Dependence of the extraction capacity of neutral bidentate organophosphorus compounds on their structure: a quantum chemical study

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Correlations between the extraction capacities and molecular structures of organophosphorus compounds (reagents for extraction of transplutonium elements from spent nuclear fuel) were studied using a quantum chemical approach. The results of calculations are in qualitative agreement with experimental data. The approach proposed can be used for analysis of the extraction properties of all classes of organophosphorus compounds and also for prediction of the most efficient organophosphorus extragents with preset properties.

Key words: spent nuclear fuel, fractionation, extraction, organophosphorus compounds, quantum chemical calculations, molecular electrostatic potential, torsion angle, effective charge, complexation, functional group, "anomalous aryl strengthening" effect.

Processing of spent nuclear fuel (SNF) in order to extract uranium and plutonium followed by recovery into fresh nuclear fuel is an important step in a closed fuel cycle. At present, the SNF processing technology used in the Russian Federation is based on the PUREX process,[1] which was initially elaborated to provide plutonium extraction for military purposes from irradiated uranium lumps. Large-scale PUREX processing of SNF for nuclear power engineering, especially at high nuclear fuel burnup, leads to accumulation of large amounts of liquid high-level waste (HLW).[2] Therefore, in connection with an increase in the amount of processed SNF and taking into account toughening of requirements for handling of HLW, in the Russian Federation it is planned to fractionate liquid HLW and extract the Cs, Sr, and long-lived actinide fractions in order to provide separate solidification and subsequent long-term storage of the corresponding products. Among methods for HLW fractionation, the leading position is occupied by the extraction techniques involving organophosphorus compounds (OPCs) as the most promising extragents.[3—6]

The search for highly efficient OPCs is an urgent scientific and practical problem. In particular, it includes establishment of the dependence of the extraction capacity (EC) of OPCs on their structure as one of the main goals. To this end, the extraction constants of various elements are often correlated with certain characteristics of the reactivity of extragents,[7,8] *e.g.*, the atomic group electronegativities,[9] the Taft constants σ^* (see Ref. 10) and the Kabachnik constants σ^P (see Refs 11 and 12, in both cases assuming additive substituent effects), the electron density (charge) on the functional atom, the ionization potential,[13] the core s-level energies,[14] as well as with the basicity established from the energies of test reactions with the simplest electron acceptors[10,15—18] or from quantum chemical calculations of the proton affinity energies or the energies of complexation with Li^+ and LiH (see Refs 14 and 19).

Neutral OPCs (NOPCs) is the first class of compounds for which the "EC—structure" correlations were studied systematically. Phosphates, phosphonates, phosphinates, and phosphine oxides have the same reaction center (phorsphoryl group) and form complexes with identical composition (actinide : NOPC ratio) while their ECs significantly increase in this order. A correlation equation was proposed, which relates the parameters $\ln K_{ex}$ (K_{ex} is the effective extraction constant) of uranyl nitrate and nitric acid to the sums of the substituent group electronegativities in this series. Analysis showed that the ECs of monodentate NOPCs (MNOPCs) reduce upon introduction of electronegative substituents. At the same time this correlation equation is inapplicable to bidentate NOPCs (BNOPCs).[7] Therefore, we propose yet another approach for the determination of the dependence of the ECs of MNOPCs and BNOPCs on the structure, which is based on quantum chemical calculations of the molecular electrostatic potentials (MEPs). We plan to employ this approach in search for the EC—structure correlations for various classes of OPCs (see above) in order to predict the structures of the most efficient extragents for elaboration

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of novel methods of SNF processing and handling of nuclear waste.

The aim of this work was to carry out quantum chemical calculations of the MEP for a number of known OPCs and to compare the results obtained with the available experimental data.

The Approach

The formation of a complex between an organic reagent molecule and a metal cation (M) can be treated (ignoring desolvation of the interacting particles) as a two-step process involving an approach of the M cation to the functional (complex-forming) group (FG) of the organic reagent followed by the interaction between these species at distances of the order of the length of a chemical bond. The second step is accompanied by electron exchange, which results in complex formation. It is commonly accepted that distant substituents of different nature only slightly change the electronic states of the FG atoms of the reagent, which should not significantly affect the reactivity of the FG toward the pre-specified metal M.

Analysis of the first step shows that although the molecules are electrically neutral, they create electrostatic fields due to the distribution of the negative electron charge over a confined region surrounding atomic nuclei. As the organic reagent molecule and cation M approach each other, their MEPs interact.

This interaction can cause polarization of atomic electron shells in the organic reagent molecules, which in turn can favor the reaction, preclude it, or even make it impossible.[20] Ignoring the kinetic energy contribution, the overlap of the MEP regions of the same sign (different signs) favors repulsion between (approach of) the molecules. The larger the product of the absolute values of the potentials at the points of the overlap region the stronger the molecular attraction. Calculations of the MEP effect on the properties of organic molecules were first used to explain different values of the first and second dissociation constants of aliphatic dicarboxylic acids.[20] Various chemical properties of organic compounds, including differences between the nitration rates of substituted arenes, were also interpreted in terms of the MEP effect. The MEP calculations became a routine procedure with the development of quantum chemical theory and computers.[20]

The MEP at a point i is defined as the superposition of potentials created by each atom with allowance for the screening effect of the electron shells of the atoms in the molecule:

$$U(r_i) = \sum \frac{Z_A}{|r_i - r_A|} + \sum P_{\mu\nu} V(r_i),$$

where Z_A is the charge of the atom A located at the point r_A; $P_{\mu\nu}$ are the density matrix elements corresponding to the AOs μ and ν; $V(r_i)$ is the integral term, which makes it possible to estimate the effect of the electron density at the point r_i with allowance for the properties and overlap of the AOs μ and ν.

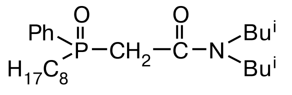
The MEP can be calculated using both semiempirical (CNDO/2, MINDO/3, AM1, PM3) and *ab initio* methods. Differences in the MEP distribution due to the accuracy of the computational methods employed were estimated in a number of studies.[21,22] In most cases the results of efficient semiempirical MEP calculations are only slightly different from those obtained using *ab initio* methods.[23] For instance, the ligand—receptor interactions were estimated[23] in the framework of analysis of the "structure—reactivity" correlations for effectors of a receptor complex of γ-aminobutyric acid using semiempirical MEP calculations. Identical MEP distributions around different molecules or conformers of the same molecule may indicate similarity of their physiological action, thus revealing their biological equivalence.[24]

Knowledge of the MEP distribution can be useful in studies of the differences of interactions at the stage of approach of the reacting molecules. Analysis of the second stage of the interaction allows one to establish the parameters whose effect can cause significant differences in reactivity. The interaction of the cation M and the electron-donor atom in the FG is proportional to the effective charge of M, namely, the larger the charge the stronger the interaction and the higher the reactivity of the compound under study. If the reagent molecule contains two FGs with an electron-donor atom in each group (*e.g.*, P=O and C=O groups), yet another parameter appears, namely, the torsion angle between the FGs. If this angle equals zero (FGs lie in the same plane) or is small, stable bidentate complexes can be formed. At large torsion angles, less stable complexes are formed.

Other parameters manifest themselves indirectly. In this work the solvation—desolvation processes and competitive protonation of electron-donor atoms (they reduce the complex-forming ability of FGs) are left out of consideration; no competing reactions and solvation shells are also assumed. This makes it possible to apply the approach proposed in this work to the interaction between the metal cation and organic reagent.

In order to construct correlations between the EC and the structure of OPCs using the MEP-based approach, we chose well-studied bidentate compounds **1—5** with the known extraction properties toward metals and strongly different reactivities toward metals; this simplifies the choice of corresponding parameters.

Octylphenyl(*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide (**1**) is basic to the TRUEX process employed for processing of HLW in the USA.[25] A Russian version of the TRUEX process[26] is based on diphenyl(*N*,*N*-dibutylcarbamoylmethyl)phosphine oxide (**2**) and assumes the



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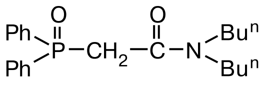

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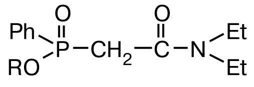
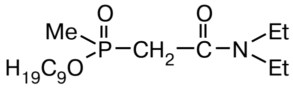


3a—f



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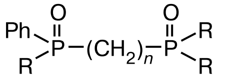


5a—c

3: R = C_nH_{2n+1}; n = 5 (**a**), 6 (**b**), 7 (**c**), 8 (**d**), 9 (**e**), 10 (**f**)

5: R = Ph, n = 1 (**a**); R = Ph, n = 3 (**b**); R = C_8H_{17}, n =1 (**c**)

use of polar diluents and (in contrast to **1**) no use of tributylphosphate as solubilizer.

Compound **2** has a higher EC in the extraction of transuranium elements from nitrate solutions compared to **1**.[26]

Recently,[27] we have systematically studied *O*-alkyl *N*,*N*-diethylcarbamoylmethylphosphinates (**3a—f**). Yet another extragent, *O*-nonyl *N*,*N*-diethylcarbamoylmethylmethylphosphinate (**4**), is structurally similar to **3**.

Elongation of the radical R in molecules **3a—f** causes nonmonotonic changes in the extraction coefficient of americium(III), which reaches a maximum at $n = 9$. The extraction capacities of compounds **3a—f** are much higher than that of **4**.[27]

Compounds **5a—c** are derivatives of methylenediphosphine dioxides (efficient bidentate extragents).[28] An "anomalous aryl strengthening" (AAS) effect was discovered in studies of the extraction properties of methylenediphosphine dioxides.[29—31] This means that, in contrast to alkyl substituents at the phosphorus atom in BNOPC molecules, the aryl substituents at the P atom in the BNOPC molecules favor a much higher degree of metal extraction in spite of increase in the electronegativities of substituents and a decrease in the basicities of compounds. The AAS effect is assumed to be due to biphilic (amphoteric) nature of the phenyl substituents capable of possessing both donor and acceptor properties depending on the nature of the complex-forming metal, reagent, and solvent.[19,32] On the contrary, disappearance of the AAS effect upon separation of the Ph group from the P atom by a CH_2 unit in the extraction with methylenebis(dibenzylphosphine) dioxide is indicative of π—π-conjugation between the Ph group and the P=O group in the formation of complex (six-membered ring) and of the electron density delocalization from the Ph group to the ring. In this case the AAS effect is due to the ring "aromatization", *i.e.*, the formation of a system of conjugated bonds. This provides arguments supporting a chemical (electronic) nature of this effect.[6] Other explanation for the AAS effect were also proposed.[30,31]

Calculation Procedure

Compiter simulation was carried out using the LEV program developed at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry (Russian Academy of Sciences). The starting conformations of the structures under study were generated using molecular image (structure) generators in such a manner that be best structurally similar to the actual structures and possess the highest possible reactivity). The O—P—C—O (or O—P—P—O for molecules **5a—c**) torsion angle was set to 0°, which implied the formation of bidentate complexes.

The generated conformations of the molecules under study were calculated by the MNDO semiempirical method. The calculations began with geometry optimization and search for the most stable conformations, construction of three-dimensional images of the optimized models, and obtaining information on the spatial arrangement of atoms, electron density values, effective atomic charges, bond lengths, and the bond and torsion angles. The second step included the MEP calculations with allowance for the results obtained at the geometry optimization step and construction of the contour maps of the MEP distribution.

The results obtained were analyzed using the following parameters: effective atomic charges of oxygens in the P=O and C=O groups, torsion angles between the P=O and C=O groups (O—P—C—O and O—P—P—O angles), and the absolute values and the extension of the MEP region around the FGs of the model molecules under study.

Results and Discussion

Test of parameters chosen in the calculations. Our calculations revealed that the changes in the electron density and in the effective charges of the electron-donor O atoms involved in complexation (Table 1) are insignificant and provide no explaination for considerable differences between the ECs of reagents.

The structures of the model molecules under study differ in the O—P—C(P)—O torsion angles (τ) that are listed below.

Molecule	τ /deg	Molecule	τ /deg	Molecule	τ /deg
1	39.64	**3c**	106.32	**4**	78.22
2	34.67	**3d**	109.08	**5a**	0.93
3a	102.55	**3e**	107.83	**5b**	1.91
3b	97.86	**3f**	103.03	**5c**	45.45

The optimum situation for the formation of complexes with cations M is when the P=O and C=O groups in the BNOPC molecules under study lie in the same plane. Here, chelation of the ion M results in planar conjugated six-membered ring while extraction results in bidentate

Table 1. Calculated atomic charges (q) of oxygens involved in chelation

Molecule	$-q$/au	
	P=O	C=O
1	0.626	0.262
2	0.632	0.286
3e	0.651	0.292
4	0.645	0.278

coordinated complexes. Alignment of the P=O and C=O groups leads to a more stable chelate and a higher reactivity of the starting reagent. At large O—P—C—O angles (tens of degrees), the bonding between the metal and extragent is weaker. This will result in less stable complexes and subsequent decrease in the partition coefficient (D) of the target ions.

According to calculations, replacement of radicals can cause significant changes in the O—P—C—O (O—P—P—O) angles from 1—5° to more than 90°. Apparently, reduction of the torsion angle (ideally, to zero) requires that substituents located on the same side of the FG be of nearly the same volume as in, *e.g.*, molecule **5a**. As a consequence, the calculated O—P—P—O angle in molecule **5a** is 0.93°. Examples of the reverse are provided by the model molecules **3a—f** characterized by large O—P—C—O torsion angles (~97—109°). This should affect the reactivity of the extragent models under study.

However, the reactivities of the compounds with similar O—P—C—O angles are significantly different and cannot be explained by differences in the molecular and electronic structures. Clearly, the reason should be searched for among the phenomena that accompany the approach of the reacting species (where the key role is played by electrostatic interactions). Therefore, it is natural to assume that distant polar substituents that determined the electrostatic field of the organic reagent molecule also affect its reactivity.

According to calculations, all the model molecules under study are characterized by unique MEPs. At the same time all of them have a common feature, namely, a region of negative potential values around the FG, which is due to the presence of two lone electron pairs of O atoms. The cation M, which creates a positive field, will tend to move to the region of negative potentials.

Although for all molecules the regions of negative MEP values are localized near the oxygen atoms of FGs, they have different shape and differ in absolute values. Seemingly, one should not expect significant changes in the MEP on going from molecule **3a** to **3b**, because both substituents (pentyl and hexyl radicals) are of the same nature and stucturally similar. However, the changes are significant (Fig. 1). Therefore, the MEP is an integrated characteristic of the molecule are "responses" to not only the change in the geometric parameters of the structure under study, namely, changes in torsion angles between O atoms (change in conjugation between lone electron pairs) but also replacement of substituents, *etc*. Indeed, introduction of an additional CH_2 fragment into the structure of the alkyl radical immediately causes a charge redistribution, which can provide an explanation for different reactivities of compounds **3a** and **3b**.

It should be noted that the MEP distribution and corresponding differences can only be studied for series of model structures under identical conditions.

Comparison of the results of quantum chemical calculations with experimental data. The O—P—C—O torsion angles calculated for molecules **1** and **2** are similar (39.64 and 34.67°, respectively) and make a small contribution to the difference in the ECs. However, the extensions of the regions of negative MEP values calculated for these molecules are significantly different (14.0 and 22.6 Å, respectively), which indicates a higher reactivity of compound **2** compared to **1**. These results were confirmed by experimental data.[25,26]

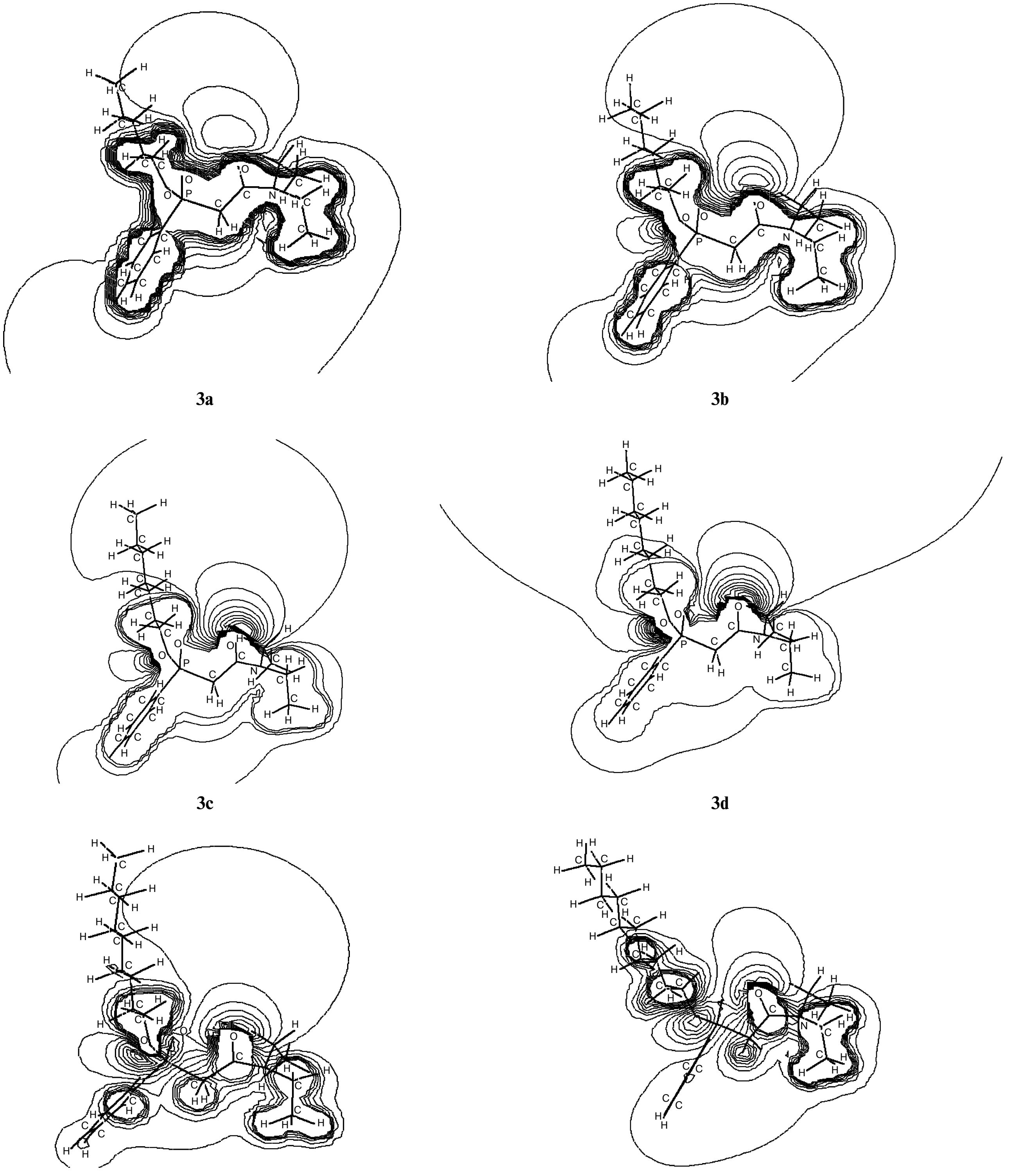
Quantum chemical calculations of the MEP distribution in molecules **3a—f** showed that these species are characterized by the same absolute value of the MEP near the FG and different extensions of corresponding MEP regions (see Fig. 1). The extensions of the negative MEP values calculated for molecules **3a—f** are listed below.

Molecule	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**
Region extension/Å	7.0	11.2	15.4	29.5	8.6	4.6

As can be seen, this parameter increases from 7.0 to 29.5 Å for molecules **3a—d** and then decreases to 4.6 Å for **3e,f** with the maximum value for **3d**. One could also expect a maximum distribution coefficient for this compound.

Taking extraction of Am^{3+} from 3 M HNO_3 solutions as an example, it was experimentally shown[27] that the ECs of compounds **3a—f** also change nonmonotonically (increase on going from **3a** to **3e** and then decreases on going to **3f**, Fig. 2). However, in the experiments the maximum D value was obtained for compound **3e**. At the same this difference is small. We believe that a small difference between the experimental data and the results of quantum chemical calculations can be explained by the influence of certain factors ignored by calculations (*e.g.*, different solubilities of the complexes with the actinide in the organic phase).

Comparison of the results of quantum chemical calculations of structures **3e** and **4** shows that the extension of the MEP region for **3e** is larger than for **4** (8.6 and 7.08 Å, respectively). According to calculations, compound **3e** is more reactive than **4**. These results were confirmed[27] by the data on extraction of americium(III) with



3a **3b**

3c **3d**

3e **3f**

Fig. 1. MEP distribution around the FG in the model structures of compounds **3a—f**; isolines were drawn with an increment of 1 Å^{-1}.

these compounds from 3 *M* HNO_3 solutions, namely, *D*(**3e**) = 2.1 *vs*. *D*(**4**) = 0.095.

In order to study the effects of symmetrical substituents and the distance between the oxygen atoms of FGs on the geometry and MEP distribution, we studied structures **5a—c**.[28]

Calculations confirmed our assumption of the effect of substituents of the same volume on the magnitude of

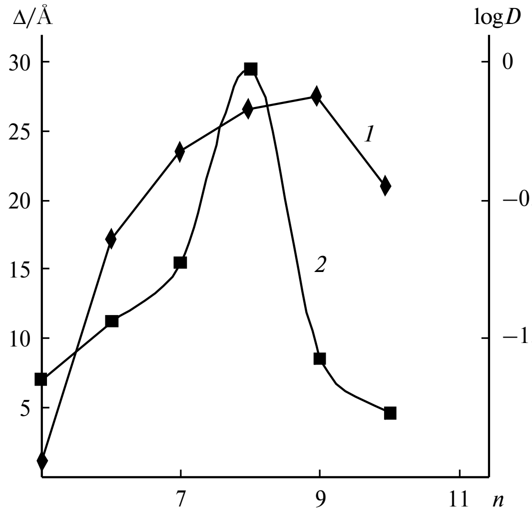


Fig. 2. Dependence of logarithm of the partition coefficient ($\log D$) in extraction of Am^{III} with solutions of compounds **3a—f** in dichloroethane[27] from 3 M HNO_3 solutions (*1*) and the extension (Δ) of the MEP (*2*) on the number of carbon atoms in the alkoxyl group (n).

the O—P—P—O angle (see above). The arrangement of substituents of the same volume on both sides of the FG favors a parallel arrangement of the P=O groups. Indeed, the O—P—P—O angle is 0.93° in molecule **5a** and 1.91° in molecule **5b** (substituents and P=O groups here are separated by the $—(CH_2)_3—$ radical), being 45.45° in molecule **5c** possessing no symmetry of bulk substituents on one side of the complex-forming group (see above).

These structural differences also affect the MEP distribution. The distances of the MEP extension calculated for molecules **5a**, **5b**, and **5c** are 30, 15.5, and 13.5 Å, respectively. Therefore, the metal cation will rapidly approach the reagent in the case of **5a**, do it somewhat slower with **5b**, and even more slower for **5c**. The last-mentioned molecule is characterized by not only weaker negative field around the FG but also a large O—P—P—O angle, which makes the formation of a bidentate complex different and reduces the reactivity of the reagent. According to calculations, replacement of aromatic substituents by alkyl ones and the lack of "substituent volume similarity" at least on one side of the FG leads to reduction of the reactivity, which is characterized by significant decrease in the extension of the MEP region around this group. This in turn reduces the probability of the interaction between the reagent and the M cation M and, therefore, makes the complex formation less probable.

Thus, the results of quantum chemical calculations of the MEP suggest that not only the biphilic nature of phenyl substituents and/or "aromatization" of the chelate ring[16,19] but also the torsion angles and the extension of the MEP region of the electron-donor groups contribute largely to the AAS effect. The interaction between them can lead to both strengthening and weakening of the BNOPC—metal complex, which in turn leads to an increase or decrease in the distribution coefficients.

Thus, in this work we proposed an approach that involves quantum chemical calculations of the MEP, which can be used for prediction of the ECs of all classes of OPCs including the ECs for extraction of transuranic elements.

Experimental data on extraction of actinides[25—28] show good correlations with the results of quantum chemical calculations of the MEP. Differences in the ECs of the structurally similar extragents studied can be explained by changes in the torsion angles and by different extension of the MEP region, which determine the ability to form complexes. The method proposed provides a convenient tool for explanation for the differences between the ECs in series of compounds. This offers prospects for quite reliable assessment of the reactivities of novel OPCs and, probably, prediction of the structures of efficient organophosphorus extragents with preset properties.

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