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Search Strategy for New Efficient Organophosphorus Extractants for Concentrating Radionuclides

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Long-term systematic studies of actinide and lanthanide extraction from acid solutions have implied that bidentate neutral organophosphorus compounds (BNOPCs) are the most efficient extractants for these metals [1]. Naturally, new, even more efficient extractants are expected to exist among these compounds. In our opinion, the most promising strategy for choosing such extractants is a systematic theoretical search for BNOPCs with high complexing abilities to 4*f* and 5*f* elements followed by experimental verification of theoretical inferences.

One major task of this search is to determine the relationship between the extraction ability and structure of organophosphorus compounds. Correlations of extraction constants with some features of structure families were used for this purpose, for example, correlations with the electronegativity [2], Taft constant σ^* [3], and Kabachnik constant σ^p [4] (on the assumption that the substituent effect is additive). In particular, it was found for various types of monodentate neutral organophosphorus compounds (MNOPCs)—phosphates, phosphonates, phosphinates, and phosphine oxides—that the reactive site (P=O group) and the composition of the complex (the ratio element : ligand) remain unchanged, while the extraction ability considerably increases in this series. Rozen et al. [5] proposed a correlation between $\ln K_{ex}$ values (where K_{ex} is effective extraction constant) of uranyl nitrate and nitric acid, on the one hand, and the sums of the electronegativities of substituents at the phosphorus atom in this series of compounds, on the other. From calculations, the extraction ability of MNOPCs decreases with increasing substituent electronegativity.

Although electronegativities can be determined autonomously, the above correlation unfortunately cannot be applied to BNOPCs, which are of the most practical importance [1]. In this context, another approach to the problem was proposed on the basis of quantum-chemical calculations of molecular electrostatic fields (MESFs); we have successfully used this approach [6]. Not only did this strategy reveal the calculation parameters that can explain distinctions in reactivities of organophosphorus compounds, but it also helped us to create a complex quantum-chemical approach to predicting the extraction ability of these compounds, including transuranic elements.

Here, we use MESF quantum-chemical calculations to choose *N*-diphenylphosphoryl-*N*'-alkylureas as the most effective BNOPCs for concentrating and separating 4*f* and 5*f* elements; we also compare theoretical predictions with experiments.

Concept of the strategy. Complexing between an organic reagent and a metal ion (with the desolvation of the reacting species being ignored) can be divided into two stages. First, the metal cation and the ligand group (LG) of the reagent come closer to each other. Second, they directly react at distances close to chemical bond lengths; this reaction involves electron exchange and the generation of the relevant complex. It is believed that the removed substituents only insignificantly alter the electronic state of the atoms in the LG of the reagent, which should not considerably affect its reactivity to the given metal atom.

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Table 1. Comparison of the MESF parameters calculated for *N*-diphenylphosphoryl-*N'*-*n*-alkylureas $Ph_2P(O)NHC(O)NHR$ (**II**) and (*N*-*n*-alkylcarbamoylmethyl)diphenylphosphine oxides $RNHC(O)CH_2P(O)Ph_2$ (**III**)

R	Torsion angles between P=O and C=O groups, deg		Relative charges *q* on oxygen atoms in LGs, au				Oxygen–oxygen distances between P=O and C=O groups, Å		MESF zone width, Å	
	(**II**)	(**III**)	(**II**)		(**III**)		(**II**)	(**III**)	(**II**)	(**III**)
			P=O	C=O	P=O	C=O				
n-C_5H_{11}	36	60	–0.638	–0.339	–0.628	–0.318	3.26	3.53	7.87	6.42
n-C_6H_{13}	39	56	–0.639	–0.340	–0.626	–0.315	3.24	3.50	8.20	6.65
n-C_7H_{15}	40	51	–0.638	–0.340	–0.624	–0.313	3.22	3.50	8.75	6.80
n-C_8H_{17}	38	56	–0.638	–0.339	–0.626	–0.315	3.25	3.51	8.13	6.95
n-C_9H_{19}	38	49	–0.638	–0.339	–0.623	–0.312	3.23	3.49	7.85	6.90
n-$C_{10}H_{21}$	39	47	–0.638	–0.339	–0.623	–0.311	3.21	3.54	7.82	6.90

Note. The bond lengths in the P=O and C=O groups in compounds II and III are equal to 1.51 and 1.23 Å, respectively.

Considering the first stage, one finds that a complex electrostatic field is generated in electrically neutral organic reagent molecules due to the specific distribution of negative electron charges in a confined region around atomic nuclei. When such a neutral organic molecule approaches the metal cation, their MESFs interact. This interaction induces the polarization of the electronic shells of organic ligand molecules, either enhancing the reaction or hindering or even inhibiting it [7]. The MESFs of the reagents are characterized by positive and negative regions with the relevant potentials. Overlapping of different-sign MESFs brings molecules closer to each other; overlapping of similar MESFs induces repulsion. Molecular attraction strengthens with an increasing product of the absolute values of potentials at points in the overlap region.

Knowledge of the MESF distribution can help in studying differences between interactions at the first and second complexing stages. A series of control parameters responsible for noticeable differences in reactivities can be distinguished. For example, the higher the effective negative charge of the electron-donating atom of the LG, the stronger the interaction between this group and the metal ion and, thus, the higher the reactivity of the compound.

In cases where there are two LGs in the reagent molecule, each containing an electron-donating atom (e.g., P=O and C=O groups), an additional control parameter appears, namely, the torsion angle between these groups. When this angle is null (that is, when both LGs are in one plane) or small, the organic reagent can form strongly bonded bidentate complexes. With greater torsion angles, less strongly bonded complexes are formed.

Here, we assume that there are no competitive reactions (e.g., the protonation of electron-donating atoms of the LG) or solvation shells. This allows us to apply the quantum-chemical approach directly to the reaction between the metal ion and organic reagent and to explain, using the chosen parameters, the different reactivities of various types of reagents.

Calculation procedure. The LEV program (developed at the Vernadsky Institute of Geochemistry and Analytical Chemistry) was used for quantum-chemical simulations. Initial conformations of the test structures that approached the real conformations as maximally as possible and ensured the highest reactivities were created using molecular imaging means. The torsion angle between the LGs (P=O and C=O) was nullified; that is, the test compounds were initially endowed with an ability to form bidentate complexes.

The conformations were calculated using the MNDO semiempirical method. The first stage included geometry optimization and a search for the most stable conformations with a minimal energy; as a result, three-dimensional images of optimized models were created. The spatial arrangement of atoms, electron densities, effective atomic charges, bond lengths, bond angles, and torsion angles were also calculated at this stage. At the second stage, MESFs were calculated and MESF distribution maps were designed, including geometry optimization data.

Choice of models. Structural modification of compounds that have already demonstrated their high efficiency seemed the most logical strategy for

Table 2. Comparison of uranium(VI) distribution ratios D_U in extraction from 2.81 M HNO_3 to 0.05 M solutions of compounds **IIb–IIf** in chloroform as a function of radical length R (phase ratio: 1 : 1)

D_U	Compound	R
62	(**IIb**)	n-C_6H_{13}
53	(**IIc**)	n-C_7H_{15}
70	(**IId**)	n-C_8H_{17}
44	(**IIe**)	n-C_9H_{19}
52	(**IIf**)	n-$C_{10}H_{21}$

Table 3. Uranium(VI) distribution ratios D_U as a function of HNO_3 concentration in extraction to 0.05 M solutions of compounds **I** and **IId** in chloroform (phase ratio: 1 : 1)

$[HNO_3]$, mol/L	D_U	
	(**I**)	(**IId**)
0.58	1.0	2.6
2.81	1.3	70
6.52	1.5	72

searching among BNOPCs for new types of potential extractants for 4*f* and 5*f* elements. At present, carbamoylmethylphosphine oxides (CMPOs) are the best organophosphorus extractants for actinide and lanthanide extraction from nitric acid solutions [8, 9]. Of them, (*N*,*N*-dibutylcarbamoylmethyl)diphenylphosphine oxide $Ph_2P(O)CH_2C(O)NBu_2$ (**I**) has the highest activity [8]; in particular, it is used in the Russian version of the TRUEX process.

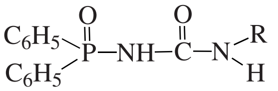
Fundamentally, there are three variants of structural modification of this compound: replacement of substituents at the phosphorus atom, variation of substituents at the nitrogen atom, and replacement of the methylene group by another spacer.

Systematic investigations of the effect of substituents at the phosphorus atom on the extraction ability of CMPOs were successfully performed under the supervision of Academicians M.I. Kabachnik and B.F. Myasoedov at the end of the last century in the course of optimization of the TRUEX process. Anomalous aryl strengthening was observed in the CMPO series; this effect, first discovered in the study of extraction properties of methylenediphosphine dioxides, consisted of the following: the replacement of alkyls at the phosphorus atom in a BNOPC molecule by more electronegative aryl substituents considerably improves the extraction characteristics of the compound, despite the attendant decrease in basicity [10]. Thus, in all probability, the existence of two phenyl radicals at the phosphorus atom in a molecule of a potential extractant is the optimal structural variant to ensure the maximal extraction efficiency.

As regards variation of substituents at the nitrogen atom, recent studies [11] showed that the CMPOs generated by the replacement of the *N*,*N*-dibutyl group in molecule **I** by an NHAlk group (where Alk = C_nH_{2n+1}) are not inferior to compound **I** in actinide extraction efficiency from nitric acid solutions and are even slightly superior to it in synthetic availability. With account for this, the BNOPC structures containing a terminal NHAlk moiety are preferred from the practical standpoint for the design of potential organophosphorus extractants.

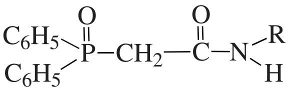
Notably, the CH_2 spacer between the phosphoryl and carbonyl complexing groups in a CMPO molecule does not ensure electronic interactions between these groups. Therefore, the replacement of the methylene spacer by a divalent radical seems, in fact, the only variant of structural modification of CMPOs that is potentially capable of radically improving the complexing properties: this replacement would ensure delocalization of the electron system of the complexing fragment, which in turn would enhance the efficiency of cation binding. An imide group –NH– can be one such bridging radical; as a result, the carbamoylmethylphosphine oxide structure would transform into the *N*-phosphorylurea structure. To achieve the best result, these urea molecules should retain the substituents at the phosphorus atom and terminal nitrogen atom that were recognized as optimal for CMPOs.

To test this idea, we carried out MESF quantum-chemical calculations for both *N*-diphenylphosphoryl-*N'*-*n*-alkyl(C_5–C_{10})ureas (**IIa–IIf**) and their closest analogues in the CMPO series, chosen to be references: [*N*-*n*-alkyl(C_5–C_{10})carbamoylmethyl]diphenylphosphine oxides **IIIa–IIIf**.



$(C_6H_5)_2P(O)\text{–NH–}C(O)\text{–}N(R)H$

(**IIa–IIf**)



$(C_6H_5)_2P(O)\text{–}CH_2\text{–}C(O)\text{–}N(R)H$

(**IIIa–IIIf**)

a: R = n-C_5H_{11}, **b**: R = n-C_6H_{13}, **c**: R = n-C_7H_{15}, **d**: R = n-C_8H_{17}, **e**: R = n-C_9H_{19}, **f**: R = n-$C_{10}H_{21}$

Because all other structural fragments in both types of compounds were identical apart from the bridge between the phosphoryl and carbonyl groups, all distinctions revealed by the calculations can be completely assigned to the replacement of the methylene spacer in CMPOs (**III**) by an imide spacer in phosphorylureas (**II**). The results are summarized in Table 1.

The quantum-chemical calculations allowed us to compare the most important parameters for the reactivity of BNOPCs. Such parameters are the effective charges on the oxygen atoms of the phosphoryl and carbonyl groups, the torsion angles between these groups, and the MESF zone width around the P=O and C=O groups of the models.

We can infer that the replacement of the methylene by an imide spacer in the model compounds renders the structure more rigid because of the decrease in the torsion angle between the P=O and C=O groups. While this torsion angle for CMPOs **IIIa**–**IIIf** is about 53°, for compounds **IIa–IIf** it is close to 38°. As a result, the distances between the phosphoryl and carbonyl oxygen atoms in phosphorylureas **II** are shorter than in related CMPOs **III**, which should evidently improve the complexing ability of such ureas.

Average relative negative charges *q* on phosphoryl and carbonyl oxygen atoms for CMPOs **III** do not exceed –0.625 and –0.314 au, respectively; for phosphorylureas **II**, the respective values are slightly higher: –0.638 and –0.339 au.

While the P=O and C=O atomic distances in the test classes of compounds are almost identical, the MESF zone widths in ureas **IIa**–**IIf** and the corresponding CMPOs **IIIa**–**IIIf** differ considerably: the MESF zone width in CMPOs **III** is 6.77 Å, whereas in ureas **II**, it is close to 8.10 Å.

The results of the MESF quantum-chemical calculations also imply that the complexing and extraction properties of *N*-diphenylphosphoryl-*N*'-*n*-alkyl(C_5–C_{10})ureas **IIa**–**IIf** should be far higher than those for related [*N*-*n*-alkyl(C_5–C_{10})carbamoylmethyl]diphenylphosphine oxides **IIIa**–**IIIf** due to the decreased torsion angles between the P=O and C=O groups, closer values of effective charges *q* on the oxygen atoms of the LG, and considerably increased width of the MESF zone. Of the aforementioned ureas, compounds with the *n*-alkyl length ranging from hexyl to octyl should have the highest efficiency.

To experimentally verify the above inference, we synthesized a set of phosphorylureas (**IIa–IIf**) using a recent three-stage one-pot process [12] and proceeding from low-cost commercially available reagents (Scheme 1). This process produces target compounds with high yield (>90%) and high purity (at least 97%).

$$\mathrm{Ph_2PCl} \xrightarrow[\mathrm{CCl_4}]{\mathrm{SO_2Cl_2},\ \approx 20^\circ\mathrm{C}} [\mathrm{Ph_2P(O)Cl}]$$

$$\xrightarrow[\mathrm{MeCN}]{\mathrm{NaOCN},\ [\mathrm{MgCl_2}],\ \approx 20^\circ\mathrm{C}} [\mathrm{Ph_2P(O)NCO}] \xrightarrow{\mathrm{RNH_2},\ \approx 20^\circ\mathrm{C}} \underset{\textbf{IIa–IIf}}{\mathrm{Ph_2P(O)NHC(O)NHR}}$$

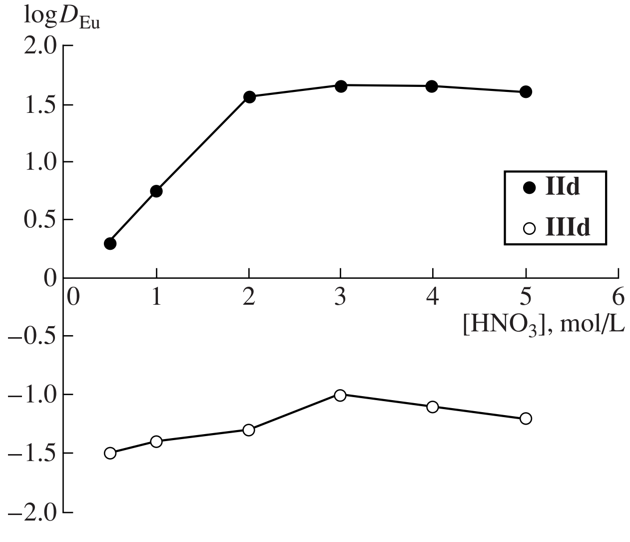
Scheme 1.

Uranium(VI) extraction by 0.05 M solutions of compounds **IIb**–**IIf**[1] from 2.81 M HNO_3 to chloroform showed that, indeed, the highest distribution ratios in this set of compounds are achieved for ureas with *N*'-*n*-alkyl radicals C_6–C_8; *N*'-*n*-octylurea **IId** has the maximal efficiency (Table 2).

The ability to extract uranium(VI) from nitric acid solutions of various strengths for this urea is far higher than for the most effective CMPO extractant (diphenyl(*N*,*N*-dibutylcarbamoylmethyl)phosphine oxide **I**); this effect is most prominent for high acid concentrations (Table 3).

Moreover, the predicted advantage of phosphorylureas (**II**) over CMPOs in extraction ability is actually observed not only for actinides but also for lanthanides: in ability to extract europium(III) from nitric acid solutions, phosphorylurea **IId** exceeds structurally related phosphine oxide **IIId** by more than two orders of magnitude (figure).

To summarize, the experimental check completely validates the high efficiency of *N*-diphenylphosphoryl-*N*'-*n*-alkylureas for separating 4*f* and 5*f* elements, inferred from MESF quantum-chemical simulations, and implies the potential of this strategy for finding



Extraction of indicator europium(III) amounts by 0.1 M solutions of $Ph_2P(O)NHC(O)NH$-*n*-C_8H_{17} (**IId**) and $Ph_2P(O)CH_2C(O)NH$-*n*-C_8H_{17} (**IIId**) in chloroform vs. HNO_3 concentration (phase ratio: 1 : 1).

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[1] Urea **IIa** is not sufficiently soluble in chloroform for obtaining solutions of the required concentration.

new, improved types of extractants for solving various engineering and analytical problems.

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