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XAS study of americium complexes with calixarene bearing carbamoylmethylphosphine oxide moieties

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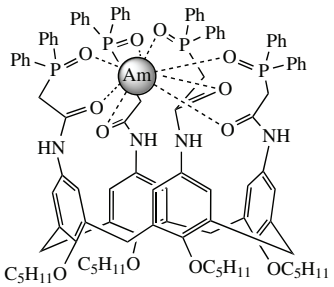
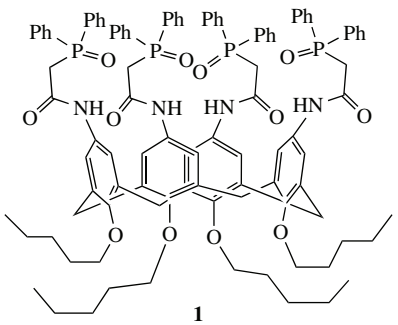
The local environment of a novel group of americium (Am^{3+}) complexes with calix[4]arene bearing carbamoylmethylphosphine oxide moieties on the upper rim has been investigated by X-ray absorption spectroscopy. The complexes were obtained by the extraction of americium from aqueous nitric or 2-(1-adamantyl)sulfoacetic acids with the 1,2-dichloroethane solution of this ligand. The correlation of the structures of the obtained complexes with americium distribution coefficients in the corresponding extraction systems is revealed.



Keywords: liquid–liquid extraction, EXAFS spectroscopy, calixarenes, americium complexes, phosphorylacetamides, carbamoylmethylphosphine oxides.

Carbamoylmethylphosphine oxides (CMPOs), or phosphorylacetamides, are currently considered to be among the most effective extractants for transuranic elements separation.[1–4] A promising approach in the new highly effective extractant production is the use of molecular platforms for the preorganization of the functional groups. Thus, the extraction efficiency grows at least 100 times when using calixarenes modified by introducing four such substituents on the lower or upper rims, compared to those with pure CMPOs.[5] Moreover, it was shown that calixarenes modified on the lower or upper rim can fractionate radioactive wastes and selectively separate cesium, strontium, lanthanides, and actinides.[6–11]

In our previous work,[12] we used solution of calixarene **1** bearing four CMPO moieties (phosphorylacetamido substituents) on the upper rim in 1,2-dichloroethane. The dependence of Am^{3+} distribution coefficients D on the acid type and concentration when using this extractant was studied. The value of D for americium grows notably during the extraction from nitrate solution as the acidity grows ($D = 2.9 \pm 1.7$ for the extraction from 0.1 M HNO_3, and $D = 22.5 \pm 3.4$ for the extraction from 3 M HNO_3). Replacement of nitric acid by 2-(1-adamantyl) sulfoacetic acid **2** significantly improves the extraction efficiency ($D = 11.9 \pm 0.9$ for the extraction from 0.01 M solution of **2**).[12]



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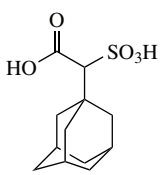

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Quantum mechanical calculations[13–15] were used in search for the most effective extraction system for the separation of lanthanides and actinides. This requires an understanding of extraction mechanisms and the creation of databases of extraction efficiencies depending on the structures of extractants, solvents, *etc*.

The study of lanthanide and actinide extraction with calixarenes bearing CMPO moieties (Calix-CMPO) requires, in particular, the information on the structure of americium complex formed in organic phase during extraction and the influence of aqueous solution composition on the complex structure.

In this paper, we present the extended X-ray absorption fine structure (EXAFS) study of two Calix-CMPO complexes **3a** and **3b** in 1,2-dichloroethane solution obtained under different conditions† in order to determine the effect of the acid type on Am^{3+} local environment in the complexes and the distances from americium ion to the nearest coordination spheres.

Since the Am^{3+} ion size is 1.97–2.18 Å in diameter depending on the coordination number,[16] and the diameter of calix[4]arene lower rim is 1.0 Å,[17] Am^{3+} cannot be coordinated with four oxygen atoms of this rim. Also, it was noted[18] that the change in the number of carbon atoms in the alkoxy substituents of the lower rim influences insignificantly on the distribution coefficients of lanthanides, and, hence, the lower rim sites can

† For details, see Online Supplementary Materials.

hardly be involved in the coordination with americium. Therefore, the modeling of the possible complex structures in the present work was accomplished for americium coordinated only within the upper rim.

The previous studies of americium extraction with CMPO with the addition of tributyl phosphate in nonpolar solvent from nitric acid solutions showed that Am ion needs three ligands per one cation (complex 1 : 3). As nitric acid concentration grows, HNO_3 molecules get also included in the extracted complex.[2]

In general, extraction of americium ions with CMPO from nitric acid solution can be described by the following equilibrium:

$$[Am(H_2O)_9]^{3+}_{(aq)} + 3\,CMPO\cdot(HNO_3)_{n(org)} + 3NO^-_{3(aq)} \leftrightarrow \quad (1)$$

$$\leftrightarrow Am(NO_3)_3\cdot(CMPO)_3\cdot(HNO_3)_{m(org)} + 9\,H_2O_{(aq)} + (3n-m)HNO_{3(aq)}$$

EXAFS spectra of Am L_{III}-edge of complexes **3a** and **3b** and their Fourier transforms are presented in Figures 1, 2. EXAFS results show that one ion of americium is coordinated with ten oxygen atoms in complex **3a**, *i.e.* coordination number of Am^{3+} (CN_{Am}) is 10, and the Am–O interatomic distance is 2.43 ± 0.03 Å (first coordination sphere radius). Also, it should be noted that the value of the Debye–Waller factor (σ^2), which characterizes the disorder of the interatomic scattering (Table 1), is high. In order to determine the average Am–N distance to three nitrogen atoms building the second coordination sphere, the Debye–Waller factor during the fitting was fixed to be 0.006 Å^2. In this case, the Am–N distance was found to be 3.18 ± 0.15 Å. The obtained distances are in satisfactory agreement with the X-ray diffraction (XRD) data published for Eu–CMPO complexes (Eu–N and Eu–O distances are 2.38–2.72 ± 0.01 and 2.93–3.01 ± 0.01 Å, respectively).[19] The obtained results are also in good agreement with the experimental data published for americium environment in complexes containing oxygen in the first coordination sphere and nitrogen in the second coordination sphere. Thus, for complexes Am with 2,6-bis[(diphenylphosphoryl)methyl]pyridine 1-oxide (NOPOPO), the XRD-determined Am–O and Am–N distances were found to be 2.34–2.51 ± 0.01 and 2.96–3.01 ± 0.01 Å, respectively.[20] From the obtained data, we can conclude that the americium ion is coordinated with six oxygen atoms from three nitrate anions and four oxygen atoms from two CMPO residues in the studied complex **3a** with Calix-CMPO [Figure 3(*a*)].

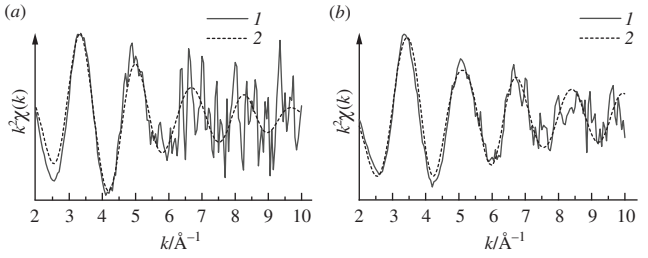

Figure 1 EXAFS spectra of Am L_{III}-edge: (*1*) experimental and (*2*) best-fit model data for (*a*) complex **3a** and (*b*) complex **3b**.

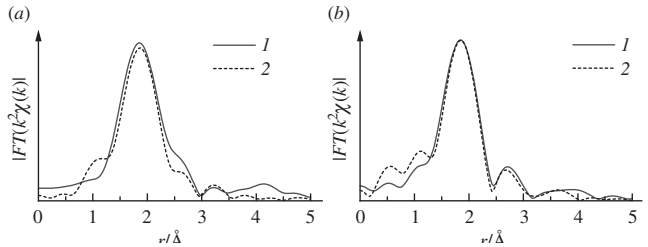

Figure 2 Fourier transforms of Am L_{III}-edge EXAFS spectra: (*1*) experimental and (*2*) best-fit model data for (*a*) complex **3a** and (*b*) complex **3b**.

Table 1 Quantitative results of the local atomic structure of complexes **3a**,**b**.

Complex	Coordination sphere number	Coordinating atom	Number of atoms in the coordination sphere	r/Å[a]	σ^2/Å^2[b]
3a	1	O	10	2.43(0.03)	0.010(0.002)
3a	2	N	3	3.18(0.15)	0.006
3b	1	O	8	2.40(0.02)	0.005(0.001)
3b	2	C	4	3.35(0.08)	0.005
		P	4	3.56(0.08)	0.016(0.011)

[a] r is the distance from ion of americium to the ions of the corresponding coordination sphere. [b] σ^2 is the Debye–Waller factor.

The study of stoichiometry of complexes of Eu with calix[4]-arene, differing from Calix-CMPO ones only by the lower rim alkoxy group length, indicates the formation of both 1 : 1[21] and 1 : 2[22] complexes depending on metal/ligand concentration ratio according to the angular coefficients of linear dependence log$D$ – log[L]. The angular coefficient equal to 1 was obtained for low calixarene concentration, and its value of 2 was found when the cation/ligand ratio reached 100.[23] Therefore, one may suggest that the 1 : 1 complex was formed under the conditions used in the present work, and the extraction can be described as follows:

$$[Am(H_2O)_9]^{3+}_{(aq)} + Calix\text{-}CMPO_{(org)} + 3\,NO^-_{3(aq)} \leftrightarrow \quad (2)$$

$$\leftrightarrow Am(NO_3)_3\cdot Calix\text{-}CMPO_{(org)} + 9\,H_2O_{(aq)}$$

Obviously, in this case, Am^{3+} coordinates two CMPO groups of one ligand molecule, *i.e.*, the ion is chelated by the macromolecule 'wall'. So, the initial conception of developing a class of extractants where the calixarene platform provides the rigid chelating structure and the metal ion coordinates within the calixarene cavity with all four CMPO fragments does not take place in this case. Comparison of stability constants of Eu–CMPO complexes (logβ_{11} = 3.6, logβ_{12} = 5.5) and Eu with Calix-CMPO (logβ_{11} = 6.2)[24] confirms it indirectly.

The suggested scheme of the coordination spheres of complex **3a** and the distances to the coordination spheres are given in [Figure 3(*a*)].

One can see that the formation of complex **3a** includes the transfer of nitrate ions to the non-polar organic phase. To increase the extraction efficiency, the employment of ionic liquids as organic phase[25–27] was studied. For example, in the course of CMPO extraction into 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide the composition of the extracted complex was LnL_3^{3+} lacking nitrate ions.[28] In the present work, when 2-(1-adamantyl)sulfoacetic acid **2** provided a hydrophobic counter ion, the extraction was facilitated as complex **3b** was formed.

From the EXAFS spectra, it is found that the americium ion is coordinated with eight oxygen ions (CN_{Am} = 8) in complex **3b**

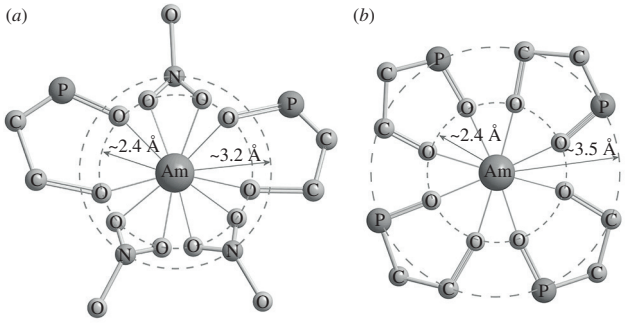

Figure 3 The local environment around americium and the distances to the first two coordination spheres in (*a*) complex **3a** and (*b*) complex **3b**.

formed during the Am extraction from aqueous solution of acid **2** [Figure 3(*b*)]. The Am–O, Am–C and Am–P distances are 2.40 ± 0.02, 3.35 ± 0.08 and 3.56 ± 0.08 Å, respectively. The value of the Debye–Waller factor for carbon atoms of the second coordination sphere is fixed. It is important for determining the distance to the phosphorous atoms of the second coordination sphere (see Table 1). The obtained distances are in a satisfactory agreement with the EXAFS data for the Eu–CMPO complex in 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)-imide solution (2.37 ± 0.01, 3.43 ± 0.02 and 4.03 ± 0.03 Å, respectively),[28] and with the XRD data for the Eu–CMPO (2.38–2.72 ± 0.01, 3.43–3.48 ± 0.01 and 3.61 ± 0.01 Å, respectively).[19] The agreement with the published experimental data on Am environment in complexes where the first coordination spheres with respect to americium were formed by oxygen, carbon, and phosphorus, was also reached. Thus, according to XRD, the Am–O and Am–P distances for the Am–NOPOPO complex are 2.34–2.51 ± 0.01 and 3.61–3.71 ± 0.01 Å,[20] and the Am–O and Am–C distances for the Am/tetramethyl-3-oxaglutaramide complex are 2.40–2.52 ± 0.01 and 3.31–3.34 ± 0.01 Å, respectively.[29]

It was found that in complex **3b** americium ion is coordinated with eight oxygen ions from four CMPO-substitutes (four carbonyl and four phosphoryl groups of the CMPO residues). The scheme of the nearest to the Am^{3+} coordination spheres of complex **3b** is shown in Figure 3(*b*). It has to be noted that unlike in complex **3a**, where Am^{3+} is coordinated both with CMPO-substitutes and anions of nitric acid from the initial solution, in complex **3b** ion Am^{3+} is not coordinated with 2-(1-adamantyl)-sulfoacetate ion but is coordinated only with the CMPO groups attached to calix[4]arene core. Since in the present work calix[4]-arene was insufficient with respect to americium, one can suggest a formation of the M : L (1 : 1) complex, which can be described as follows:

$$[Am(H_2O)_9]^{3+}_{(aq)} + \text{Calix-CMPO}_{(org)} + 3\,Ad^{-}_{(aq)} \leftrightarrow \quad (3)$$

$$\leftrightarrow [Am \cdot \text{Calix-CMPO}]Ad_{3\,(org)} + 9\,H_2O_{(aq)}$$

Thus, unlike the nitrate ion, a more lipophilic counter ion of acid **2** is not included in the first coordination sphere of the Am–calixarene complex. Probably, this is energetically more favorable compared to the extraction from the nitric acid solution and provides a higher extraction efficiency. Besides, the comparison of the EXAFS data with the stoichiometric composition allows one to conclude that in the case of complex **3b** we observe the chelation of americium with participation of all four CMPO-groups of the macrocycle. It is possible only if Am is incorporated into the calixarene cavity. Unlike in complex **3a**, in complex **3b** first coordination sphere of Am^{3+} ion does not contain oxygen atoms from nitrate as well as 2-(1-adamantyl)-sulfoacetate anions, and Am^{3+} chelates with four CMPO moieties of one cavitand macromolecule. This important fact explains a significant increase in the distribution coefficients with the change of extraction conditions. The obtained data can be used for the optimization of extractant selection and composition of the extraction system for selective separation of americium from the mixture of lanthanide and actinide compounds.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.014.

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