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Study of the State of Uranoarsenates $M^{II}(AsUO_6)_2{\cdot}nH_2O$ ($M^{II} = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}$) in Aqueous Solutions

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Abstract—State of uranoarsenates $M^{II}(AsUO_6)_2{\cdot}nH_2O$ (M^{II} = Mn, Co, Ni, Cu, Zn, Cd, Pb) in aqueous solutions in a wide range of acidity (pH 0–14) was studied. Acid–base boundaries of existence of the compounds were estimated, products of conversion were identified, and solubility of $M^{II}(AsUO_6)_2{\cdot}nH_2O$ was determined. On the basis of the obtained data the solubility products and Gibbs functions of formation of uranoarsenates, and the solubility curves were calculated, phase diagrams of uranium(VI) and arsenic(V) in solutions and in equilibrium solid phases were constructed with the use of the equilibrium thermodynamics technique.

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Earlier we have published [1, 2] results of physicochemical study of the state of uranoarsenates and uranophosphates of alkali and alkaline-earth metals in aqueous solutions and have calculated solubility products of low-soluble compounds on this basis. The attention to the compounds $M^k\,(B^VUO_6)_k{\cdot}nH_2O$ (M^k are of various metals with the oxidation states +1, +2, +3; B^V = As, P) is caused by the fact that many of them are minerals and there is a probability of their formation when radioactive uranium-containing waste penetrates into natural environment. Published works devoted to the determination of solubility of uranophosphates of some 3d transition elements [3, 4] are known. The problem of the state of uranoarsenates of d elements and lead in heterogeneous aqueous–salt systems was not studied. In this communication we present the results of a complex study of the state of manganese, cobalt, nickel, copper, zinc, cadmium, and lead uranoarsenates in water and aqueous solutions of perchloric acid and sodium hydroxide at 25°C.

The state of the heterogeneous aqueous-salt systems depends on a number of factors related to the composition of an aqueous solution and the nature of a metal M^{II}. The acidity of aqueous solutions influences the most essentially on the chemical stability of $M^{II}(AsUO_6)_2{\cdot}nH_2O$ compounds. The value of pH defines the direction and depth of conversion of uranoarsenates in the bottom phase, the concentration and form of existence of uranium(VI), arsenic(V), and M(II) in aqueous solutions. It was found that uranoarsenates of *d* elements and lead retain their individuality in the heterogeneous systems under study only in a limited acidity range at pH from 2 up to 8. In acid media at pH < 2 as a result of ion exchange the crystalline solid phases convert to uranoarsenic acid by reaction (1).

$$M^{II}(AsUO_6)_2{\cdot}nH_2O(cr) + 2H^+(sol) \rightleftarrows M^{2+}(sol) + 2HAsUO_6{\cdot}4H_2O(cr) + (n-8)H_2O(l). \quad (1)$$

The formation of an acid was estimated by the X-ray method (Fig. 1) and confirmed by the appearance in the IR spectrum of an intensive band $\delta(H_3O^+)$ at 1737 cm^{-1}, which is characteristic for $HAsUO_6{\cdot}4H_2O$ [5]. Calculations based on Table 1 where the concentrations of U(VI), As(V), and M(II) in heterogeneous systems are presented also confirm the fact that under these conditions M(II) completely passes into solution. In alkaline media at pH > 8 uranoarsenates are decomposed owing to the formation of amorphous $M^{II}(OH)_2$ hydroxides. Aresic(V) is completely leached from the solid phase, and its concentration in the solution becomes constant (Table 1). Under these conditions U(VI) remains in the solid phase in the form of the low-soluble compounds $UO_3{\cdot}2H_2O$ (8 < pH < 11) and $Na_2U_2O_7$ (pH > 11). The conversion of uranoarsenates in alkaline region can be represented by Eqs. (2), (3).

$$M^{II}(AsUO_6)_2{\cdot}nH_2O(cr) + 6NaOH(sol) \rightleftarrows 2UO_3{\cdot}2H_2O(cr) + M^{II}(OH)_2(cr) + 2Na_3AsO_4(sol) + (n-2)H_2O(l)\ (8 < pH < 11). \quad (2)$$

$$M^{II}(AsUO_6)_2{\cdot}nH_2O(cr) + 6NaOH(sol) \rightleftarrows Na_2U_2O_7(cr) + M^{II}(OH)_2(cr) + 2Na_2HAsO_4(sol) + (n+1)H_2O(l)\ (pH > 11). \quad (3)$$

The formation of low-soluble compounds of a secondary origin was determined by comparison of X-ray patterns of the bottom phase annealed at 280°C with a set of X-ray maxima of reflection for the corresponding compounds (Fig. 1) [5–9]. In the range of $2 < pH < 8$ the structure of uranoarsenates is retained and the concentrations of U(VI), As(V), M(II) in saturated solutions are defined by uranoarsenates solubility, which varies from 10^{-6} M in neutral solutions up to 10^{-3} M in acid media. The difference in the solubility of uranoarsenates of 3*d*-transition elements lies within the experimental error limits. Sizes of ions of cadmium ($r_{Cd^{2+}}$ 0.99 nm) and especially lead ($r_{Pb^{2+}}$ 1.29 nm) are already of such a value that the solubility of the corresponding compounds decreases (Table 1).

In the present work using the equilibrium thermodynamics techniques we have fulfilled the quantitative description of the equilibria established in the aqueous-salt systems under study. It allowed us to use the obtained experimental data for the calculation of solubility products of low-soluble compounds $M^{II}(AsUO_6)_2{\cdot}nH_2O$, thermodynamic functions of formation of uranoarsenates of *d*-elements and lead, and phase diagrams of uranium(VI) and arsenic(V) in aqueous solutions and in solid phases. Let us consider the essence of the developed physicochemical description and principles of calculation using it. Passing of a low-soluble uranoarsenate into solution can be presented in the form of generally accepted formal reaction (4).

$$M^{II}(AsUO_6)_2{\cdot}nH_2O(cr) \rightleftarrows M^{2+}(sol) + 2UO_2^{2+}(sol) + 2AsO_4^{3-}(sol) + nH_2O(l). \quad (4)$$

The equilibrium constant of this reaction is the solubility product K_s [Eq. (5)].

$$K_s = a(M^{2+}){\cdot}a(UO_2^{2+})^2{\cdot}a(AsO_4^{3-})^2. \quad (5)$$

When calculating activities of ions appearing in Eq.(5) we took into account the fact that U(VI), As(V), and M(II) exist in aqueous solutions as various ion-molecular forms presented in Table 2 [10–14]. Activity

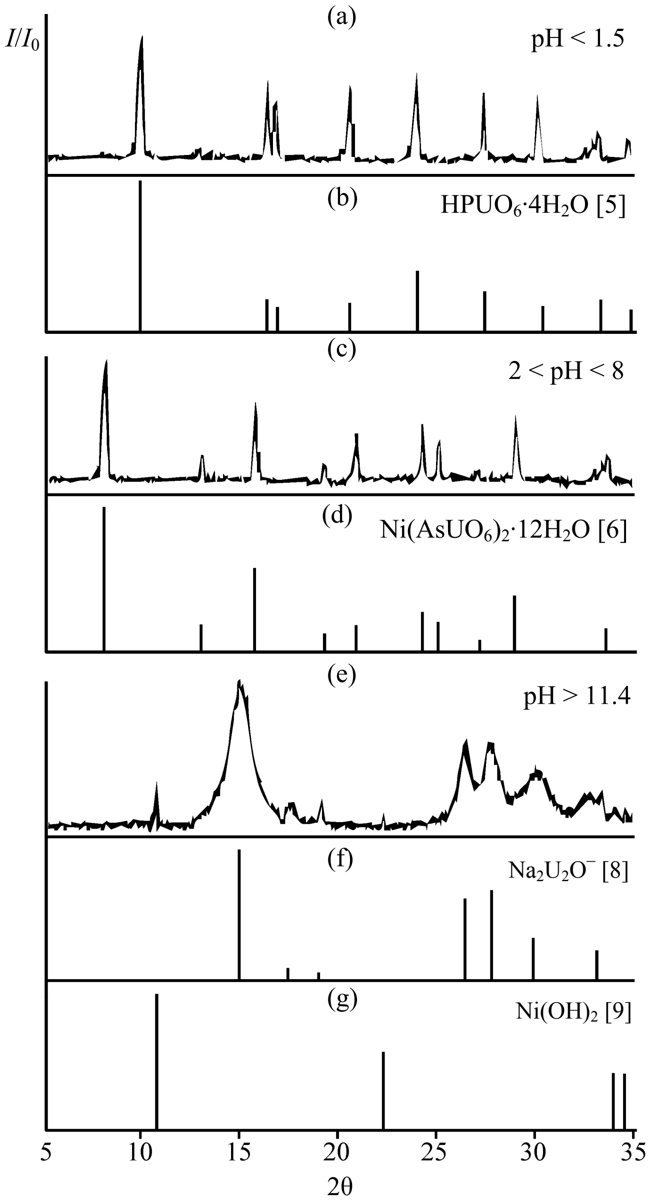

Fig. 1. X-ray patterns of bottom phases in the system $Ni(AsUO_6)_2{\cdot}12H_2O(cr)$–aqueous solution: (a), (c), (e) our data; (b), (d), (f), (g) published data.

coefficients of ions were calculated by Debye–Höckel equation (6) in view of the specific ionic interaction theory [11].

$$\log \gamma_{z\pm} = -z^2{\cdot}[(0.5090\sqrt{\mu}/(1 + 1.5\sqrt{\mu})] + \sum_m \varepsilon_{(z\pm,m,\mu)}{\cdot}c_m. \quad (6)$$

Here μ is an ionic strength of a solution; $\varepsilon_{(z\pm,m,\mu)}$ is a coefficient of ionic interaction of an ion having a charge $z^{\pm}$ with counterions (a total number of the considered ions is *m*) [11]; c_m is a molar concentration of the *m*th counterion in the solution.

Table 1. Concentrations of U(VI), As(V), and M(II) in saturated aqueous solutions obtained by dissolving of $M^{II}(AsUO_6)_2\cdot nH_2O$ compounds (25°C)

Solvent	pH, c_{As}, c_U, c_M, M	M^{II}, n^a						
		Mn, 12	Co, 12	Ni, 12	Cu, 8	Zn, 12	Cd, 10	Pb, 8
1×10^{-1} M $HClO_4$	pH	1.40	1.45	1.45	1.42	1.42	1.32	1.32
	$c_U\times10^3$	8.51±0.26	7.41±0.22	7.18±0.22	7.59±0.22	8.34±0.25	10.0±0.3	9.33±0.28
	$c_{As}\times10^3$	8.91±0.27	8.51±0.26	7.48±0.22	7.76±0.23	7.38±0.22	8.91±0.27	8.13±0.24
	$c_M\times10^3$	5.13±0.26	4.57±0.23	5.13±0.26	5.25±0.26	5.01±0.25	5.62±0.28	4.65±0.23
1×10^{-2} M $HClO_4$	pH	2.16	2.01	2.10	2.02	1.93	2.11	2.00
	$c_U\times10^3$	1.21±0.05	1.21±0.05	1.05±0.04	2.09±0.08	2.24±0.09	1.13±0.05	0.86±0.03
	$c_{As}\times10^3$	1.02±0.04	1.08±0.04	0.85±0.03	2.10±0.08	2.40±0.10	1.05±0.04	0.97±0.04
	$c_M\times10^3$	0.51±0.04	0.51±0.03	0.46±0.03	1.02±0.05	1.15±0.07	0.48±0.03	0.46±0.03
1×10^{-3} M $HClO_4$	pH	3.08	3.06	3.08	3.17	3.05	3.06	3.10
	$c_U\times10^4$	1.02±0.05	1.18±0.06	0.94±0.05	0.85±0.04	1.35±0.07	0.93±0.05	0.56±0.03
	$c_{As}\times10^4$	1.25±0.06	1.03±0.05	0.95±0.05	0.99±0.05	1.17±0.06	1.07±0.05	0.57±0.03
	$c_M\times10^4$	0.52±0.03	0.50±0.03	0.47±0.03	0.46±0.03	0.56±0.05	0.49±0.03	0.29±0.02
1×10^{-4} M $HClO_4$	pH	4.48	4.52	4.68	4.74	4.65	4.54	4.36
	$c_U\times10^6$	9.12±0.46	6.03±0.30	5.50±0.28	5.01±0.30	5.61±0.28	7.41±0.45	8.51±0.51
	$c_{As}\times10^6$	14.5±0.9	9.12±0.55	5.75±0.35	6.76±0.41	8.45±0.51	10.0±0.6	8.71±0.44
H_2O	pH	6.24	6.41	6.45	5.98	6.32	6.21	6.21
	$c_U\times10^6$	2.00±0.14	1.23±0.08	1.29±0.09	1.51±0.12	1.10±0.09	1.32±0.11	1.45±0.12
	$c_{As}\times10^6$	3.98±0.24	2.34±0.14	2.00±0.12	2.88±0.17	2.00±0.12	2.00±0.12	1.51±0.09
1×10^{-4} M NaOH	pH	7.20	7.64	7.05	7.47	7.15	7.50	7.50
	$c_U\times10^6$	1.78±0.12	1.86±0.13	1.35±0.09	1.95±0.14	1.20±0.10	1.58±0.13	2.06±0.14
	$c_{As}\times10^6$	3.24±0.23	2.82±0.20	2.19±0.15	5.01±0.35	2.29±0.16	3.16±0.22	1.98±0.14
1×10^{-3} M NaOH	pH	7.64	8.87	7.85	9.55	7.99	8.80	9.89
	$c_U\times10^6$	2.24±0.13	4.47±0.27	1.51±0.09	6.99±0.42	1.51±0.11	5.89±0.41	93.3±5.6
	$c_{As}\times10^6$	4.17±0.17	8.32±0.33	2.29±0.09	1380±50	2.51±0.10	11.2±0.5	158±6
1×10^{-2} M NaOH	pH	10.77	11.60	10.91	11.10	10.79	11.60	10.95
	$c_U\times10^5$	5.25±0.26	11.5±0.6	7.76±0.38	13.5±0.5	0.73±0.03	18.2±0.7	14.8±0.6
	$c_{As}\times10^3$	3.31±0.10	2.95±0.09	2.33±0.07	2.51±0.08	3.31±0.10	2.40±0.07	2.33±0.07
1×10^{-1} M NaOH	pH^b	13.00	13.00	13.00	13.00	13.00	13.00	13.00
	$c_U\times10^5$	3.47±0.17	3.55±0.18	0.41±0.02	4.07±0.20	3.98±0.20	4.68±0.23	6.31±0.32
	$c_{As}\times10^3$	2.88±0.09	2.75±0.08	2.57±0.08	2.75±0.08	2.63±0.08	2.48±0.06	2.55±0.08
1 M NaOH	pH^b	14.00	14.00	14.00	14.00	14.00	14.00	14.00
	$c_U\times10^5$	8.51±0.34	9.12±0.37	10.5±0.4	9.55±0.38	13.8±0.6	11.7±0.5	10.5±0.4
	$c_{As}\times10^3$	2.63±0.11	2.75±0.11	2.34±0.09	3.02±0.12	2.57±0.10	2.63±0.11	2.53±0.10

[a] *n* is the coordination number. [b] Calculated proceeding from NaOH concentration.

Table 2. Equilibrium constants of reactions of As(V), U(VI), and M(II) in aqueous solution

Reaction equation	*K*	References	Reaction equation	*K*	References
$H_3AsO_4^0 \rightleftarrows H^+ + H_2AsO_4^+$	$5.75{\times}10^{-3}$	[10]	$Cu^{2+} + H_2O \rightleftarrows CuOH^+ + H^+$	$4.76{\times}10^{-8}$	[13]
$H_2AsO_4^- \rightleftarrows H^+ + HAsO_4^{2-}$	$1.74{\times}10^{-7}$	″	$Cu^{2+} + 2H_2O \rightleftarrows Cu(OH)_2^0 + 2H^+$	$1.07{\times}10^{-28}$	″
$HAsO_4^{2-} \rightleftarrows H^+ + AsO_4^{3-}$	$2.51{\times}10^{-12}$	″	$Zn^{2+} + H_2O \rightleftarrows ZnOH^+ + H^+$	$1.14{\times}10^{-09}$	″
$UO_2^{2+} + H_2O \rightleftarrows UO_2OH^+ + H^+$	$5.62{\times}10^{-6}$	[11, 12]	$Zn^{2+} + 2H_2O \rightleftarrows Zn(OH)_2^0 + 2H^+$	$1.07{\times}10^{-28}$	″
$UO_2^{2+} + 2H_2O \rightleftarrows UO_2(OH)_2^0 + 2H^+$	$7.08{\times}10^{-13}$	″	$Zn^{2+} + 3H_2O \rightleftarrows Zn(OH)_3^- + 3H^+$	$4.38{\times}10^{-29}$	″
$UO_2^{2+} + 3H_2O \rightleftarrows UO_2(OH)_3^- + 3H^+$	$5.62{\times}10^{-21}$	″	$Zn^{2+} + 4H_2O \rightleftarrows Zn(OH)_4^{2-} + 4H^+$	$6.98{\times}10^{-42}$	″
$UO_2^{2+} + 4H_2O \rightleftarrows UO_2(OH)_4^{2-} + 4H^+$	$3.98{\times}10^{-33}$	″	$Cd^{2+} + H_2O \rightleftarrows CdOH^+ + H^+$	$6.60{\times}10^{-11}$	″
$2UO_2^{2+} + 2H_2O \rightleftarrows (UO_2)_2OH^{3+} + H^+$	$2.00{\times}10^{-3}$	″	$Cd^{2+} + 2H_2O \rightleftarrows Cd(OH)_2^0 + 2H^+$	$1.86{\times}10^{-20}$	″
$2UO_2^{2+} + 2H_2O \rightleftarrows (UO_2)_2(OH)_2^{2+} + 2H^+$	$2.40{\times}10^{-6}$	″	$Cd^{2+} + 3H_2O \rightleftarrows Cd(OH)_3^- + 3H^+$	$2.05{\times}10^{-33}$	″
$3UO_2^{2+} + 5H_2O \rightleftarrows (UO_2)_3(OH)_5^+ + 5H^+$	$2.82{\times}10^{-16}$	″	$Cd^{2+} + 4H_2O \rightleftarrows Cd(OH)_4^{2-} + 4H^+$	$6.61{\times}10^{-48}$	″
$3UO_2^{2+} + 7H_2O \rightleftarrows (UO_2)_3(OH)_7^- + 7H^+$	$6.31{\times}10^{-33}$	″	$Pb^{2+} + H_2O \rightleftarrows PbOH^+ + H^+$	$7.10{\times}10^{-07}$	″
$4UO_2^{2+} + 7H_2O \rightleftarrows (UO_2)_4(OH)_7^+ + 7H^+$	$1.26{\times}10^{-22}$	″	$Pb^{2+} + 2H_2O \rightleftarrows Pb(OH)_2^0 + 2H^+$	$7.59{\times}10^{-18}$	″
$UO_2^{2+} + AsO_4^{3-} + H^+ \rightleftarrows UO_2HAsO_4^0$	$5.77{\times}10^{18}$	[10]	$Pb^{2+} + 3H_2O \rightleftarrows Pb(OH)_3^- + 3H^+$	$9.40{\times}10^{-29}$	″
$UO_2^{2+} + AsO_4^{3-} + 2H^+ \rightleftarrows UO_2H_2AsO_4^+$	$9.12{\times}10^{21}$	″	$HAsUO_6{\cdot}4H_2O(cr.) \rightleftarrows UO_2^{2+} + AsO_4^{3-} + 4H_2O$	$1.00{\times}10^{-23}$	[14]
$UO_2^{2+} + 2AsO_4^{3-} + 4H^+ \rightleftarrows UO_2(HAsO_4)_2^0$	$3.39{\times}10^{41}$	″	$UO_3{\cdot}2H_2O(cr.) \rightleftarrows UO_2^{2+} + 2OH^- + H_2O$	$1.91{\times}10^{-22}$	Our data
$Mn^{2+} + H_2O \rightleftarrows MnOH^+ + H^+$	$1.80{\times}10^{-11}$	[13]	$Na_2U_2O_7(cr.) + 3H_2O \rightleftarrows 2Na^+ + 2UO_2{}^{2+} + 6OH$	$8.55{\times}10^{-56}$	The same
$Mn^{2+} + 2H_2O \rightleftarrows Mn(OH)_2^0 + 2H^+$	$1.07{\times}10^{-28}$	″	$Mn(OH)_2(cr.) \rightleftarrows Mn^{2+} + 2OH^-$	$1.44{\times}10^{-13}$	[13]
$Mn^{2+} + 3H_2O \rightleftarrows Mn(OH)_3^- + 3H^+$	$7.11{\times}10^{-35}$	″	$Co(OH)_2(cr.) \rightleftarrows Co^{2+} + 2OH^-$	$1.49{\times}10^{-15}$	″
$Mn^{2+} + 4H_2O \rightleftarrows Mn(OH)_4^{2-} + 4H^+$	$9.95{\times}10^{-51}$	″	$Ni(OH)_2(cr.) \rightleftarrows Ni^{2+} + 2OH^-$	$5.86{\times}10^{-18}$	″
$Co^{2+} + H_2O \rightleftarrows CoOH^+ + H^+$	$6.53{\times}10^{-12}$	″	$Cu(OH)_2(cr.) \rightleftarrows Cu^{2+} + 2OH^-$	$4.39{\times}10^{-20}$	″
$Co^{2+} + 2H_2O \rightleftarrows Co(OH)_2^0 + 2H^+$	$1.07{\times}10^{-28}$	″	$Zn(OH)_2(cr.) \rightleftarrows Zn^{2+} + 2OH^-$	$2.67{\times}10^{-16}$	″
$Ni^{2+} + H_2O \rightleftarrows NiOH^+ + H^+$	$1.77{\times}10^{-11}$	″	$Cd(OH)_2(cr.) \rightleftarrows Cd^{2+} + 2OH^-$	$2.00{\times}10^{-14}$	″
$Ni^{2+} + 2H_2O \rightleftarrows Ni(OH)_2^0 + 2H^+$	$1.07{\times}10^{-28}$	″	$Pb(OH)_2(cr.) \rightleftarrows Pb^{2+} + 2OH^-$	$4.70{\times}10^{-16}$	″

Solubility products of uranoarsenates were calculated by the data on the solubility of compounds in 10^{-2} and 10^{-3} M solutions of perchloric acid (Table 1), as under these conditions the equilibrium bottom phase contains more than 99% of $M^{II}(AsUO_6)_2{\cdot}nH_2O$ and a stoichiometric passing of U(VI), As(V), and M^{II}(II) in a solution is observed. Average values of solubility products of the compounds under study K_s are given in Table 3. Values of K_s for uranoarsenates of 3*d*-transition elements and cadmium coincide within the limits of the experimental error. The solubility product of lead uranoarsenate is lower by an order of magnitude, which corresponds to a lattice energy increase caused by an increase in the ionic component of the M^{II}–O bond in the structure of lead uranoarsenate. The Gibbs functions of formation of uranoarsenate calculated by Eqs. (7), (8) are also presented in Table 3.

$$\Delta G_r^0 = -RT\ln K_s, \tag{7}$$

$$\Delta G_f^0[M^{II}(AsUO_6)_2{\cdot}nH_2O_{cr}] = \Delta G_f^0(M^{2+}) + 2\Delta G_f^0(UO_2^{2+}) + 2\Delta G_f^0(AsO_4^{3-}) + n\Delta G_f^0(H_2O_l) - \Delta G_f^0. \tag{8}$$

Here ΔG_f^0 are the standard Gibbs functions of formation of UO_2^{2+} (–952.551), AsO_4^{3-} (–648.360), Mn^{2+} (–230.965), Co^{2+} (–53.638), Ni^{2+} (–45.563), Cu^{2+} (65.563), Zn^{2+} (–147.163), Cd^{2+} (–77.655), Pb^{2+} (–24.392), and H_2O (–237.140) kJ mol^{-1} [10, 11, 13]; ΔG_r^0 is Gibbs function of reaction (4).

To simulate the state of the aqueous–salt systems under study in a wide range of acidity and to construct phase diagrams of aqueous solutions and solid phases within the limits of the developed physicochemical description, we have set up a system of Eqs. (9)–(19).

$$c_U = \Sigma f[a(UO_2^{2+})] + \Sigma f[a(UO_2^{2+}), a(AsO_4^{3-})], \tag{9}$$

$$c_P = \Sigma f[a(AsO_4^{3-})] + \Sigma f[a(UO_2^{2+}), a(AsO_4^{3-})], \quad (10)$$

$$c_M = \Sigma f[a(M^{2+})], \quad (11)$$

$$K_s[M^{II}(AsUO_6)_2{\cdot}nH_2O] = a(M^{2+}){\cdot}a(UO_2^{2+})^2{\cdot}a(AsO_4^{3-})^2, \quad (12)$$

$$K_s(HAsUO_6{\cdot}4H_2O) = a(H^+){\cdot}a(UO_2^{2+}){\cdot}a(AsO_4^{3-}), \quad (13)$$

$$K_s(UO_3{\cdot}2H_2O) = a(UO_2^{2+}){\cdot}[K_w^2/a(H^+)^2], \quad (14)$$

$$K_s[M^{II}(OH)_2] = a(M^{2+}){\cdot}[K_w^2/a(H^+)^2], \quad (15)$$

$$K_s(Na_2U_2O_7) = a(Na^+)^2{\cdot}a(UO_2^{2+})^2{\cdot}[K_w^6/a(H^+)^6], \quad (16)$$

$$n\{m[M^{II}(AsUO_6)_2{\cdot}nH_2O]/M[M^{II}(AsUO_6)_2{\cdot}nH_2O]\} = c_U{\cdot}V + \sum_L[(m_L{\cdot}\omega_{U,L})/M(U)], \quad (17)$$

$$n\{m[M^{II}(AsUO_6)_2{\cdot}nH_2O]/M[M^{II}(AsUO_6)_2{\cdot}nH_2O]\} = c_{As}{\cdot}V + \sum_L[(m_L{\cdot}\omega_{As,L})/M(As)], \quad (18)$$

$$m[M^{II}(AsUO_6)_2{\cdot}nH_2O]/M[M^{II}(AsUO_6)_2{\cdot}nH_2O] = c_M{\cdot}V + \sum_L[(m_L{\cdot}\omega_{M,L})/M(M)]. \quad (19)$$

Here f shows the presence of a functional dependence; $m[M^{II}(AsUO_6)_2{\cdot}nH_2O]$ is the weight of a primary uranoarsenate phase; V is the volume of aqueous solution of $HClO_4$, H_2O, or NaOH; M is a molar weight; m_L is the weight of compound L in the bottom phase; L = $M^{II}(AsUO_6)_2{\cdot}nH_2O$, $HAsUO_6{\cdot}4H_2O$, $UO_2{\cdot}2H_2O$, $Na_2U_2O_7$, $M^{II}(OH)_2$; $\omega_{U,L}$ is the weight fraction of uranium in the compound L.

The system of Eqs. (9)–(19) makes it possible to take into account along with $M^{II}(AsUO_6)_2{\cdot}nH_2O$ the presence of low-soluble compounds of secondary origin in a bottom phase: $HAsUO_6{\cdot}4H_2O$, $UO_3{\cdot}2H_2O$, $Na_2U_2O_7$, and $M^{II}(OH)_2$. Equations (9)–(11) consider homogeneous equilibria involving various ion-molecular forms of U(VI), As(V), and M(II), Eqs. (12)–(16) represent equilibrium constants of heterogeneous reactions between solid-phase primary and secondary compounds and equilibrium solutions, whereas Eqs. (17)–(19) show the relation between the amounts of U(VI), As(V), and M(II) in the solid phase and in the solution.

Table 3. Solubility products and standard Gibbs functions of formation of $M^{II}(AsUO_6)_2{\cdot}nH_2O$ compounds

Compound	pK_s	$-\Delta_fG^0$, kJ mol^{-1}
$Mn(AsUO_6)_2{\cdot}12H_2O$	45.14±0.40	6305±20
$Co(AsUO_6)_2{\cdot}12H_2O$	45.52±0.40	6307±20
$Ni(AsUO_6)_2{\cdot}12H_2O$	45.56±0.40	6308±20
$Cu(AsUO_6)_2{\cdot}8H_2O$	44.97±0.40	5356±20
$Zn(AsUO_6)_2{\cdot}12H_2O$	45.05±0.40	6305±20
$Cd(AsUO_6)_2{\cdot}10H_2O$	45.42±0.50	5833±20
$Pb(AsUO_6)_2{\cdot}8H_2O$	46.25±0.30	5363±20

The system of Eqs. (9)–(19), which we have developed, allows us the calculation of various parameters of the studied heterogeneous systems $M^{II}(AsUO_6)_2{\cdot}nH_2O$(cr)–aqueous solution in a wide range of acidity of a medium. At preset values of pH and volume V of an equilibrium solution and weight m of primary uranoarsenate $M^{II}(AsUO_6)_2{\cdot}nH_2O$ in a bottom phase, we have calculated activities of ionic forms $a(UO_2^{2+})$, $a(AsO_4^{3-})$, $a(M^{2+})$ and total concentrations c_U, c_{As}, and c_M in solution, and also weights of solid phase components of primary and secondary origin m(L). Using the calculated values of weights we have constructed the phase diagrams of solid phases and estimated the acid–base intervals of existence of separate components. The activities of ions in aqueous solutions calculated by solving this set of equations were used for the calculation of phase diagrams of U(VI), As(V), and M(II) in saturated aqueous solutions.

Let us consider the results of the physicochemical state simulation for heterogeneous systems, using Eqs. (9)–(19). Figures 2–4 show: (a) calculated diagrams of solid phases and (b) the corresponding calculated concentrations of U(VI), As(V), and M(II) in equilibrium solutions of certain uranoarsenates under study in a wide pH range. The variation of ion-molecular composition of saturated aqueous solutions is shown by the example of lead uranoarsenate (Fig. 5). It is seen from Figs. 2a–4a that acid–base intervals, in which uranoarsenates retain their composition and structure in solutions, depend on the nature of an interlayer element M^{II}. The lower boundary of the stability of compounds under study varies in a narrow pH range from 1.5 for lead uranoarsenates up to 2.2 for the manganese derivative and correlates with K_s values (Table 3). The upper boundary of the pH range has a scatter from pH 7.5 up to 9.8 and is displaced in the alkaline region in the series of Cu–Ni–Zn–Co–Cd–Mn derivatives according to the increase in the solubility products of hydroxides $M^{II}(OH)_2$ of *d*-elements (Table 2). Concentrations of uranium(VI) and arsenic(V) in aqueous solutions of heterogeneous systems under study originate from the acidity of the medium and the composition of an equilibrium bottom phase. In the acid–base range where the uranoarsenates retain their individuality the concentration dependences c_U and c_{As} coincide, which is caused by congruent dissolution of the compounds and corresponds to their stoichiometry. The concentration of M(II) in this pH range is twice less

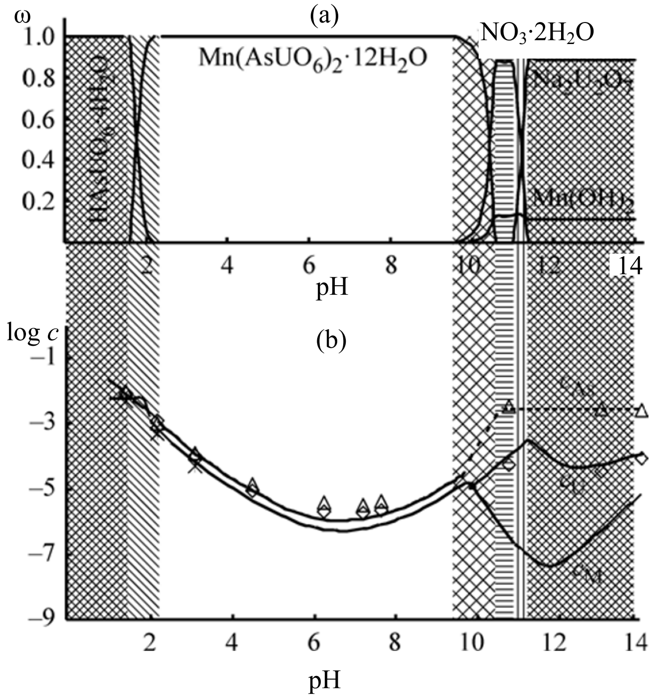

Fig. 2. Dependence of (a) weight fractions ω of bottom phase components (m 0.15 g, V 0.1 l) and (b) concentrations of U(VI), As(V), and M(II) in solution on the acidity of medium in the system $Mn(AsUO_6)_2 \cdot 12H_2O$(cr)–aqueous solution. Here and herinafter: lines are calculated curves, points are experimental values, rhombs are U(VI), triangles are As(V), crosses are M(II).

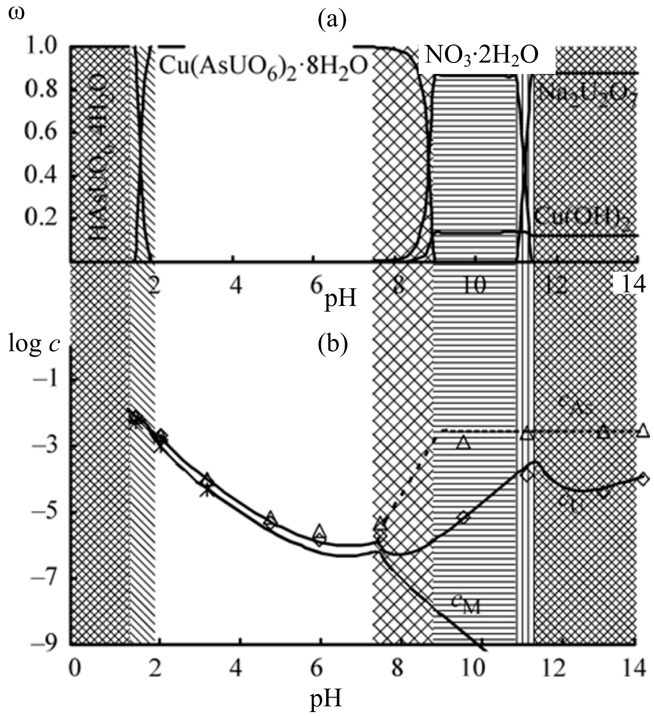

Fig. 3. Dependence of (a) weight fractions ω of bottom phase components (m 0.15 g, V 0.1 l) and (b) concentrations of U(VI), As(V), and M(II) in solution on the acidity of medium in the system $Cu(AsUO_6)_2 \cdot 8H_2O$(cr)–aqueous solution.

than c_U and c_{As} that also corresponds to their ratio in the compounds under study. The solubility of the $M^{II}(AsUO_6)_2 \cdot nH_2O$ compounds is minimal in neutral solutions and increases in acid and alkaline media. In alkaline media the curves of c_U and c_{As} diverge, which is a consequence of the conversion of uranoarsenates with the formation of secondary bottom phases, the nature and weight fraction of which is shown in Figs. 2a–4a. The concentration of As(V) in the equilibrium solution corresponds to its amount in the initial phase of an uranoarsenate $M^{II}(AsUO_6)_2 \cdot nH_2O$, and the concentration of U(VI) in the solution is caused by the solubility of hydrated uranium(VI) oxide or of sodium diuranate, and the concentration of M(II), by the solubility of $M^{II}(OH)_2$. To check the adequacy of the description of the heterogeneous system and the calculated dependences, the experimental concentrations of uranium, arsenic, and a corresponding element M^{II} (Table 1) are shown in Figs. 2b–4b. The coincidence of calculated curves and experimental data within the whole investigated range of acidity points to the reliability of the results obtained and allows us to recommend the developed description for prediction of the state of systems in a region, which was not studied experimentally.

EXPERIMENTAL

Samples of $M^{II}(AsUO_6)_2 \cdot nH_2O$ compounds were synthesized, using reaction (20) of ion exchange between crystals of $HAsUO_6 \cdot 4H_2O$ and a 0.05 M aqueous solution of a salt of the corresponding element [6].

$$2HAsUO_6 \cdot 4H_2O(cr) + M^{2+} + (n-8)H_2O \rightleftarrows M^{II}(AsUO_6)_2 \cdot nH_2O(cr) + 2H^+. \quad (20)$$

To reach a complete exchange, the equilibrium in this reaction was displaced to the right by adding freshly precipitated metal M^{II} hydroxide with intensive stirring in an amount equivalent to the amount of formed H^+ ions. The resulting compounds were washed with distilled water and dried in air at 25°C.

Uranoarsenic acid $HAsUO_6 \cdot 4H_2O$ necessary for the synthesis of salts was obtained by reaction (21) of equivalent amounts of 0.15 M solution of $UO_2(NO_3)_2$ and 0.1 M solution of H_3AsO_4 [15].

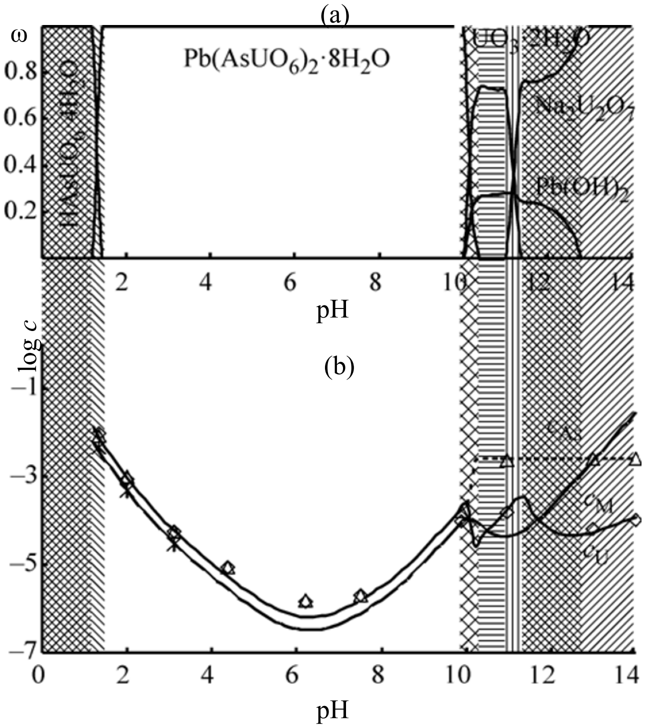

Fig. 4. Dependence of (a) weight fractions ω of bottom phase components (m 0.15 g, V 0.1 l) and (b) concentrations of U(VI), As(V), and M(II) in solution on the acidity of medium in the system $Pb(AsUO_6)_2{\cdot}8H_2O$(cr)–aqueous solution.

$$UO_2(NO_3)_2 + H_3AsO_4 + 4H_2O \rightleftarrows HAsUO_6{\cdot}4H_2O(\text{cr.}) + 2HNO_3. \quad (21)$$

To increase the crystallinity degree of the product $HAsUO_6{\cdot}4H_2O$ and its yield, the prepared solution with the precipitate was boiled for 3 days.

Phase individuality of the synthesized samples and the absence of crystalline admixtures were checked by the powder X-ray diffraction analysis. The resulting X-ray patterns were compared with the known published data [6]. The weight fraction of water in all samples was determined by the weight method, annealing them at 600°C within 10 h. Amounts of uranium, arsenic, and an element M(II) were determined by the method of X-ray fluorescence spectroscopy. For this purpose we applied the method of fundamental parameters with correcting sensitivity coefficients deduced from standard samples. The standard samples were prepared by mixing UO_3, As_2O_5, and $M^{II}O$ in molar ratios 2:1:1 with grinding the resulting mixture. To remove moisture, the oxides were preliminarily annealed at appropriate temperatures [16]. The found concentrations of the specified elements in a solid phase coincided with calculated values within the error limits of 0.5%.

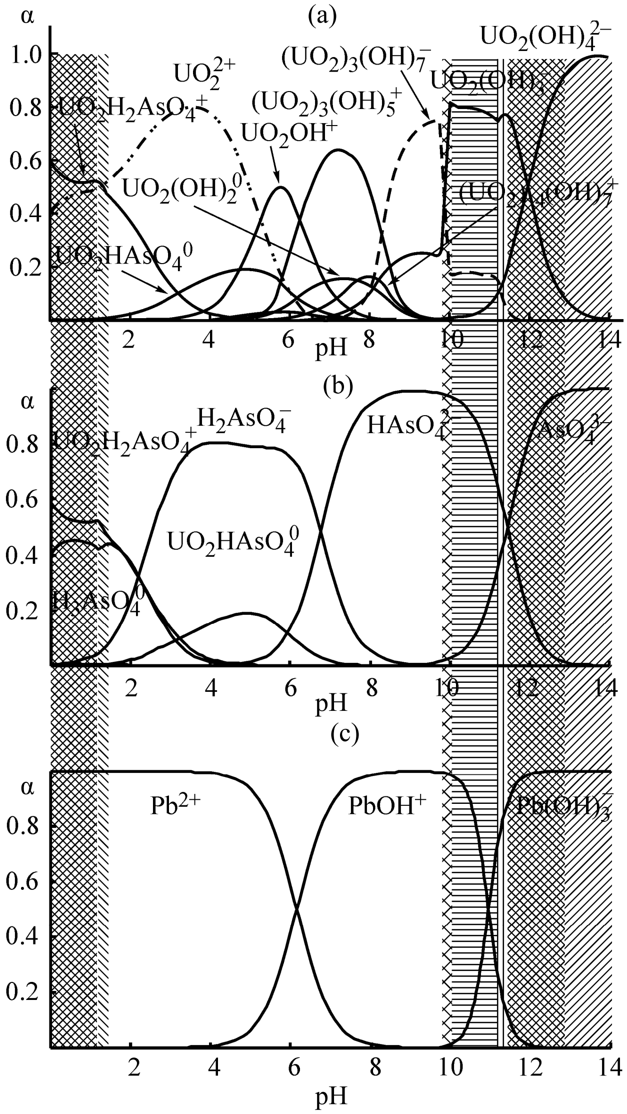

Fig. 5. Phase diagrams of (a) U(VI), (b) As(V), and (c) Pb(II) () in aqueous solutions of $Pb(AsUO_6)_2{\cdot}8H_2O$.

To determine the solubility of uranoarsenates of transition elements and lead, a weighted sample of a substance (~0.1 g) was placed into an aqueous solution (5–100 ml) of $HClO_4$ (10^{-4}–1 M), NaOH (10^{-4}–1 M) or in twice-distilled water. Experiments were carried out in plastic leakproof containers with a minimal free space (less than 1–2 ml) in order to prevent the contact of solutions with carbon dioxide, which is present in atmosphere. The solutions with precipitates were intermittently stirred over several months, and pH was controlled. After reaching a constant pH value in the system, a precipitate was separated from the solution by centrifugation, washed with distilled water, dried at 25°C, and studied by the methods of X-ray phase and X-ray fluorescence analyses and by IR spectroscopy.

The concentrations of U(VI), As(V), and M(II), and also the presence of suspended and colloidal particles were determined in saturated aqueous solutions by the photometry, nephelometry and turbidimetry methods.

The concentration of As(V) in aqueous solutions was determined by photometric measurements of the absorption of the arsenomolybdic heteropolyacid reduced form (λ_{max} 900 nm, reducing agent – ascorbic acid) [17]. The working solution of As(V) was prepared by dissolution of NaH_2AsO_4 in water. The concentration of uranium(VI) in solutions was determined by the reaction with arsenazo III (λ_{max} 650 nm, pH 3) [18.] A standard uranium (VI) solution was prepared by dissolution of $UO_2(NO_3)_2 \cdot 6H_2O$ in water. The concentration of M(II) in solutions was determined by the reaction with sulfarsazene (λ_{max} 535 nm, pH 9.4). Working solutions of M(II) were obtained as described in [19-25]. Concentrations of all standard solutions were 10^{-2} M. Less concentrated solutions used for constructing calibration curves were prepared by sequential dilution. Completeness of solid phase separation from equilibrium solution and the absence of suspended and colloidal particles in aqueous solutions were confirmed by the nephelometry method, comparing intensity of radiation scattered by saturated aqueous solutions and distilled water, and also by the turbidimetry method, measuring turbidity of solutions in the range of wavelengths 300–1100 nm.

The X-ray patterns of powdered samples were recorded on a Shimadzu XRD-6000 diffractometer (CuK_α radiation). The elemental analysis of solid samples was carried out with the use of a Shimadzu EDX-900 HL energy-dispersive X-ray-fluorescent spectrometer. The IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer. Samples were prepared in the form of tablets with KBr and suspensions in mineral oil. All the synthesized compounds and the reagents used in this work corresponded to the chemically-pure grade. Bidistilled water free of CO_2 admixture [26, 27] was used in all experiments. Solutions of sodium hydroxide free of CO_2 were prepared by the procedure described in [27]. Values of pH of solutions were determined with a pH 410 pH-meter (“Akvilon” company) and an ESK-10601/7 glass electrode. The electrode was calibrated using standard buffer solutions with pH 1.68, 3.56, 4.01, 6.86, 9.18, and 12.45. To separate a solid phase from saturated solution, a TSLN-2 centrifugal machine was used. The centrifuging was carried out at a velocity of 9000 rpm. Photometric measurements were carried out on a Shimadzu UV-1650 spectrophotometer. Intensity of scattered radiation was measured by means of a NFM nephelometer (Russia). Statistical treatment of results and mathematical simulation of the state of heterogeneous systems were fulfilled using the Mathcad 8.0 computer program.

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