 (0.05%)	$(UO_2)_5(OH)_9^+$	–6746.838 ± 5.8

could hardly have resulted in such considerable uranium losses.

The room-temperature solubility of U(VI) hydroxides in various media has been studied by many authors [22, 30–34]. Figure 3 shows experimental data that were not included in the compilation of [11] and the results of model calculations. Noteworthy is that the experimental data from all of these studies show significant discrepancies. It is known that the solubilities of amorphous and crystalline phases are different, and

Table 7. Free energies of formation of U(VI) (hydroxide) complexes with $Z = +2$

Species	$\Delta_f G^0_{298.15}$, kJ/mol (fraction in mU_{T+2})	Species	$\Delta_f G^0_{298.15}$, kJ/mol
H^+	0	–	–
UO_2^{2+}	–952.635 ± 0.15* (91.26%)	UO_2^{2+}	–952.635 ± 0.15
$U_2O_5^{2+}$	–2110.109 ± 1.4 (8.16%)	$(UO_2)_2(OH)_2^{2+}$	–2347.250 ± 1.4
$U_3O_8^{2+}$	–3267.583 ± 3.0 (0.55%)	$(UO_2)_3(OH)_4^{2+}$	–3741.865 ± 3.0
$U_4O_{11}^{2+}$	–4425.057 ± 4.6 (0.03%)	$(UO_2)_4(OH)_6^{2+}$	–5136.480 ± 4.6
$U_5O_{14}^{2+}$	–5582.531 ± 6.1 (0.00%)	$(UO_2)_5(OH)_8^{2+}$	–6531.095 ± 6.1

* Based on the value $\Delta_f G^0_{298.15}$ (UO_2^{2+}) = –952.613 kJ/mol [25].

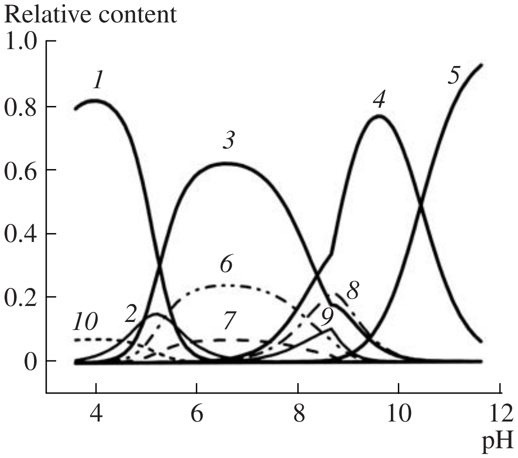

Fig. 2. Contributions of various U(VI) (hydroxide) complexes to the solubility of schoepite and clarkeite according to calculations: *1*, UO_2^{2+}; *2*, UO_2OH^+; *3*, $UO_2(OH)_2^0$; *4*, HUO_4^-; *5*, UO_4^{2-}; *6*, $H_2U_2O_7^0$; *7*, $H_2U_3O_{10}^0$; 8, $HU_2O_7^-$; *9*, $HU_3O_{10}^-$; and *10*, $(UO_2)_2OH^{3+}$.

the solubility of the metastable phase $UO_2(OH)_2(s)$ must be different from that of thermodynamically stable schoepite, $UO_3 \times 2H_2O(s)$. The degree of crystallinity also affects the solubility of a solid phase through a parameter depending on the specific surface area of the material, because the free energy of a compound depends on the crystal radius [35] or the specific surface [36].

According to [22, 34], a change in the phase state of a material (amorphous–finely crystalline) is accompanied by an order of magnitude change in $UO_3 \times 2H_2O$ solubility over a pH range from 7.0 to 7.5. The subsequent recrystallization of schoepite may additionally reduce the solubility of this phase by one order of magnitude [34]. On the other hand, according to the data of [11, 31], the solubility of $UO_3 \times 2H_2O(cr)$, which is stable up to 60°C [1], differs from that of β-$UO_2(OH)_2(cr)$, which is metastable at 25°, by less than 0.1 order of magnitude. The solubility of schoepite (probably, finely crystalline) in water is estimated to be 4×10^{-6} mol/kg H_2O on the basis of our experimental data (Table 1) and model calculations (Fig. 3). This estimate corresponds to the value constrained by the experiments of Nikitin et al. [31] and Giammar [32] and recommended by the Nuclear Energy Agency [11]. However, in our opinion, this estimate corresponds to the solubility of finely crystalline schoepite with a free energy of formation $\Delta_f G^0_{298.15}(UO_3 \times 2H_2O(s)) = -1639.47 \pm 0.6$ kJ/mol, whereas the solubility of the well-crystallized phase in water is $(1–2) \times 10^{-6}$ M [22, 31] and $\Delta_f G^0_{298.15}(UO_3 \times 2H_2O(cr)) = -1640.4 \pm 0.9$ kJ/mol. The predominant aqueous species in equilibrium with such a phase is $UO_2(OH)_2^0$ (70–80%).

Using experimental data (five experiments) reported in [33] for acidic solution with pH from 4.1 to 5.0 in equilibrium with the phase $UO_2(OH)_2(s)$, we calculated the concentrations of species and Gibbs free energy of formation of this phase: $\Delta_f G^0_{298.15}(UO_2(OH)_2(s)) = -1398.355 \pm 0.110$ kJ/mol. Grenthe et al. [11] reported $\Delta_f G^0_{298.15} = -1398.7 \pm 1.1$ kJ/mol for β-$UO_2(OH)_2$. As for the solubility of sodium uranate estimated in [33], it has to be concluded that these data are strongly underestimated at pH values of 7.8 and 10. The values of $\Delta_f G^0_{298.15}(Na_2U_2O_7\ (cr))$ calculated using these parameters are –3016.756 kJ/mol at pH = 7.8 and –3021.043 kJ/mol at pH = 10.0. All of the available $\Delta_f G^0_{298.15}$ estimates for this phase fall within the range from –3003.171 [6] to –3011.454 kJ/mol [11]. Thus, it can be supposed that equilibrium was not reached in these experiments, or part of the dissolved uranium was lost during analytical operations.

The free energy of formation of metaschoepite, $\Delta_f G^0_{298.15} = -1601.4 \pm 3.2$ kJ/mol [37], was estimated from the enthalpy of formation, $\Delta_f G^0_{298.15} = -1791.4 \pm 3.2$ kJ/mol (calorimetric measurements), and third-law entropy $S^0_{2981.5}$ = 174 J/mol K [11]; however, in our opinion, this value is erroneous. It can be supposed that the material used for the thermochemical investigation was not a well-crystallized schoepite or metaschoepite, because of the short duration of its synthesis (one day at 50°C).

In addition, we attempted to evaluate and use the data of other authors, including [22, 38]. Unfortunately, these papers (Fig. 3) do not provide information on the results of the phase analysis of schoepite, the solid to solution ratios in the experiments, and, most importantly, on the content of carbonate in the alkaline system studied. Note that the continuous passage of N_2 through an alkaline solution cannot liberate completely dissolved CO_2. It should be concluded that the above-cited data on the solubility of amorphous and crystalline schoepite cannot be satisfactorily described either using the database of [11] or by refining the constants of formation of the hydroxide complexes $UO_2(OH)_3^-$ and $(UO_2)_3(OH)_7^-$ and limiting the number of species to six, considering also UO_2^{2+}, UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ in accordance with the recommendations of [38].

The constants of hydrolysis and complexation of aqueous species should not depend on the state of the solid phase. The discrepancy of half an order of magnitude between the estimates of the respective constants

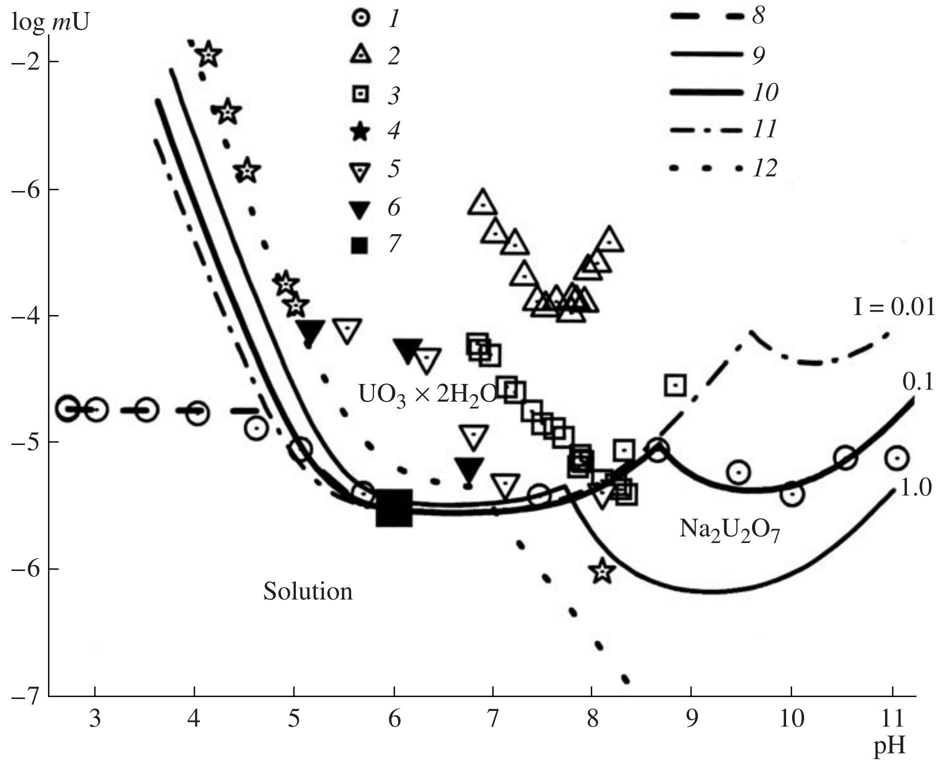

Fig. 3. Solubility of U(VI) hydroxides and clarkeite at 25°C according to experimental data and calculations. (*1*) and (*8*) results of titration of 0.1 mNaCl + 0.002 mHCl + 1.9×10^{-5} $m\mathrm{UO_2(NO_3)_2}$ solution with 0.1 mNaOH solution (experiment and model calculations with the participation of schoepite and clarkeite, our data); (*9*)–(*11*) solubility of schoepite and clarkeite in 0.01, 0.1, and 1.0 mNaCl solutions in a system without CO_2 (model calculations, our data); (*2*) and (*3*) solubility of amorphous and crystalline schoepite in 0.5 $m\mathrm{NaClO_4}$ [22]; (*4*) and (*12*) solubility of $UO_2(OH)_2$(s) in 0.5 M NaCl in air [33] and model calculations of the solubility of $UO_2(OH)_2$(cr) and $Na_2U_2O_7$ according to the data of [11]; (*5*) and (*6*) precipitation of "amorphous" schoepite from the solution of 10^{-4} M $UO_2(NO_3)_2$ in 0.1 M $NaNO_3$ in a system with quartz and from pure solution, N_2 atmosphere [34]; and (*7*) solubility of crystalline schoepite in 0.01 and 0.1 M $NaNO_3$ at pH = 6.0 [32].

of dissolved species can be explained only by the influence of a third component. Analysis of the method of synthesis of the solid phase suggests that the titration of $UO_2(ClO_4)_2$ solution with concentrated NaOH must be accompanied by the precipitation of hydrous sodium uranate (clarkeite) from the solution [39], despite the fact that the solution showed pH ≤ 7. Within the pH range from 6.8 to at least 7.5, the concentration of uranium in solution is controlled by the most soluble phase, clarkeite, even if its content is very low and it cannot be identified by X-ray phase analysis. In the case of chemical equilibrium, the univariant association schoepite–clarkeite buffers the acidity–alkalinity of solution. However, since the pH value of solution changed, it can be supposed that equilibrium was not reached in the experiments of [22], and the concentration of uranium in the solution corresponded to the solubility of clarkeite (amorphous and crystalline) rather than schoepite. However, even in such a case, we failed to find a satisfactory agreement between the calculations and experiments. All of the experimental data could be adequately interpreted only when CO_2 and related species were introduced into the system: HCO_3^- and CO_3^{2-} from the SUPCRT-92 database [40], $NaCO_3^-$ and $NaHCO_3^0$ from the UNITHERM [26], and carbonate complexes of U(VI) from Table 2 were included. The calculations showed that the content of CO_2 was $(3.0 \pm 1.2) \times 10^{-3}$ mol/kg H_2O in the experiments with amorphous schoepite, whereas $m\mathrm{CO_2} = (6.6 \pm 1.4) \times 10^{-4}$ mol/kg H_2O in the experiments with crystalline schoepite, and clarkeite was a dissolving phase. Figure 4 shows the CO_2 to alkali ratio in the titrant, which controls the desired pH value of solution and the corresponding solubility of the solid phase (Fig. 3). Noteworthy is the narrow range of $m\mathrm{CO_2(aq)}/m\mathrm{NaOH}$ values, from 0.87 to 1.15. This indicates that CO_2 occurred mainly as sodium bicarbonate in the starting suspension, and the addition of NaOH, even free of CO_2, could not strongly affect this ratio.

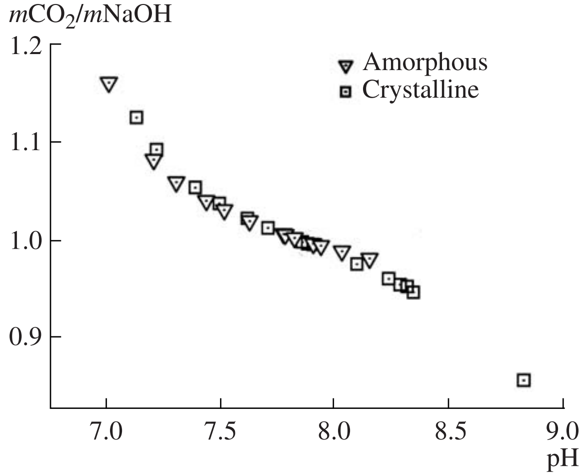

Fig. 4. Relation of the bulk concentrations of CO_2 and NaOH in solution in equilibrium with clarkeite showing the same solubility as was observed in 0.5 m solution of $NaClO_4$ in experiments with "amorphous and crystalline schoepite" [22].

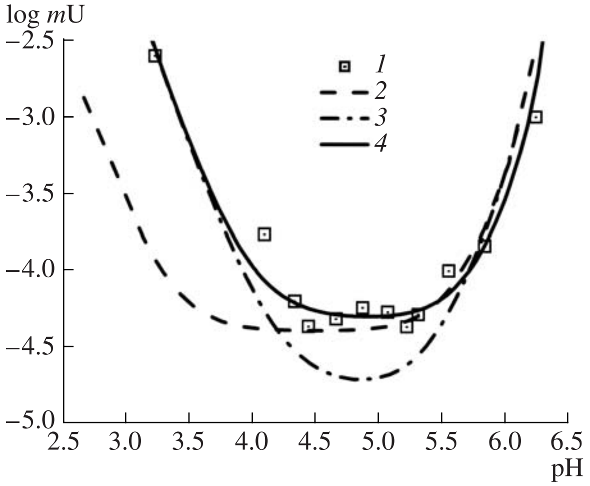

Fig. 5. Solubility of uranyl carbonate at 25°C and $P(CO_2)$ = 1 bar according to (*1*) experimental data [41] and model calculations of (*2*) [41], (*3*) [11], and (*4*) this study.

ADEQUACY IN OTHER SYSTEMS

Table 2 also shows data for uranyl carbonate complexes. Model calculations based on the recommended thermodynamic properties of these complexes appeared to be inconsistent with experimental data on the solubility of uranyl carbonate [41]. Therefore, the constants of formation of the carbonate complexes of uranyl, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ were revised to achieve consistency with the experimental data of Sergeeva et al. [41]. The results of model calculations for these experiments are shown in Fig. 5. The adjustment of the stability constants of uranyl carbonate complexes resulted in the narrowing of the stability field of $UO_2(CO_3)_2^{2-}$, which is probably in agreement with [42]. The fraction of the $(UO_2)_3(CO_3)_2^{2-}$ species in the system considered at pH from 3.2 to 6.3 is no higher than 1%, while USO_2^{2+}, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are the major species contributing to the solubility of uranyl carbonate at 25°C and P = 1 bar CO_2. The value $\Delta_f G^0_{298.15}$ (UO_2CO_3, cr) = –1563.046 ± 1.8 kJ/mol [11] that was used in our calculations is significantly (by 26.5 kJ/mol) different from the $\Delta_f G^0_{298.15}$ (UO_2CO_3, cr) value of rutherfordine obtained from the data of [43]. It seems that, similar to the above-discussed case of schoepite, the fine-grained rutherfordine that was synthesized from amorphous UO_3 at room temperature under a CO_2 pressure of 0.7 bar for one day was not completely transformed and the product was dominated by amorphous UO_3. This is probably why the heats of solution of "metaschoepite" and "rutherfordine" are equal. Another serious source of controversy is the constant of formation of rutherfordine from metaschoepite (reaction S5 in Table 2). According to the data of [37, 43], $\log K$ (S5) = –11.9, which indicates that rutherfordine must be the most stable U(VI) mineral under crustal conditions. This is not the case, and the formation of U(VI) carbonate requires a CO_2 pressure from 0.01 [44] to 0.3 bar (our estimate). Therefore, we believe that the heats of formation of rutherfordine and metaschoepite reported by Kubatko et al. [37, 43] are erroneous.

Our data from Table 2 were used to calculate the incongruent solubility of uranophane, $CaH_2(UO_2)_2(SiO_4)_2 \times 5H_2O(s)$, in bicarbonate solutions based on the experimental data of [45]. The results of calculations are compared in Fig. 6 with the data tabulated by Perez et al. [45], who used the thermodynamic data of Grenthe et al. [11]. The calculations were carried out for 25°C, whereas the experiments were conducted at 20 ± 2°C in air. The values of solubility and solution pH are not very sensitive to temperature variations of 3–5°C, whereas diurnal variations in CO_2 partial pressure could be the main factor affecting the solution pH. Our calculations showed that corrections to the values of the thermodynamic properties of uranyl-bearing complexes provide an adequate agreement with the experiments. The value of $\log K$ (S6) is 12.23 ± 0.4 according to our calculations and 11.7 ± 0.6. according to the data of [11].

Figure 7 shows the results of thermodynamic calculations describing the results of potentiometric titration of uranyl sulfate solution in sulfuric acid with NaOH solution [30]. The thermodynamic properties of SO_4^{2-} and HSO_4^- were taken from SUPCRT-92; those of $NaSO_4^-$, from UNITHERM [26]; and those of $UO_2SO_4^0$

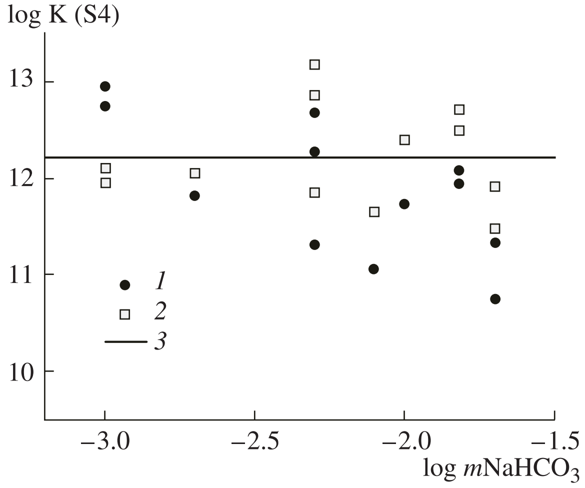

Fig. 6. Estimation of the solubility constant of uranophane, $Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \times 3H_2O + 6H^+ \longleftrightarrow Ca^{2+} + 2UO_2^{2+} + 2SiO_{2,\,aq} + 9H_2O$, in bicarbonate solutions in air according to experimental data of [45], (*1*) calculations of [11], (*2*) this study, and (*3*) average value.

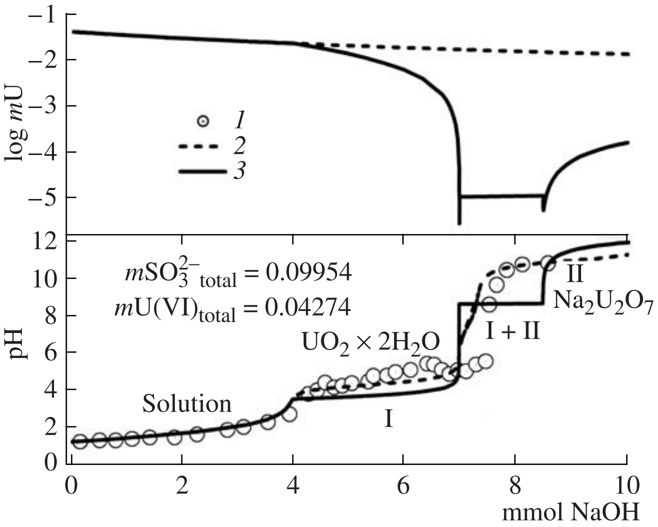

Fig. 7. Experimental and thermodynamic modeling of the potentiometric titration of UO_2SO_4/H_2SO_4 solution with NaOH solution at 25°C and 1 bar in an N_2 atmosphere: (*1*) experimental data of [30]; (*2*) and (*3*) calculated curves of the titration of the same solution (*2*) for the homogeneous system and (*3*) for the case of the precipitation of schoepite (I) and clarkeite (II).

and $UO_2(SO_4)_2^{2-}$, from [11]. The calculations were performed for homogenous (dashed line) and heterogeneous (solid line) systems. In the latter case, schoepite (phase I) and clarkeite (phase II) precipitated from the solution $\log K(S1) = 4.30$ and $\log K(S2) = 7.51$. As can be seen from Fig. 7, the calculations for the homogenous system are in better agreement with the potentiometric titration curve. Inflections at pH = 4 (4 mmol NaOH) and pH = 5 (7 mmol NaOH) are not necessarily related to the precipitation of $UO_2(OH)_2 \times xH_2O$ and $Na_2U_2O_7$ from the solution (explanation proposed in [30]) but may be due to a change in the dominant complexes of U(VI). According to the calculations, the main contribution is from the species $UO_2SO_4^0$, UO_2^{2+}, and $UO_2(SO_4)_2^{2-}$ at pH < 3.7; polymeric hydroxide complexes with Z = +1 at 4 < pH < 5; polymeric hydroxide complexes with $Z = 0$ at 5 < pH < 7.0; polymeric species with $Z = -1$ at 7.0 < pH < 11.0; and UO_4^{2-} at pH > 11. The results of calculations diverge from the experimental data at pH values from 7 to 9, which indicates that the role of negatively charged polymer uranyl complexes with $n > 5$ is underestimated. The system is metastable, and schoepite must crystallize first from the solution already at pH = 3.6, followed by clarkeite at pH > 8.7. The upper panel of Fig. 7 shows the trend of changes in the concentration of uranium in solution. The complete replacement of schoepite by clarkeite requires the addition of 1.5 mmol NaOH into the reaction vessel. The boundaries of precipitation of uranyl hydroxide and sodium diuranate will depend on their phase state and the degree of crystallinity.

The calculations showed that the most abundant U(VI) hydroxide complexes are polymeric species ($n > 3$) in metastable solutions with pH 5–8 strongly oversaturated with respect to thermodynamically stable phases and monomeric species in strongly diluted solutions ($m\mathrm{U} < 1 \times 10^{-7}$). This inference is of fundamental significance for the investigation of the composition of adsorbed particles on mineral surfaces. Samples for spectral investigations (AFM, EXAFS, FTIR, and XANES) are usually prepared from solutions with high contents of U(VI). Owing to this, polymeric species provide the major contribution to spectral lines. Therefore, any conclusions on the composition of surface complexes must be drawn taking into account the initial concentration of metal in the solution from which sorption occurred.

CONCLUSIONS

Based on the analysis of experimental and thermodynamic data, we refined a number of constants of formation of U(VI) hydroxide complexes necessary for the description of the solubility of solid uranium phases within a wide range of acidity of water solutions.

Thermochemical increments were determined for the polymeric species of U(VI) with charges from –1 to +2. They are used for the calculations of the Gibbs free energy of formation of corresponding homologue series.

It was shown that calculations based on the proposed thermodynamic properties of U(VI) polymer hydroxide complexes are in adequate agreement with experimental data obtained in other more complex systems.

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