ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 11, pp. 1976–1984. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © O.V. Nipruk, N.G. Chernorukov, N.S. Zakharycheva, E.L. Kostrova, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 11, pp. 1772–1780.

Study of the State of Uranogermanates $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ in Aqueous Solutions (M^{II} = Mn, Co, Ni, Cu, Zn)

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Received December 25, 2012

Abstract—The state of *d*-elements uranogermanates $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ in aqueous salt solutions in a wide range of ionic strength, ionic composition, and acidity has been investigated. The pH ranges of the uranogermanates stability have been determined, and products of their transformation have been identified. Solubility, solubility equilibrium constant, and Gibbs energy of formation have been determined for the studied uranogermanates. Diagrams of uranium(VI), germanium(IV), and M(II) state in aqueous solutions and in equilibrium solid phases have been plotted.

DOI: 10.1134/S1070363213110029

The studied uranogermanates are representatives of wide class of uranium compounds $M^k(UO_2An)_k \cdot nH_2O$ with M^k being a metal ion and An being PO_4^{3-}, AsO_4^{3-}, VO_4^{3-}, $HSiO_4^{3-}$, or $HGeO_4^{3-}$. From this class, germanium derivatives have been least studied, as germanium is a trace element, and its minerals are scarce. Information to be found in the literature is majorly devoted to preparation and properties of mono- and divalent metals uranogermanates [1–5]. Extending the knowledge, in this paper we report on the state of 3*d*-elements uranogermanates in heterogeneous aqueous systems.

The stationary equilibrium between solid phase(s) and solution is required to properly study heterogeneous aqueous saline systems. In this work, the constancy of pH of the aqueous solution over precipitate was chosen as criterion of equilibration. Indeed, all the ion-molecular interactions in the studied systems involved hydrogen ions uptake or release; thus, pH reflected the state of a system as a whole, and its constancy with time assured the equilibrium state of the system, in particular, no further changes in the solution or solid phase composition [6]. Kinetics of pH change in the case of zinc uranogermanate in the presence of various concentrations of $HClO_4$ or NaOH is presented in Fig. 1. Equilibration time in the $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ – aqueous solution heterogeneous system varied in the range of several days to several months depending on the initial acidity. From Fig. 1, after about 75 days the equilibrium state was attained in all the studied conditions.

Solubility (*S*) of the studied uranogermanates could be defined via the concentration of uranium(VI) c_U, germanium(IV) c_{Ge}, or M^{II} c_M in the saturated aqueous solution equilibrated over the solid phase of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ ($S = 0.5$, $c_U = 0.5б$ $c_{Ge} = c_M$). The aqueous solutions compositions as function of pH are collected in Table 1. All the analyzed liquids were true solutions and did not contain any significant fraction of

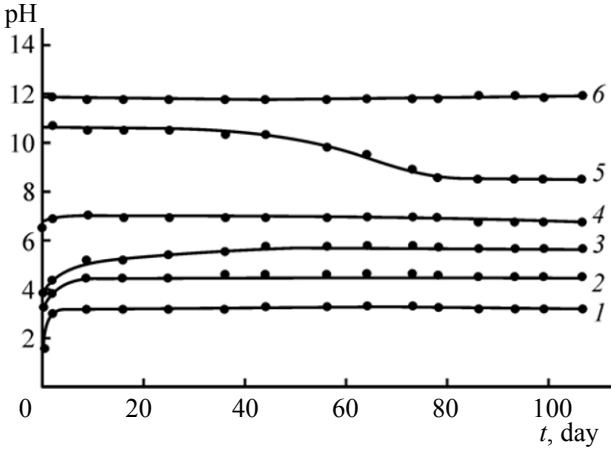

Fig. 1. Kinetics of pH change in aqueous phase of the $Zn(GeUO_6)_2 \cdot 6H_2O_{cr}$–solution system in the presence of (*1*) 10^{-1} mol L^{-1} $HClO_4$, (*2*) 10^{-2} mol L^{-1} $HClO_4$, (*3*) 10^{-3} mol L^{-1} $HClO_4$, (*4*) H_2O, (*5*) 10^{-3} mol L^{-1} NaOH, (*6*) 10^{-2} mol L^{-1} NaOH.

Table 1. Concentrations of U(VI), Ge(IV), and M(II) (mol L^{-1}) in the saturated aqueous solutions of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ [M^{II} = Mn, Co, Ni, Cu, or Zn] at 25°C

Solvent	pH, c_{Ge}, c_U, c_M, mol L^{-1}	Mn	Co	Ni	Cu	Zn
1 mol L^{-1} $HClO_4$	pH[a]	0	0	0	0	0
	$c_U \times 10^2$	5.79±0.09	4.79±0.07	5.48±0.08	5.35±0.08	4.78±0.07
	$c_{Ge} \times 10^2$	5.85±0.10	5.19±0.09	5.00±0.08	5.84±0.09	5.07±0.09
	$c_M \times 10^2$	2.12±0.04	2.14±0.04	2.88±0.05	2.91±0.05	2.22±0.04
1×10^{-1} mol L^{-1} $HClO_4$	pH	2.14	2.64	2.06	2.86	2.95
	$c_U \times 10^2$	4.99±0.08	5.44±0.07	4.01±0.07	5.74±0.09	1.44±0.03
	$c_{Ge} \times 10^2$	5.18±0.08	5.86±0.08	4.19±0.07	4.96±0.08	2.08±0.04
	$c_M \times 10^2$	2.31±0.04	2.79±0.05	2.28±0.04	2.60±0.05	1.90±0.04
1×10^{-2} mol L^{-1} $HClO_4$	pH	3.80	3.93	4.01	3.68	4.46
	$c_U \times 10^3$	19.60±0.43	7.93±0.33	14.80±0.34	1.53±0.02	1.76±0.05
	$c_{Ge} \times 10^3$	15.80±0.30	4.69±0.12	11.00±0.23	2.37±0.07	2.69±0.09
	$c_M \times 10^3$	5.12±0.17	1.22±0.03	4.37±0.14	0.97±0.04	0.52±0.02
1×10^{-3} mol L^{-1} $HClO_4$	pH	5.73	4.95	4.48	4.64	5.69
	$c_U \times 10^4$	4.27±0.18	5.60±0.29	13.60±0.39	4.15±0.19	1.62±0.07
	$c_{Ge} \times 10^4$	9.82±0.46	7.54±0.28	16.30±0.49	2.90±0.09	4.22±0.19
	$c_M \times 10^4$	2.64±0.13	3.58±0.14	6.77±0.27	1.76±0.08	2.07±0.10
H_2O	pH	7.04	6.78	6.59	5.55	6.70
	$c_U \times 10^5$	2.82±0.15	6.75±0.42	15.80±0.68	8.66±0.42	1.23±0.06
	$c_{Ge} \times 10^5$	8.52±0.42	7.54±0.28	16.90±0.52	7.63±0.36	1.02±0.05
	$c_M \times 10^5$	1.38±0.07	1.69±0.10	4.89±0.25	4.07±0.18	3.50±0.18
1×10^{-3} mol L^{-1} NaOH	pH	10.16	10.87	10.19	7.10	8.47
	$c_U \times 10^4$	0.12±0.02	1.38±0.06	1.93±0.09	0.27±0.01	0.10±0.01
	$c_{Ge} \times 10^4$	0.15±0.03	1.02±0.05	2.98±0.13	0.27±0.01	0.32±0.02
1×10^{-2} mol L^{-1} NaOH	pH	11.81	11.94	11.97	8.41	11.90
	$c_U \times 10^4$	1.53±0.08	1.91±0.06	0.99±0.05	0.35±0.02	0.57±0.03
	$c_{Ge} \times 10^4$	9.77±0.37	81.40±2.20	40.40±1.60	0.13±0.07	32.70±1.24
1×10^{-1} mol L^{-1} NaOH	pH	12.09	12.29	12.17	10.68	12.42
	$c_U \times 10^5$	3.50±0.19	2.94±0.16	5.89±0.26	31.50±1.32	6.31±0.37
	$c_{Ge} \times 10^3$	9.42±0.24	3.57±0.12	9.12±0.28	0.24±0.01	7.08±0.30
1 mol L^{-1} NaOH	pH[b]	14	14	14	14	14
	$c_U \times 10^4$	1.99±0.10	3.50±0.12	2.15±0.10	5.56±0.22	1.99±0.08
	$c_{Ge} \times 10^3$	7.18±0.19	3.49±0.11	7.60±0.20	6.68±0.17	7.18±0.19

[a] Calculated from $HClO_4$ concentration. [b] Calculated from NaOH concentration.

Table 2. Equilibrium constants (K) of uranium(VI), germanium(IV), and M(II) reactions in aqueous solutions

Reaction equation	K	References	Reaction equation	K	References
$UO_2^{2+} + H_2O \leftrightarrow UO_2OH^+ + H^+$	5.62×10^{-6}	[7, 8]	$Co^{2+} + 2H_2O \leftrightarrow Co(OH)_2^0 + 2H^+$	1.07×10^{-28}	[10, 11]
$UO_2^{2+} + 2H_2O \leftrightarrow UO_2(OH)_2^0 + 2H^+$	7.08×10^{-13}		$Ni^{2+} + H_2O \leftrightarrow NiOH^+ + H^+$	1.77×10^{-11}	
$UO_2^{2+} + 3H_2O \leftrightarrow UO_2(OH)_3^- + 3H^+$	5.62×10^{-21}		$Ni^{2+} + 2H_2O \leftrightarrow Ni(OH)_2^0 + 2H^+$	1.07×10^{-28}	
$UO_2^{2+} + 4H_2O \leftrightarrow UO_2(OH)_4^{2-} + 4H^+$	3.98×10^{-33}		$Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+$	4.77×10^{-8}	
$2UO_2^{2+} + 2H_2O \leftrightarrow (UO_2)_2OH^{3+} + H^+$	2.00×10^{-3}		$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2^0 + 2H^+$	1.07×10^{-28}	
$2UO_2^{2+} + 2H_2O \leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+$	2.40×10^{-6}		$Zn^{2+} + H_2O \leftrightarrow ZnOH^+ + H^+$	1.14×10^{-9}	
$3UO_2^{2+} + 5H_2O \leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+$	2.82×10^{-16}		$Zn^{2+} + 2H_2O \leftrightarrow Zn(OH)_2^0 + 2H^+$	1.07×10^{-28}	
$3UO_2^{2+} + 7H_2O \leftrightarrow (UO_2)_3(OH)_7^- + 7H^+$	6.31×10^{-33}		$Zn^{2+} + 3H_2O \leftrightarrow Zn(OH)_3^- + 3H^+$	4.38×10^{-29}	
$4UO_2^{2+} + 7H_2O \leftrightarrow (UO_2)_4(OH)_7^+ + 7H^+$	1.26×10^{-22}		$Zn^{2+} + 4H_2O \leftrightarrow Zn(OH)_4^{2-} + 4H^+$	6.98×10^{-42}	
$Ge(OH)_4 \leftrightarrow GeO(OH)_3^- + H^+$	4.79×10^{-10}	[9]	$Mn(OH)_2 \leftrightarrow Mn^{2+} + 2OH^-$	1.44×10^{-13}	
$GeO(OH)_3^- \leftrightarrow GeO_2(OH)_2^{2-} + H^+$	1.91×10^{-13}		$Co(OH)_2 \leftrightarrow Co^{2+} + 2OH^-$	1.49×10^{-15}	
$Mn^{2+} + H_2O \leftrightarrow MnOH^+ + H^+$	1.80×10^{-11}	[10, 11]	$Ni(OH)_2 \leftrightarrow Ni^{2+} + 2OH$	5.86×10^{-18}	
$Mn^{2+} + 2H_2O \leftrightarrow Mn(OH)_2^0 + 2H^+$	1.07×10^{-28}		$Cu(OH)_2 \leftrightarrow Cu^{2+} + 2OH^-$	4.39×10^{-20}	
$Mn^{2+} + 3H_2O \leftrightarrow Mn(OH)_3^- + 3H^+$	7.12×10^{-35}		$Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-$	2.67×10^{-16}	
$Mn^{2+} + 4H_2O \leftrightarrow Mn(OH)_4^{2-} + 4H^+$	9.95×10^{-51}		$GeO_2 + 2H_2O \leftrightarrow Ge(OH)_4^0$	4.51×10^{-2}	[9]
$Co^{2+} + H_2O \leftrightarrow CoOH^+ + H^+$	6.54×10^{-12}		$Na_2U_2O_{7\,к} + 3H_2O \leftrightarrow 2Na^+ + 2UO_2^{2+} + 6OH^-$	8.55×10^{-56}	

colloid particles, as revealed by nephelometry and turbidimetry. The light scattering of the $M^{II}(HGeUO_6)_2\cdot 6H_2O$ saturated solutions did not exceed that of distilled water; the opacification of the solutions at 450–750 nm was below 0.005 with respect to distilled water.

Using the data from Table 1, we calculated the equilibrium constants of heterogeneous dissolution process. The calculations were performed according to reaction equation (1).

$$M^{II}(HGeUO_6)_2\cdot 6H_2O_{cr} + 2H^+_{sol} \leftrightarrow M^{2+}_{sol} + 2UO_2^{2+}{}_{sol} + 2H_2GeO_4^{2-}{}_{sol} + 6H_2O_L. \quad (1)$$

The equilibrium constant K_S of that reaction was defined by Eq. (2).

$$K_S = a(M^{2+})\, a(UO_2^{2+})^2\cdot a(2H_2GeO_4^{2-})^2\cdot a(H^+)^{-2}. \quad (2)$$

When calculating activities of the ions appearing in Eq. (2), we took into account that the elements could exist in various ion-molecular forms in aqueous solutions (Table 2) [7–11]. The ions activity coefficients were calculated according to the Debye-Hückel equation and the specific ionic interaction theory [7]. The calculation principle is described in detail in [12].

The log K_S values for the studied uranogermanates are collected in Table 3; log K_S increased in the series Cu→Co→Zn→Ni→Mn in accordance with the Goldschmidt atomic radii of M. However, due to the structural similarity and close physico-chemical properties of M(II), the changes of K_S values in that series was not dignificant.

From the determined equilibrium constants of dissolution, the Gibbs free energy of the uranogermanates formation was calculated according to Eq. (3).

$$\Delta G_r = -RT\ln K_S,$$
$$\Delta_f G^0[M^{II}(HGeUO_6)_2\cdot 6H_2O_{cr}] = \Delta_f G^0(M^{2+}) + 2\Delta_f G^0(UO_2^{2+}) + 2\Delta_f G^0(H_2GeO_4^{2-}) + 6\Delta_f G^0(H_2O) - \Delta G^0_r. \quad (3)$$

In Eq. (3), ΔG_f^0 is standard Gibbs energy of the corresponding ions and molecules formation [7–9];

ΔG_r^0 is the Gibbs energy of reaction (1). The calculation results are given in Table 3.

The above-described results did not account for possibility of processes other than dissolution. We further theoretically studied the state of the uranogermanates in aqueous solutions including the processes of the secondary compounds formation [GeO_2, $M(OH)_2$, and $Na_2U_2O_7$] in the model. The calculation method was described in detail in [6, 12]. Here, we present the results of the state of the $M^{II}(HGeUO_6)_2 \cdot 6H_2O$–aqueous solution systems simulation at pH of 0–14. The calculated phase compositions of U(VI), Ge(IV), and M(II) species in the solid phases and in the saturated aqueous solutions are given in Figs. 2–5 along with theoretical solubility curves for cobalt and zinc uranogermanates. The shading marks the pH ranges at which the uranogermanates decomposed into secondary compounds (various shading types correspond to various qualitative compositions of the bottom phase).

The experimental study and simulation of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ state showed that the behavior of 3*d*-elements uranogermanates in aqueous solutions was in general identical to that of alkaline metal derivatives studied previously [5]. It particular, the effect of various factors on the stability of alkaline and 3*d*-elements uranogermanates was similar, due to their structural and functional similarity. Of the considered factors (acidity, ionic strength, and anionic composition), it was acidity that majorly influenced the state of 3*d*-elements uranogermanates in aqueous solutions. The pH value defined composition and structure of the equilibrium solid phase, solubility of the crystalline compound, and the primary form of U(VI), Ge(V), and M(II) in solution. The studied uranogermanates were stable in a limited pH range (from 2 to 8–10), expanding in the Cu→Co→Ni→Zn→Mn series along with increasing M radius. Outside that pH range, uranogermanates decomposed with formation of various compounds, their nature depending on pH. From Fig. 2a, in the acidic medium (at pH 3–4) the studied uranogermanates were transformed into crystalline germanium oxide [Eq. (4)].

$$M^{II}(HGeUO_6)_2 \cdot 6H_2O_{cr} + 2H^+_{sol} \leftrightarrow M^{2+}_{sol} + 2GeO_{2s} + 2UO_2^{2+}{}_{sol} + 10H_2O_L. \quad (4)$$

In the alkaline solutions, at pH 8–10, the studied compounds were transformed into less soluble 3*d*-elements hydroxides; in the strongly alkaline media the transformation was complete. As a result, the solid phase was converted into a mixture of $M^{II}(OH)_2$ and $Na_2U_2O_7$ [Eq. (5)].

$$M^{II}(HGeUO_6)_2 \cdot 6H_2O_{cr} + 6NaOH_{sol} \leftrightarrow M^{II}(OH)_{2\,am} + Na_2U_2O_{7\,cr} + Na_2H_2GeO_{4,sol} + 7H_2O_L. \quad (5)$$

Table 3. Equilibrium constant of dissolution reactions K_S and standard Gibbs energy of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ formation

Compound	log K_S	$-\Delta_f G^0$, kJ mol^{-1}
$Mn(HGeUO_6)_2 \cdot 6H_2O$	–31.41±0.25	5403±20
$Co(HGeUO_6)_2 \cdot 6H_2O$	–32.19±0.28	5249±20
$Ni(HGeUO_6)_2 \cdot 6H_2O$	–31.95±0.34	5239±20
$Cu(HGeUO_6)_2 \cdot 6H_2O$	–33.56±0.19	5137±20
$Zn(HGeUO_6)_2 \cdot 6H_2O$	–32.14±0.38	5342±20

In the case of zinc salt, at $c_{NaOH} \geq 0.1$ mol L^{-1} amphoteric $Zn(OH)_2$ was dissolved, and $Na_2U_2O_7$ was the only solid phase constituent. The formation of secondary sparingly soluble compounds such as GeO_2, $M^{II}(OH)_2$, and $Na_2U_2O_7$ was confirmed by X-ray diffraction patterns of the calcined bottom phase [13–15], and by the calculated composition diagrams of solid phases (Fig. 2).

The composition of the saturated aqueous solutions agreed well with the reaction equations shown above and with composition of the equilibrium bottom phases (Fig. 2). In the pH range of the studied uranogermanates stability, U(IV), Ge(IV), and M(II) were transferred into solution in the stoichiometric ratio of 2 : 2 : 1. The calculated pH profiles of c_U and c_{Ge} coincided, whereas the c_M curve of the similar shape was shifted towards lower log *c* values by log 2. The solubility of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ ($S = 0.5$, $c_U = 0.5$, $c_{Ge} = c_M$) in that pH range was changed by several orders, from 10^{-6}–10^{-5} mol L^{-1} at pH 8–9 to 10^{-2} mol L^{-1} at pH 3–4. In the alkaline medium, upon formation of even small amount ($\omega < 0.01$) of $M^{II}(OH)_2$ in the solid phase, the concentration curves were no longer matching, and c_M was defined by $M^{II}(OH)_2$ solubility. At pH > 11, germanium was leached, and its concentration in solution became constant. Uranium concentration in solution was determined by solubility of $Na_2U_2O_7$ formed in the solid phase from the initial uranogermanates. Upon decay of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ in the acidic medium with formation of germanium oxide, U(VI) and M(II) completely passed into the solution, and their concentrations became constant (Fig. 2). The pH profile of germanium(IV) concentra-

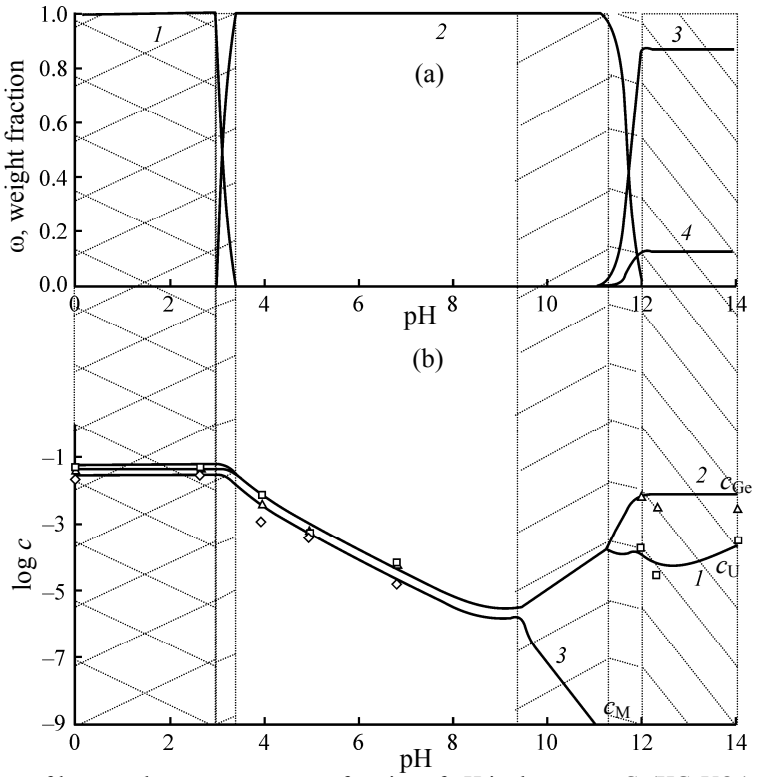

Fig. 2. (a) Weight fraction ω of bottom phase components as function of pH in the system $Co(HGeUO_6)_2 \cdot 6H_2O_{cr}$–water ($m$ = 0.15 g, V = 0.1 L): (*1*) GeO_2, (*2*) $Co(HGeUO_6)_2 \cdot 6H_2O$. (b) U(VI), Ge(IV), and Co(II) concentrations in solution as function of pH in the system $Co(HGeUO_6)_2 \cdot 6H_2O_{cr}$–water. Calculated curves are in lines, experimental values are in symbols; (*1*) c_U, (*2*) c_{Ge}, (*3*) c_{Co}.

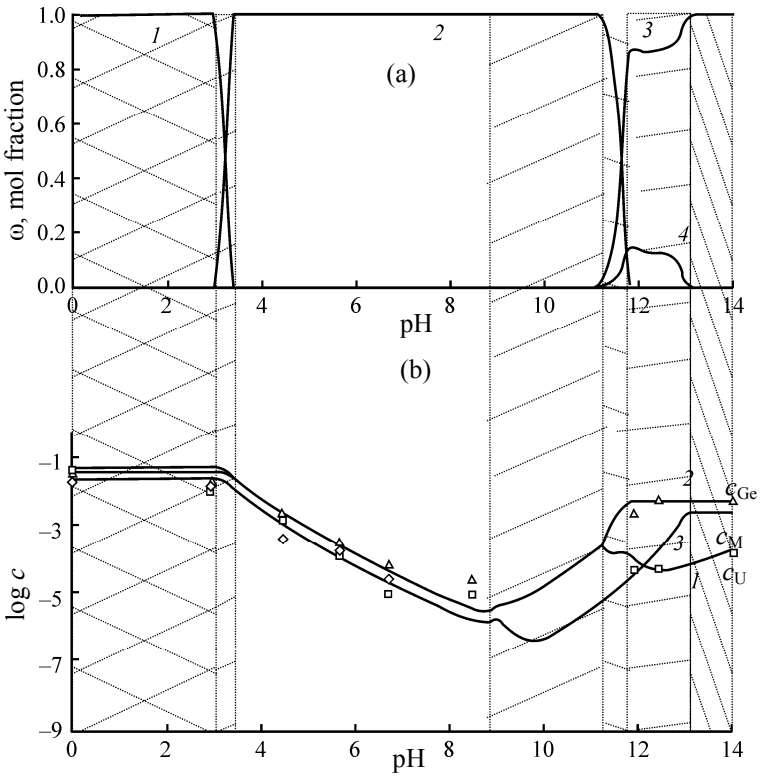

Fig. 3. *(a)* Weight fraction ω of bottom phase components as function of pH in the system $Zn(HGeUO_6)_2 \cdot 6H_2O_{cr}$–water ($m$ = 0.15 g, V = 0.1 L): (*1*) GeO_2, (*2*) $Zn(HGeUO_6)_2 \cdot 6H_2O$. (b) U(VI), Ge(IV), and Zn(II) concentrations in solution as function of pH in the system $Zn(HGeUO_6)_2 \cdot 6H_2O_{cr}$–water. Calculated curves are in lines, experimental values are in symbols (*1*) c_U, (*2*) c_{Ge}, (*3*) c_{Zn}.

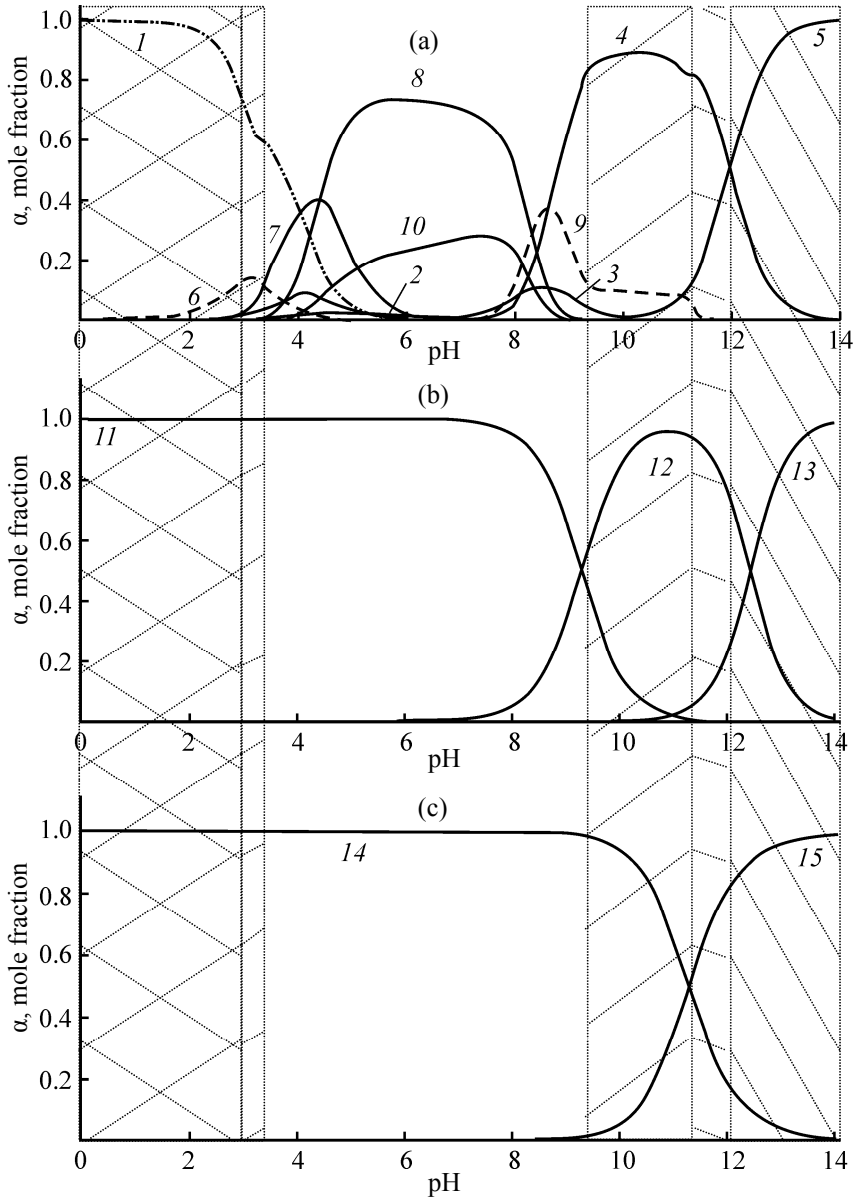

Fig. 4. The state of (a) U(VI), (b) Ge(IV), and (c) Co(II) in aqueous solutions of $Co(HGeUO_6)_2 \cdot 6H_2O$ as function of pH: (*1*) UO_2^{2+}, (*2*) $UO_2(OH)^+$, (*3*) $UO_2(OH)_2^0$, (*4*) $UO_2(OH)_3^-$, (*5*) $UO_2(OH)_4^{2-}$, (*6*) $(UO_2)_2(OH)^{3+}$, (*7*) $(UO_2)_2(OH)_2^{2+}$, (*8*) $(UO_2)_3(OH)_5^+$, (*9*) $(UO_2)_3(OH)_7^-$, (*10*) $(UO_2)_4(OH)_7^+$, (*11*) $H_4GeO_4^0$, (*12*) $H_3GeO_4^-$, (*13*) $H_2GeO_4^{2-}$, (*14*) Co^{2+}, (*15*) $CoOH^+$.

tion under those conditions was determined by GeO_2 solubility.

The medium acidity not only influenced the bottom phase composition, it also determined the ionic-molecular composition of saturated aqueous solutions (Figs. 4 and 5). Upon uranogermanates decomposition in the acidic medium to form germanium oxide, the cationic species of uranium UO_2^{2+} and metal M^{2+} predominated in solution, whereas germanium state was the most protonated form $H_4GeO_4^0$. In the region of uranogermanates stability, with increasing pH the charges of the dissolved species decreased. In even more alkaline medium, more of hydroxyl groups were added to the soluble species, and finally the corresponding hydroxides precipitated into the bottom phase. In strongly alkaline solutions, the following anionic species predominated in the solution: $UO_2(OH)_4^{2-}$, $GeO_2(OH)_2^{2-}$, $Mn(OH)_3^-$, and $Zn(OH)_4^{2-}$ (M = Mn, Zn). In the cases of cobalt, nickel, and copper uranogermanates, $M(OH)^+$ was majorly present in the solutions.

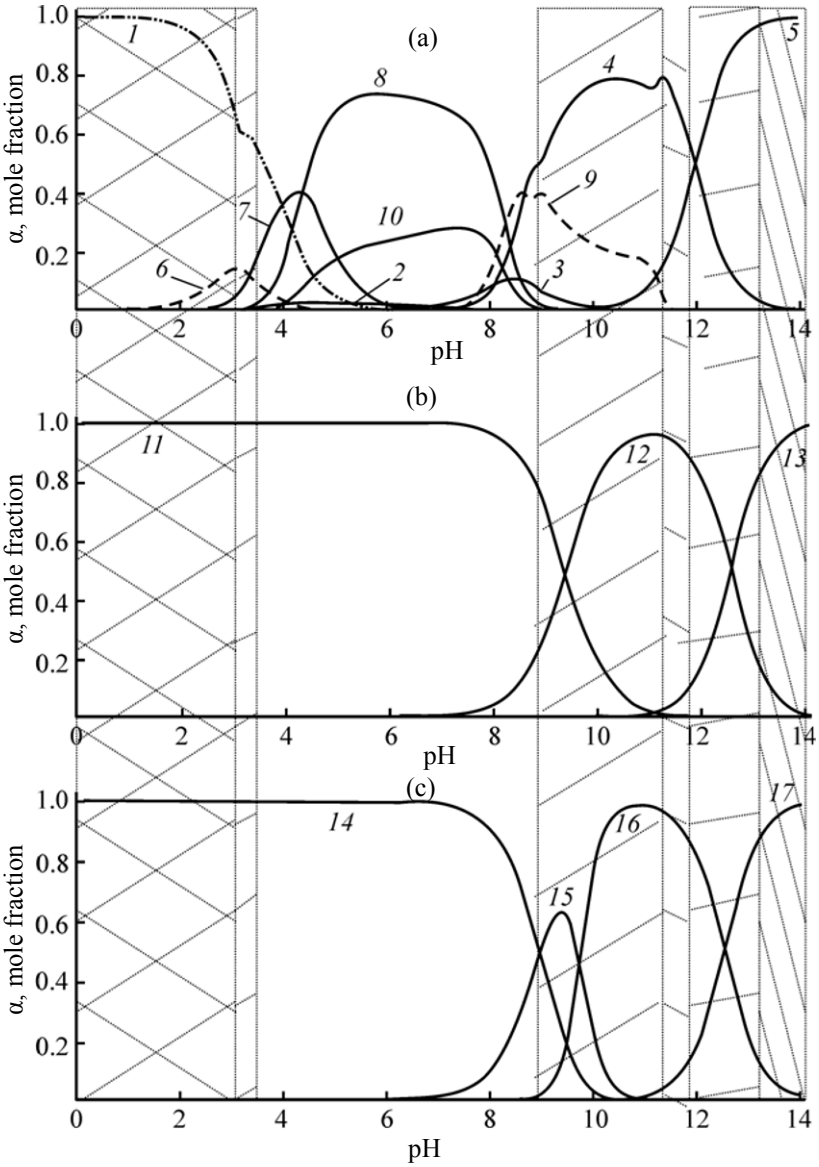

Fig. 5. The state of (a) U(VI), (b) Ge(IV), and (c) Zn(II) in aqueous solutions of $Zn(HGeUO_6)_2 \cdot 6H_2O$ as function of pH: (*1*) UO_2^{2+}, (*2*) $UO_2(OH)^+$, (*3*) $UO_2(OH)_2^0$, (*4*) $UO_2(OH)_3^-$, (*5*) $UO_2(OH)_4^{2-}$, (*6*) $(UO_2)_2(OH)^{3+}$, (*7*) $(UO_2)_2(OH)_2^{2+}$, (*8*) $(UO_2)_3(OH)_5^+$, (*9*) $(UO_2)_3(OH)_7^-$, (*10*) $(UO_2)_4(OH)_7^+$, (*11*) $H_4GeO_4^0$, (*12*) $H_3GeO_4^-$, (*13*) $H_2GeO_4^{2-}$, (*14*) Zn^{2+}, (*15*) $Zn(OH)_4^{2-}$.

To check the validity of the reported results, we plotted the experimental values of uranium, germanium, and cobalt or zinc concentrations in Figs. 2 and 3. The calculated curves were in good agreement with the experimental data over a wide range of pH. Thus, the proposed physico-chemical description can be applied to theoretically predict the states of compounds in their aqueous solutions at the conditions not accessible experimentally.

To conclude, the studied 3*d*-elements uranogermanates were stable in aqueous media at pH 3 to pH 8–10. Outside that region they decomposed to to form GeO_2, $M^{II}(OH)_2$, and $Na_2U_2O_7$. The solubility of $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ varied from 10^{-6}–10^{-5} mol L^{-1} in weakly alkaline solutions up to 10^{-2} mol L^{-1} in acidic or strongly alkaline media.

EXPERIMENTAL

The X-ray powder diffraction patterns were recorded with Shimadzu XRD-6000 diffractometer (CuK_α radiation). The constant temperature was maintained with Lauda alpha F 24 thermostat. The photometric measurements were performed with Shimadzu UV-1650 spectrophotometer. Intensity of scattered light

was measured with NFM nephelometer (Russia). The solid phase was separated from saturated solution using TSLN-2 centrifuge. The solutions pH was determined with pH 410 pH-meter (Akvilon) equipped with ESK-10601/7 glass electrode. CO_2-free twice-distilled water [26, 27] was used for all the experiments. CO_2-free solutions of sodium hydroxide were prepared as described in [16]. The reagents used in this work were of the chemical pure grade. Mathematical simulation and was performed using the Mathcad 8.0 software.

Uranogermanates $M^{II}(HGeUO_6)_2 \cdot 6H_2O$ (M^{II} = Mn, Co, Ni, Cu, or Zn) were prepared by precipitation from aqueous solutions containing soluble GeO_2 modification, chloride of the corresponding 3*d*-element, and uranyl acetate in the ratio of M^{II} : Ge : U = 1 : 2 : 2 [Eq. (6)].

$$M^{2+}_{sol} + UO_2^{2+}{}_{sol} + GeO_{2\,sol} + 10H_2O_L \rightarrow M^{II}(HGeUO_6)_2 \cdot 6H_2O_{cr} + 6H^+. \quad (6)$$

100 mg of germanium oxide was dissolved in 20 mL of water at 90°C, and solutions of uranyl acetate and 3*d*-element chloride (10 mL of each) were added. The resulting solution was transferred to the quartz ampoule and kept at 90°C during 2 days (M = cobalt, nickel, copper, and zinc). Manganese uranogermanate was obtained at 5°C because of redox instability of Mn^{2+} ions. The so prepared amorphous compounds were crystallized in mother liquor at 60°C during 20 h. The precipitated crystals were washed with distilled water and dried in air [4].

Phase homogeneity of the synthesized samples was confirmed by X-ray powder diffraction analysis. The resulting X-ray patterns were compared with the available published data [4].

In a typical experiment on the state of the prepared compounds, a weighted sample of the substance (0.1–0.3 g) was put in water or in the solution of $HClO_4$ or NaOH ($c = 10^{-3}$–1 mol L^{-1}, 5–100 mL). In order to prevent contact with atmospheric carbon dioxide, the experiments were performed in plastic leakless containers filled as full as possible. The containers were kept at (25.00±0.05)°C, periodically stirred, and pH was measured to check the approach to equilibrium state. After pH became constant, the precipitate was separated from a solution by centrifuging, washed with distilled water, dried at room temperature, and studied by X–ray diffraction.

Concentrations of uranium(VI), germanium(IV), and M(II) in the saturated aqueous solutions were determined by photometry. U(VI) was determined after its reaction with arsenazo III (λ_{max} = 650 nm, pH = 3) [17]. A standard solution of U(VI) was prepared by dissolution of $UO_2(NO_3)_2 \cdot 6H_2O$ in water [18]. Ge(IV) was determined by photometry of the reduced heteropolymolybdate (λ_{max} = 810 nm, ascorbic acid as reducing agent) [19]. Ge(IV) standard solution was prepared by fusion of GeO_2 calcined powder with Na_2CO_3 in platinum crucible with subsequent cooling and dissolution in water [18]. Concentrations of Mn, Co, Ni, Cu, and Zn were determined after their reactions with 4-(pyridin-2-ylazo)resorcin [20], nitroso-R-salt [21], dimethylglyoxime [22], diethyldithiocarbamate [23], and sulfasarsazen [24], respectively. Standard solutions of the elements were prepared as described in [18].

ACKNOWLEDGMENTS

This work was performed in the frame of the Federal Target Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia" for 2009–2013.

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