

“Extraction of *f*-elements by oligodentate organophosphorus compounds”

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Abstract. Dissertation work is devoted to the actual problem of searching for extraction ligands and one’s mixtures for isolating *f*-elements from nitric acid solutions, which would have satisfactory extraction quantitative characteristics in terms of efficiency and selectivity for solving various technological problems.

The search for new effective and selective extractants for the concentration, separation and isolation of lanthanides, actinides, as well as other valuable components, is of great scientific value and practical relevance. In addition, the design of compounds that differ in the number of coordinating centers that create optimal ligand complex formation ensembles with target actinides and lanthanides opens up great opportunities for purposeful modification of their extraction properties, compared to carbon analogues.

The purpose of the dissertation work is to develop the physicochemical basis of the extraction of actinides and lanthanides from technological solutions of processing various types of mineral raw materials and industrial wastes with oligodentate organophosphorus extractants: phosphorylureas, phosphoryl ketones and phosphorylated acid podands.

To achieve this purpose, it is necessary to solve the following scientific and technical **tasks**:

1. To determine the optimal structure of the linker separating the coordination centers to increase the reactivity of the extractants under study during complexation with *f*-elements;
2. To investigate the influence of electronic nature of substituents at phosphorous atom on extraction properties in relation to *f*-elements;
3. To investigate the influence of the electronic nature of substituents on the phosphorus atom on extraction properties in relation to *f*-elements;

4. To establish the influence of the nature and number of donor centers on the extraction ability of the extractant in relation to actinides and lanthanides;
5. To identify the structures of phosphorylureas, phosphoryl ketones and phosphorylated acid podands that have the greatest extraction ability with respect to actinides and lanthanides in a series of presented classes;
6. To determine the composition and structure of the extracted complexes of the above ligands with actinides and lanthanides;
7. To make the approbation of the most effective extractants from phosphorylureas, phosphoryl ketones and acid phosphoryl podands, including as part of binary mixtures with quaternary ammonium salts (QAS) for the extraction of f-elements and other REEs from solutions of eudialyte ore concentrate and phosphogypsum.

Scientific novelty.

1. For the first time, the influence of the nature of substituents on the phosphorus atom and the structure of the linker on the extraction ability of phosphorylureas, phosphoryl ketones and phosphorylated acid podands, which provide the highest possible ability to form complexes with f-elements, has been systematically studied. It has been established that in the case of phosphorylureas and phosphoryl ketones, the optimal substituents on the phosphorus atom are P,P-phenyl groups, and for phosphorylated acidic podands - alkyl substituents of a linear structure with a number of carbon atoms ≥ 16 . In the case of phosphoryl ketones and acidic phosphoryl podands, the extraction efficiency increases in the presence of as a linker of sterically unhindered ethylene moieties and diethylene glycol chains, respectively
2. For the first time, the structures of extractants of the classes of phosphorylureas, phosphoryl ketones and phosphorylated acid podands, which exhibit better extraction properties for f-elements, have been established. It has been established that from the series of phosphorylureas studied, N-Diphenylphosphoryl-N'-n-octylurea has the best properties, from the series of phosphoryl ketones - 5-(Diphenylphosphoryl)hexan-3-one, and in the series of

acidic phosphorylpodands - 1,5-Bis[o- (hydroxy-ethoxyphosphoryl)-p-ethylphenoxy]-3-oxapentane

3. For the first time, a number of individual complexes of actinides and lanthanides with phosphorylureas, phosphoryl ketones and phosphorylated acid podands have been isolated. Using a complex of physicochemical methods, the structural features of complex formation in extracted compounds were studied and described. It was shown that N-diorganylphosphorylated ureas have bidentate coordination for the block of f-elements; Phosphoryl ketones are predominantly coordinated to actinides monodentately, and to lanthanides mono- and bidentately; phosphorylated acid podands form intracomplex salts with cations of f-elements.

4. Using the example of complexes of the uranyl cation with 4-(diphenylphosphoryl)-4-dimethylbutan-2-one and 4-(diphenylphosphoryl)but-3-en-2-one, verification of quantum chemical modeling of the structure of complexes of f-elements with phosphoryl-containing ligands was carried out – N-diorganylphosphorylated ureas, phosphoryl ketones and phosphorylated acid podands, reliably reproducing the structural parameters determined by X-ray diffraction.

5. The features of extraction of f-elements with stoichiometric binary mixtures of acidic phosphorylpodands and QAS were determined. It has been shown that in nitric acid media of more than 4 M, the extraction ability of the mixture is determined by the properties of the acidic phosphorylpodande with the formation of an intra-complex salt with cations of f-elements in the organic phase, and QAS participates in the mixture as a solubilizer, increasing the lipophilicity of the acidic phosphorylpodande and extracted compounds.

Theoretical and practical significance.

Theoretical significance:

1. Modifications of the structures of organophosphorus extractants of various classes are substantiated to increase the reactivity during complex formation with

actinides and lanthanides, which contribute to increasing the efficiency and selectivity of the isolation of f-elements from nitric acid media.

2. The composition and structures of extractable complexes of f-elements with phosphoryl-containing ligands - N-diorganylphosphorylated ureas, phosphoryl ketones and phosphorylated acid podands in nitric acid media - were determined.

Provisions for defense:

1. Conditions for effective extraction and separation of valuable target components (actinides, zirconium, scandium and rare earth elements - REE) from leaching solutions of eudialyte ore concentrate and phosphogypsum using oligodentate extractants of the classes phosphorylureas, phosphoryl ketones and phosphorylated acid podands have been identified.

2. Conditions for the use of a stoichiometric binary mixture of acid phosphorylpodande and QAC for the extraction of uranium(VI), thorium(IV), zirconium(IV), hafnium(IV), scandium(III) and titanium(III) from leaching solutions of eudialyte ore concentrate with obtaining REE concentrate have been developed. The results obtained can become the basis for a new industrial technology for waste conditioning in the production of rare and rare earth metals from natural and man-made raw materials.