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Structure and Thermodynamics of Solid Solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$

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Abstract—Solid solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$ were prepared and studied by X-ray diffraction, IR spectroscopy, and calorimetry. The enthalpy and Gibbs energy of mixing were determined. In calculation of the thermodynamic properties, these solid solutions can be considered as regular solutions.

The compounds $HPUO_6 \cdot 4H_2O$ and $HAsUO_6 \cdot 4H_2O$ are well known as natural minerals: hydrogen forms of metaautunite and uranospinite. Their structure and physicochemical properties were studied in detail in [1–5]. In the nature, they often form isomorphous mixtures which are also of interest for uranium chemistry. In this work we studied conditions of formation, structure, and thermodynamics of solid solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$.

We prepared samples of $HP_{1-x}As_xUO_6 \cdot 4H_2O$ with x = 0.00, 0.19, 0.44, 0.72, 0.90, and 1.00, as determined by elemental analysis.

X-ray diffraction study showed that each of the samples is crystalline and single-phase. Both the individual compounds and the solid solutions are full X-ray analogs, which allowed us to index the X-ray diffraction patterns and calculate the unit cell parameters. The composition dependences of the unit cell parameters follow the Vegard rule without noticeable deviations (Fig. 1), which confirms the fact that specifically solid solutions, rather than mechanical mixtures, are formed in the system.

The IR spectra show that the solid solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$ and the individual compounds $HP(As)UO_6 \cdot 4H_2O$ are fully similar in functional composition (Fig. 2). Stretching vibrations of water in all the spectra give rise to a broad band at 3400 cm^{-1}, which suggests formation of a network of hydrogen bonds. In the range 1600–1800 cm^{-1}, the hydrogen derivatives show two absorption maxima: at 1730 and 1645 cm^{-1}, due to bending vibrations of the hydroxonium ion and molecular water, respectively.

The IR spectra of the solid solutions contain bands due to stretching vibrations ν_3 of the phosphate (1000 cm^{-1}) and arsenate (800 cm^{-1}) tetrahedra; their relative intensity is proportional to the content of the corresponding element B^V. In samples with x 0.44 and 0.19, the arsenate stretching band is split, and in samples with x 0.72 and 0.90 is split the phosphate stretching band. The band splitting suggests a lower symmetry of the corresponding groups in the solid solutions as compared to the individual compounds and strain of chemical bonds in the mixed structures.

To quantitatively evaluate the energy effects of mutual substitution of phosphorus and arsenic in the systems under consideration, we determined experimentally the enthalpies of mixing.

For this purpose, we measured the enthalpies of reaction of the solid solutions and individual compounds with an HF solution. For the phase with x 0.00, 0.19, 0.44, 0.72, 0.90, and 1.00, the enthalpy of

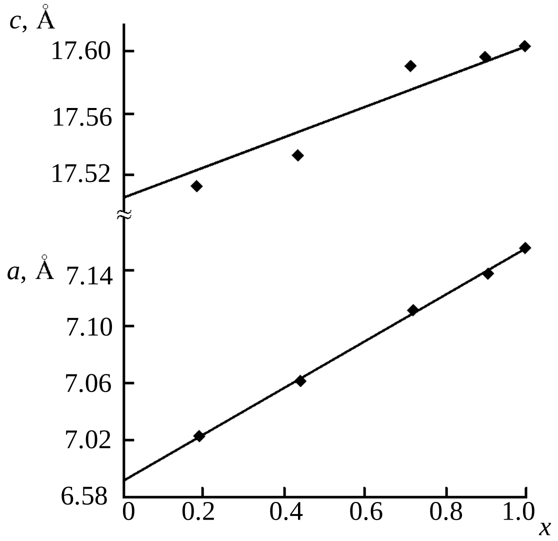

Fig. 1. Unit cell parameters (space group $P4/ncc$) of solid solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$ vs. composition.

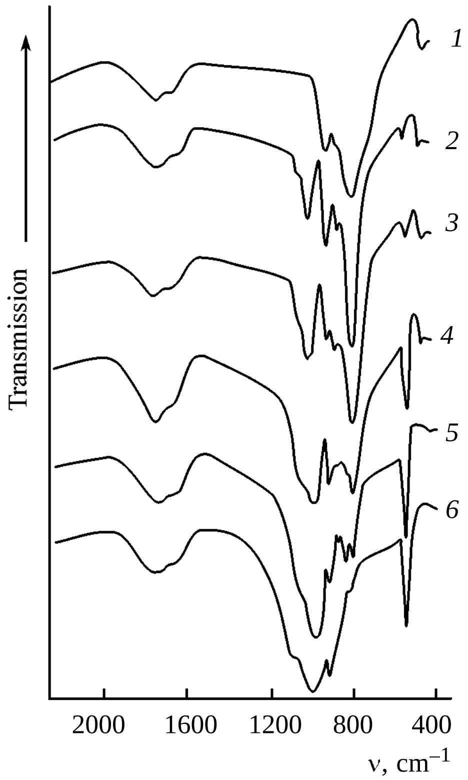

Fig. 2. IR spectra of solid solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$. *x*: (*1*) 1.00, (*2*) 0.90, (*3*) 0.72, (*4*) 0.44, (*5*) 0.19, and (*6*) 0.00.

this reaction is –10.67±0.02, –20.87±0.06, –33.71±0.11, –47.60±0.19, –56.27±0.15, and –60.98±0.26 kJ mol^{-1}, respectively. The enthalpy of mixing was calculated as the difference between the enthalpy of solution in aqueous HF of a mechanical mixture of the individual compounds and that of the solid solution of the same composition. The enthalpies of solution of the mechanical mixtures were calculated by the additive scheme from the enthalpies of solution of the individual components. For the solid solutions with x 0.19, 0.44, 0.72, and 0.90, the enthalpies of mixing are 650±270, 910±280, 720±320, and 320±300 J mol^{-1}, respectively.

The measured enthalpies of mixing have small positive values, which suggests that the strains of chemical bonds arising in the solid solution owing to replacement of phosphorus by arsenic, though being manifested in the IR spectra, are insignificant from the energy viewpoint. This may be due to the compensating effect of water of crystallization, as each of the oxygen atoms of the orthophosphate (or orthoarsenate) groups has a neighboring H_2O molecule [3, 4]. These molecules make the effect of the force field of interlayer H^+ cations more balanced and relieve in part the strain of chemical bonds.

To determine the activity coefficients of the solid solution components and the Gibbs energy of mixing, we studied the solution–precipitate equilibrium attained in the course of coprecipitation of hydrogen uranophosphate and hydrogen uranoarsenate. This process can be represented as a sum of half-reactions (1) and (2):

$$H_3PO_4 + UO_2(NO_3)_2 + 4H_2O = HPUO_6 \cdot 4H_2O + 2HNO_3, \quad (1)$$

$$H_3AsO_4 + UO_2(NO_3)_2 + 4H_2O = HAsUO_6 \cdot 4H_2O + 2HNO_3. \quad (2)$$

Their difference from the reactions of formation of the individual compounds is that the species in the right side are components of the solid solution and not individual compounds. From the thermodynamic viewpoint, this means that the activities of the solid phases in the right side of Eqs. (1) and (2) differ from unity. By subtracting Eq. (1) from (2), we obtain

$$HPUO_6 \cdot 4H_2O + H_3AsO_4 = HAsUO_6 \cdot 4H_2O + H_3PO_4. \quad (3)$$

The equilibrium constant K_a of Eq. (3) is given by

$$K_a = \frac{a^s_{HAs}\, a^l_{HP}}{a^l_{HAs}\, a^s_{HP}} = \frac{n^s_{HAs}\, c^l_{HP}}{c^l_{HAs}\, n^s_{HP}} \cdot \frac{\gamma^s_{HAs}\, \gamma^l_{HP}}{\gamma^l_{HAs}\, \gamma^s_{HP}} = K_c K_\gamma,$$

where a^l_i, c^l_i, γ^l_i (a^s_i, n^s_i, γ^s_i) are the activity, concentration, and activity coefficient of component i in the liquid (solid) phase, respectively; $n^s_{HP} = 1 - x$, $n^s_{HAs} = x$, and K_c is the distribution factor.

The thermodynamic analysis of equilibria similar to reaction (3) was made in [6] for aluminosilicates. Because in our system the concentration of HNO_3 remains constant (1 M) and the concentration of uranyl ions and total concentration of phosphate and arsenate ions vary within a narrow range from 0.205 to 0.302 M, the ratio $\gamma^l_{HP}/\gamma^l_{HAs}$ in this range can be assumed to be constant. Then the conclusions made in [6] can be applied to equilibrium (3); as a result, we obtain the relations

$$\ln \gamma^s_{HP} = RT\int_0^x x d\ln K_c, \quad (4)$$

$$\ln \gamma^s_{HAs} = -RT\int_0^{1-x} (1-x) d\ln K_c. \quad (5)$$

Equations (4) and (5) can be used to calculate the activity coefficients of the components of the solid solutions. For this purpose, we determined by chemical analysis the distribution factors K_c. For the solid solutions with x 0.19, 0.44, 0.72, and 0.90 they are 0.241, 0.517, 0.993, and 1.323, respectively (Fig. 3).

According to [6], if the partial excess Gibbs energies of mixing of solid solution components are represented in the form of power series (Margules series) restricted to the x^3 terms (which is usually sufficient), then the composition dependence of $\ln K_c$ will be a quadratic function. On this basis, we calculated the coefficients a, b, and c for the dependence $\ln K_c = ax^2 + bx + c$, expressed x through K_c, and substituted the resulting expression in Eqs. (4) and (5). The values of $\ln\gamma$ and γ are listed in Table 1.

It is seen that, when the content of a component in the solid solution is less than ~50 mol %, its activity coefficient significantly differs from unity, which should be taken into account when calculating the chemical equilibria involving hydrogen uranophosphates and uranoarsenates.

The partial and integral excess Gibbs functions of mixing of the components (Table 2) were calculated by the formulas

$$\Delta^E_{\mathrm{mix}}G_i = RT\ln\gamma_i,$$

$$\Delta^E_{\mathrm{mix}}G = x^{\mathrm{s}}_{\mathrm{HP}}\Delta^E_{\mathrm{mix}}G^{\mathrm{s}}_{\mathrm{HP}} + x^{\mathrm{s}}_{\mathrm{HAs}}\Delta^E_{\mathrm{mix}}G^{\mathrm{s}}_{\mathrm{HAs}}.$$

From these quantities and the enthalpies of mixing, we calculated the excess entropies of mixing, which are also listed in Table 2. It should be noted that the value of $T\Delta^E_{\mathrm{mix}}S = \Delta^E_{\mathrm{mix}}G - \Delta_{\mathrm{mix}}H$ is within the error of determination of the enthalpy of mixing; therefore, in the subsequent calculations of the entropy of mixing of the solid solutions under consideration the excess entropy was neglected. Thus, the solid solutions $\mathrm{HP}_{1-x}\mathrm{As}_x\mathrm{UO}_6\cdot 4\mathrm{H}_2\mathrm{O}$ were considered as regular solutions [6], and the entropy of mixing was calculated as the configuration entropy ($\Delta^{\mathrm{conf}}_{\mathrm{mix}}S$), and the Gibbs energy of mixing, by the relation $\Delta_{\mathrm{mix}}G = \Delta_{\mathrm{mix}}H - T\Delta^{\mathrm{conf}}_{\mathrm{mix}}S$ (Table 2).

These data show that the enthalpy ($\Delta_{\mathrm{mix}}H$) constituent of the Gibbs energy of mixing of components at formation of solid solutions $\mathrm{HP}_{1-x}\mathrm{As}_x\mathrm{UO}_6\cdot 4\mathrm{H}_2\mathrm{O}$ is less than the entropy constituent ($T\Delta_{\mathrm{mix}}S$), which leads to negative $\Delta_{\mathrm{mix}}G$ and makes formation of solid solutions under standard conditions at T 298.15 K thermodynamically feasible over the entire range of x from 0 to 1. The feasibility of formation of solid solutions, in turn, may be due to the fact that hydrogen uranophosphate and uranoarsenate are isostructural and the crystallochemical properties of phosphorus and arsenic are similar.

It should be noted in conclusion that the hydrogen forms can be converted by ion exchange into various metal derivatives $\mathrm{A}^k[(\mathrm{P,As})\mathrm{UO}_6]_k\cdot n\mathrm{H}_2\mathrm{O}$. Since the hydrogen form acts as an ion-exchange matrix, the

Table 1. Activity coefficients of components of solid solutions $\mathrm{HP}_{1-x}\mathrm{As}_x\mathrm{UO}_6\cdot 4\mathrm{H}_2\mathrm{O}$ and partial excess Gibbs energies of mixing of the components (J mol^{-1}) at T 298.15 K

x	$\mathrm{HPUO}_6\cdot 4\mathrm{H}_2\mathrm{O}$			$\mathrm{HAsUO}_6\cdot 4\mathrm{H}_2\mathrm{O}$		
	$\ln\gamma$	γ	$\Delta^E_{\mathrm{mix}}G^{\mathrm{s}}_{\mathrm{HP}}$	$\ln\gamma$	γ	$\Delta^E_{\mathrm{mix}}G^{\mathrm{s}}_{\mathrm{HP}}$
0.19	0.064	1.066	158.6	0.873	2.394	2163
0.44	0.301	1.351	746.1	0.346	1.413	857.8
0.72	0.675	1.964	1673	0.0667	1.069	165.1
0.90	0.904	2.470	2241	0.00912	1.009	22.60

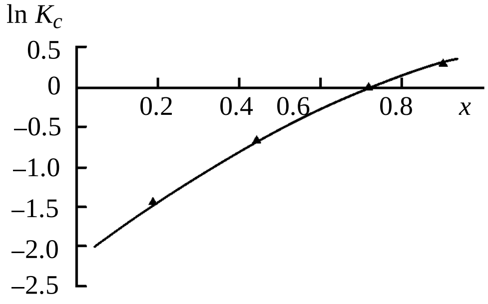

Fig. 3. Logarithm of the distribution factor ($\ln K_c$) as a function of the composition of the solid solutions $\mathrm{HP}_{1-x}\mathrm{As}_x\mathrm{UO}_6\cdot 4\mathrm{H}_2\mathrm{O}$.

Table 2. Thermodynamic functions of mixing of the components in solid solutions $\mathrm{HP}_{1-x}\mathrm{As}_x\mathrm{UO}_6\cdot 4\mathrm{H}_2\mathrm{O}$ at T 298.15 K

x	$\Delta_{\mathrm{mix}}H$, J mol^{-1}	$\Delta^E_{\mathrm{mix}}G$, J mol^{-1}	$T\Delta^E_{\mathrm{mix}}S$, J mol^{-1}	$\Delta^E_{\mathrm{mix}}S$, J mol^{-1} K^{-1}	$\Delta^{\mathrm{conf}}_{\mathrm{mix}}S$, J mol^{-1} K^{-1}	$-\Delta_{\mathrm{mix}}G$, J mol^{-1}
0.19	650 ± 270	540	110	0.442	4.042	555
0.44	910 ± 280	795	115	0.386	5.703	790
0.72	720 ± 320	588	132	0.443	4.930	750
0.90	320 ± 300	244	76	0.255	2.703	486

composition and structure of its anionic part do not change on hydrogen replacement [1–5]; therefore, the distribution of phosphate and arsenate groups can be assumed to be the same as in the hydrogen form, and the entropy of mixing of the solid solutions $A^k(P_{1-x}As_xUO_6)_k \cdot nH_2O$ can also be calculated in the regular solution approximation.

EXPERIMENTAL

The powder X-ray diffraction patterns were recorded with a DRON-3.0 diffractometer (CuK_α radiation). The unit cell parameters were refined by the least-squares method. The IR absorption spectra were taken with a Specord IR-75 spectrophotometer in the 400 – 4000 cm^{-1} range from mulls in mineral oil (KBr cell).

Crystalline solid solutions $HP_{1-x}As_xUO_6 \cdot 4H_2O$ were prepared by reaction of a 1 M solution of uranyl nitrate with a mixture of 1 M solutions of phosphoric and arsenic acids, following the procedure in [7]. The products were washed with distilled water and dried in an air box for 24 h.

To determine the composition of the mixed crystals, we developed a procedure for determination of uranium, phosphorus, and arsenic present simultaneously. A sample was treated with 1 M KOH; in the process, uranium remained in the precipitate in the form of $K_2U_2O_7$, in which the uranium content was determined, and phosphorus and arsenic passed into the solution. Arsenic was determined by reduction of arsenate ions with KI in acid solution, followed by titration of the released iodine with a standard solution of sodium thiosulfate. The total content of P and As was determined by the reaction of the phosphate and arsenate ions with Mg^{2+} in the presence of ammonia; the precipitate of magnesium ammonium phosphate/arsenate was calcined to magnesium pyrophosphate/pyroarsenate and weighed. The content of water of crystallization was determined gravimetrically.

To determine the composition of the solution in equilibrium with the precipitate, a 20-ml sample of the solution was taken and analyzed as described above.

The enthalpies of reaction of the individual compounds and solid solutions with aqueous HF (10.7 M) at 298.15 K were determined in an adiabatic calorimeter designed by S.M. Skuratov; the device and procedure are described in [8]. The random and fixed errors were evaluated in a series of experiments on determination of the enthalpy of solution of KCl (ultrapure grade) in double-distilled water. The total error of the enthalpy did not exceed 1.0 – 2.0%.

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