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EXTRACTION OF TRIVALENT LANTHANIDES AND ACTINIDES BY "CMPO-LIKE" CALIXARENES

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ABSTRACT

Extractive properties of calix[4]arenes bearing carbamoylmethylphosphine oxide moieties on their upper rim toward trivalent lanthanide and actinide cations were investigated. The study revealed that these molecules selectively extract light lanthanides and actinides from heavy lanthanides. All parameters present in the extraction system were varied to determine the origin of the selectivity. It was found that this selectivity requires a calix[4]arene platform and acetamidophosphine oxide groups containing phenyl substituents on the four phosphorus atoms.

INTRODUCTION

As part of the research being conducted in France on separations of long half-life radionuclides, the separation of minor actinides and fission products with a

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perspective toward transmutation or specific processing and storage is currently under study. Extraction and separation of trivalent lanthanides and actinides are top priorities.

Carbamoylmethylphosphine oxide (CMPO) compounds, which have been used in the TRUEX process (1), are known to extract trivalent cations from highly acidic and saline media (2). Such extraction requires three molecules per complex (3). Parent calixarenes are excellent platforms for functionalization with specific groups. Attachment to the calixarene platform adds preorganization to the specificity of these functional groups, which decreases the energy needed to gather the extractant molecules during the extraction. Exceptional properties of cesium extraction and selectivity over sodium have been exhibited for calixarenes bearing crown ethers (4,5). Following the same line of thought, CMPO molecules and calix[4]arene have been associated.

Calixarenes in the cone conformation bearing acetamidophosphine oxide groups on their upper rim were synthesized and gave interesting results for the extraction of europium and some trivalent or tetravalent actinides (6). To determine the stoichiometry of the species involved in the complexation of europium, a full study dealing with the extraction of this metallic cation by this ligand was also performed (7). This paper reports the behavior of the "CMPO-like" calixarenes toward several of the lanthanides and actinides, with an emphasis on selectivity.

EXPERIMENTAL

N-octyl(phenyl)diisobutylcarbamoylmethylphosphine oxide (CMPO derivative) was provided by Xymax, Inc., Boca Raton, Florida, and used as received. All calixarenes and other ligands used in this study (cf. Figure 1) were synthesized according to procedures described previously (8) or to be published (9).

Organic phases were prepared by dissolving a precisely weighed amount of ligand into chloroform (99.9% GC grade, Aldrich) or 1-octanol (99.9% GC grade, Aldrich). Lower calixarene concentrations were obtained by dilution of more concentrated solutions in volumetric flasks.

Aqueous phases were prepared by dissolving lanthanide nitrates (>99%, Aldrich) in an aqueous solution containing either 4 *M* sodium nitrate (99.9%, Aldrich) and 10⁻² *M* nitric acid or 3 *M* nitric acid. The acids were obtained by dilution of concentrated nitric acid (65%, Carlo Erba) with deionized water. Acid concentrations

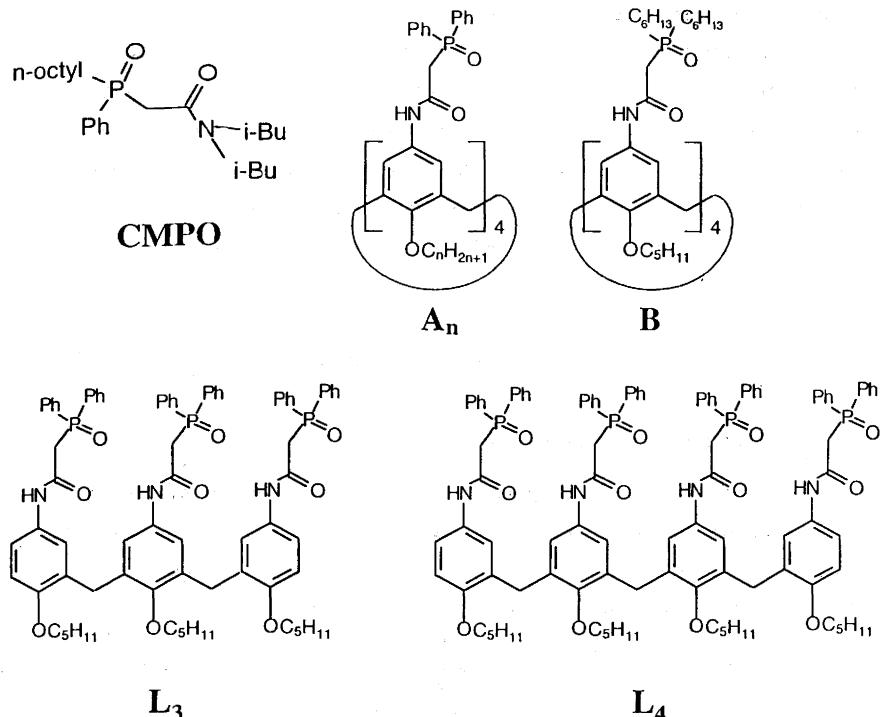


FIGURE 1. Chemical structures and names of the extractants studied.
Ph = phenyl group. A_n refers to a family of calix[4]arenes that have O-alkyl chains on their lower rim containing n atoms of carbon.

were checked by titrating a known volume of acid with a freshly prepared solution of sodium hydroxide Titrisol Merck. Lanthanide concentrations as low as $10^{-3} M$ were measured by a potentiometric method with an Ag/Hg electrode using EDTA as a titrant (10). A titroprocessor Mettler DL25 was used for all titrations. All other lower concentrations were prepared by dilution.

Extraction experiments were monitored by spiking trace concentrations of radioisotopes. The ^{140}La , ^{166}Ho , and ^{160}Tb were provided by Polatom (Poland); ^{153}Sm by Cis Bio International (France); and ^{147}Pm , ^{152}Eu , ^{153}Gd , ^{169}Er , ^{169}Yb , ^{241}Am , and ^{244}Cm by DAMRI (CEA, France).

Experiments were performed in glass-stoppered tubes where 1.5 mL of organic and aqueous phases were contacted; the aqueous phases contained a spike of

radioisotope corresponding to the stable trivalent cation, when available. Extraction was carried out by gently rocking the tubes for 30 min. (preliminary experiments have shown that equilibrium was reached after 5 min) and centrifuging for 5 min at 3000 rpm. Then, 1 mL of each phase was removed to be counted either with a γ counter (pure Ge, Eurysis), or with an α, β -scintillation counter (Packard) by adding the aliquot to 14 mL of a scintillation cocktail (Packard).

All experiments were performed at 25°C in a controlled temperature chamber (SANYO).

RESULTS AND DISCUSSION

Extraction and Stripping of Europium

Our first goal was to compare the extraction efficiencies of calixarene A_5 (containing four CMPO groups on the upper rim and four O-pentyl chains on the lower rim) with the CMPO molecule alone. This comparison is based on the values of the distribution coefficient, D, of the species M to extract :

$$D = \frac{\sum [\bar{M}]_{\text{org}}}{\sum [M]_{\text{aq}}}.$$

Europium was chosen to represent the behavior of all trivalent cations. Figure 2 shows that all europium distribution coefficients obtained with the calixarene A_5 are much higher than those obtained with the CMPO molecule alone, even after correcting the ligand concentration to account for the four CMPO extracting groups on the calixarene. Extraction efficiencies differ by about five orders of magnitude. This improvement is most likely due to the cone conformation of A_5 , which allows preorganization of the four extracting groups on the upper rim. An increase in the extraction properties was observed when the CMPO molecule was substituted on a calixarene platform. A similar effect was noted when crown ethers were bonded to a calixarene in a 1,3-alternate conformation (4,5,11).

Previous studies relating to transport experiments with these "CMPO-like" calixarenes dissolved in nitrophenylhexyl ether (NPHE) (6) (instead of chloroform) suggested that stripping was difficult since an aqueous complexant was necessary. Table 1 summarizes the results obtained for extraction and stripping of europium into $10^{-2} M$ nitric acid. A low concentration of acid was chosen instead of deionized water to avoid hydrolysis of the trivalent cation.

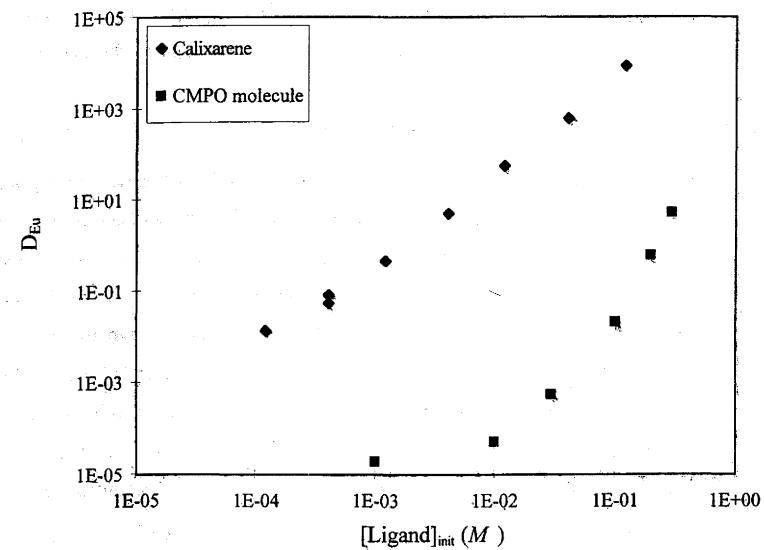


FIGURE 2. Comparison of extraction efficiencies of CMPO and calixarene A₅. Initial calixarene concentration is corrected to take into account the fact that this molecule has four CMPO moieties. Organic diluent: chloroform, aqueous phase: 4 M sodium nitrate, 10⁻² M nitric acid, 10⁻⁶ M europium nitrate; T = 25°C.

TABLE 1. EXTRACTION AND STRIPPING OF EUROPIUM^a

[A ₅]	[Eu ³⁺] = 10 ⁻⁶ M		[Eu ³⁺] = 10 ⁻⁴ M	
	10 ⁻³ M	10 ⁻² M	10 ⁻³ M	10 ⁻² M
% ext.	77.3	99.8	76.6	99.8
% strip.	99.8	99.6	~100	99.6

^a Extraction: organic phase: chloroform, [A₅]_{init} = 10⁻³ M or 10⁻² M; aqueous phase: 4 M sodium nitrate, 10⁻² M nitric acid, 10⁻⁶ M or 10⁻⁴ M europium nitrate; T = 25°C.

Stripping: organic phase: from extraction; aqueous phase: 10⁻² M nitric acid.

Stripping was extremely efficient in our experiments, which presents a major advantage regarding the diluent used. Almost all the metallic cation was released into the aqueous phase after a single contact. Therefore, it can be easily deduced that only the ionic strength of the initial aqueous phase plays a dominant role in the values of distribution coefficients and there are no major side interactions due to the diluent.

Extraction of Trivalent Lanthanides and Actinides

Our assumption to this point was that europium could represent all f-group trivalent cations. Extraction experiments using several lanthanides and actinides were performed in order to determine the potential intragroup and intergroup separation of these calixarenes. We compared the extraction behavior afforded by CMPO alone (at 0.2 M) with that of calixarene A₅ (at 10⁻³ M). The results are shown in Figure 3. The extractant concentrations were selected to obtain comparable distribution coefficient values in both cases. The results of these experiments allowed us to determine the distribution coefficient of each cation. Identical results were obtained when all cations were mixed in the aqueous phase. Indeed, their concentrations are not high enough, as compared with the concentration of the ligand, to exhibit a competition. The results are summarized in Table 2. CMPO behavior is consistent with previously reported results (12,13). What is most remarkable is the selectivity exhibited by the calixarene A₅. There are almost three orders of magnitude between the distribution coefficients of lanthanum (the lightest and largest lanthanide) and ytterbium (the heaviest and smallest trivalent cation we have studied).

The decrease in extraction efficiencies along the lanthanide series suggests a size recognition. Such selectivity is surprising since the CMPO groups on the upper rim of the calix[4]arene are conformationally flexible. The only comparable intra-lanthanide selectivity can be found with the phosphoric acid HDEHPA (diethylhexylphosphoric acid), but the trend is opposite to that reported here (i.e., the more efficiently extracted elements are the heavier lanthanides) (14).

Two trivalent elements of the actinide series, americium and curium, were also studied. For comparable radii (15), actinides are extracted somewhat more readily than lanthanides. This may be the result of a more covalent character in the bonding developed between cation and ligand. Similar results were not observed with CMPO, but we can reasonably assume that the trend was very small and not noticeable in this case. There are numerous cases in which the functional groups attached to a calixarene tend to have their initial properties enhanced. In order to better

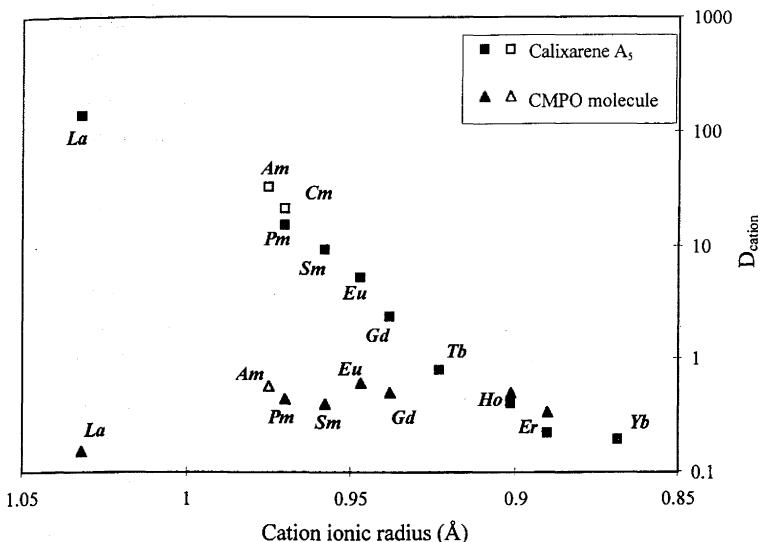


FIGURE 3. Comparison of extraction efficiencies of CMPO molecule and calixarene A₅. Organic phase: chloroform containing either $[CMPO]_{init} = 0.2\text{ M}$ or $[A_5]_{init} = 10^{-3}\text{ M}$; aqueous phase: 4 M sodium nitrate, 10^{-2} M nitric acid, 10^{-6} M metallic cation nitrate (except for promethium, americium, and curium used at trace level); $T = 25^\circ\text{C}$. Filled symbols: lanthanides; open symbols: actinides.

TABLE 2. DISTRIBUTION COEFFICIENTS OF TRIVALENT LANTHANIDES AND ACTINIDES VERSUS THEIR IONIC RADII^a

Cation	La	Pm	Sm	Eu	Gd	Tb	Ho	Er	Yb	Am	Cm
Ionic radius, Å (15)	1.032	0.97	0.958	0.947	0.938	0.923	0.90	0.89	0.868	0.975	0.97
D _{cation}	140	15.2	9.3	5.2	2.4	0.80	0.41	0.22	0.19	32	21

^aOrganic phase: chloroform containing $[A_5]_{init} = 10^{-3}\text{ M}$. Aqueous phase: 4 M sodium nitrate, 10^{-2} M nitric acid, 10^{-6} M metallic cation nitrate (except for promethium, americium, and curium used at trace level); $T = 25^\circ\text{C}$.

understand the observed selectivities, different parameters of this extraction system were varied.

Extraction efficiencies are usually directly related to the properties of the aqueous and organic phases. We changed the diluent for our system and used a nitric acid phase instead of a high-saline aqueous solution. We expected different distribution coefficients but wanted to check the influence these changes had on selectivity. By independently changing the two phases, we could compare four systems, all containing the calixarene A_5 as the extractant (Figure 4). The four plots are parallel, which shows the independence of the selectivity to the conditions. It is important to note that the calixarene remained efficient in separating the different elements, even at high acid concentrations (3 M nitric acid). The D_{Am}/D_{Eu} ratio so often used to show the separation potential of an extractant toward the lanthanides and actinides is high (~10) for an aqueous medium with a pH below 0. Most ligands designed to accomplish this separation do not extract when the acid is greater than 0.1 M (16,17). Probable protonation of the calixarene does not affect its ability to selectively extract trivalent cations. These experiments show that selectivity is due to the calixarene. The modifications discussed below consist of changes on the ligand itself.

The macrocyclic effect of the calixarene structure was tested using the two non-macrocyclic ligands L_3 and L_4 (Figure 1). The latter corresponds directly to the calixarene A_5 , except for the linkage between the end arene groups, while L_3 and L_4 are used to determine the influence of the number of extracting units (Figure 5). Several lanthanides and actinides were extracted to illustrate the relative behavior of the two ligands. The extraction behavior observed for these ligands was found to be far different from what had been found for the calixarene. The greatest separation factor (ratio of the distribution coefficients of two elements) only equals 10. In addition, the shape of the curve is quite different. There is no evidence of a size effect; thus, the calixarene structure is mandatory to obtain the selectivity.

The lower rim of the calixarene A_5 is comprised of four O-pentyl chains. We have also investigated calixarenes A_n with identical upper rims, but with O-alkyl chains of different lengths. We chose to study chains containing 3 to 14 carbon atoms. Less than 3 does not guarantee the cone conformation, while more than 14 tends to create solubility problems. Figure 6 shows that the chain length does not induce any change in the distribution coefficients of the lanthanides.

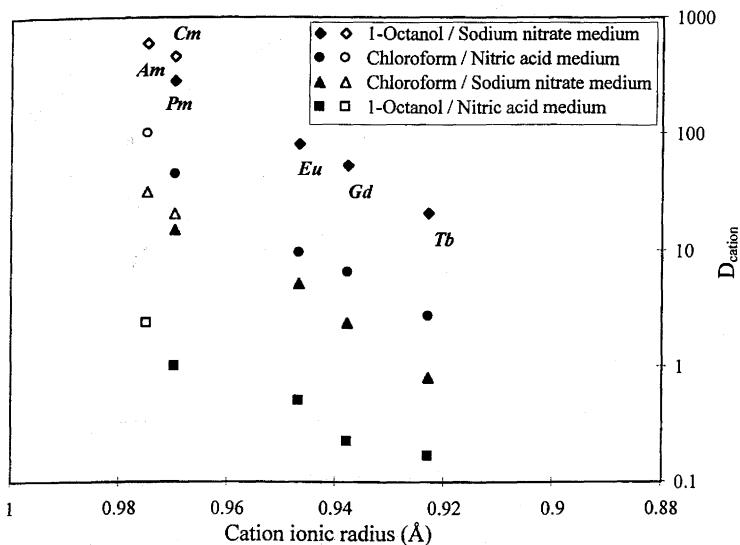


FIGURE 4. Extraction of lanthanides(III) and actinides(III) by calixarene A_5 from two different aqueous and organic media. Comparison between 4 M sodium nitrate and 3 M nitric acid (aqueous conditions) and between chloroform and 1-octanol (organic diluents). Organic phase: diluent containing $[A_5]_{\text{init}} = 10^{-3} M$; aqueous phase: aqueous solution containing $10^{-6} M$ metallic cation nitrate (except for promethium, americium, and curium used at trace level); $T = 25^\circ\text{C}$. Filled symbols: lanthanides; open symbols: actinides.

Finally, we were interested in changing the substituents present on the upper rim of the calixarene, particularly those on the four phosphorus atoms of the CMPO. The two phenyl groups were replaced by two hexyl groups (compound B). Figure 7 shows that this compound does not have any selectivity toward different trivalent cations. This is in agreement with Litvina's observations (18) on two CMPO-type molecules, one having two phenyl groups on the phosphorus atoms and the other having two butyl groups. The phenyl derivative exhibited slight selectivity (the La/Lu separation factor equaled about 10), whereas no selectivity was observed for the butyl derivative. As shown earlier, attaching four CMPO moieties (containing phenyl groups on the phosphorus atoms) to a calixarene platform (A_n) enhanced the extraction properties of the moieties as compared with the "unattached" analog (CMPO itself). Their discrimination abilities increased by a factor of 100.

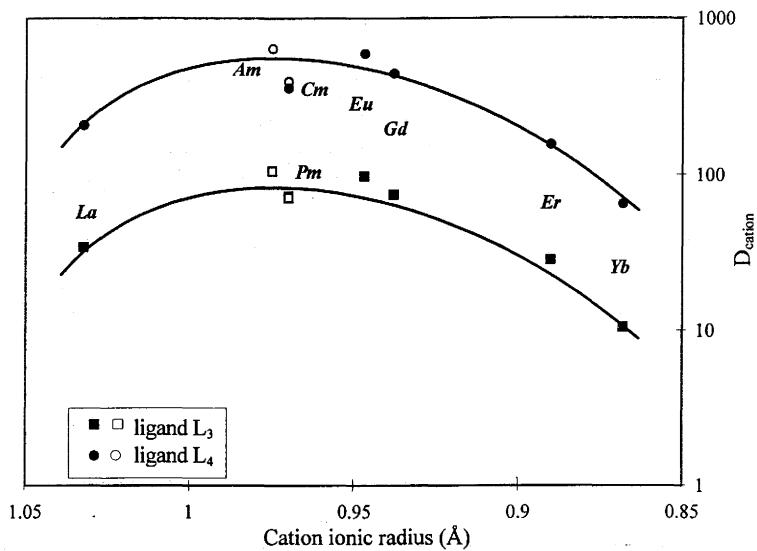


FIGURE 5. Extraction by the ligands L_3 and L_4 . Organic phase: chloroform containing either $[L_3]_{\text{init}} = 10^{-2} M$ or $[L_4]_{\text{init}} = 10^{-2} M$; aqueous phase : 4 M sodium nitrate, $10^{-2} M$ nitric acid, $10^{-6} M$ metallic cation nitrate (except for promethium, americium and curium used at trace level). $T = 25^\circ\text{C}$. Filled symbols: lanthanides; open symbols: actinides.

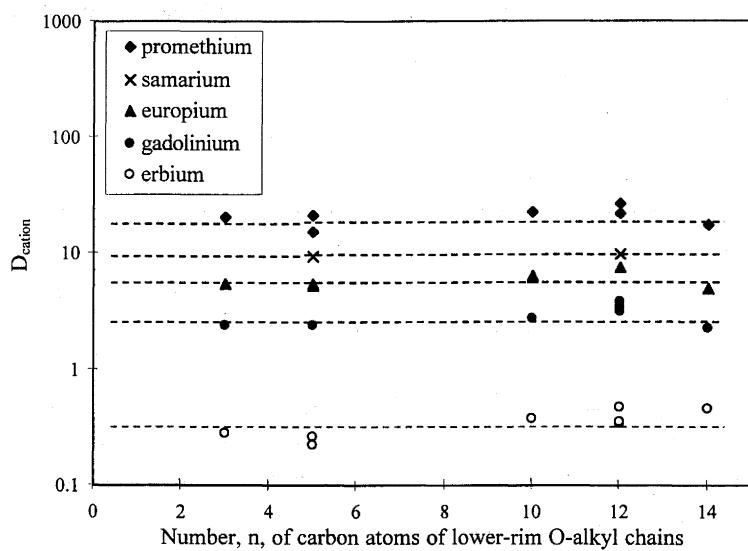


FIGURE 6. Variation of lanthanide distribution coefficient vs the number n of carbon atoms present in the four O-alkyl chains present at the lower rim. Organic phase: chloroform containing $[A_n]_{\text{init}} = 10^{-3} M$; aqueous phase : 4 M sodium nitrate, $10^{-2} M$ nitric acid, $10^{-6} M$ metallic cation nitrate (except for promethium used at trace level); $T = 25^\circ\text{C}$.

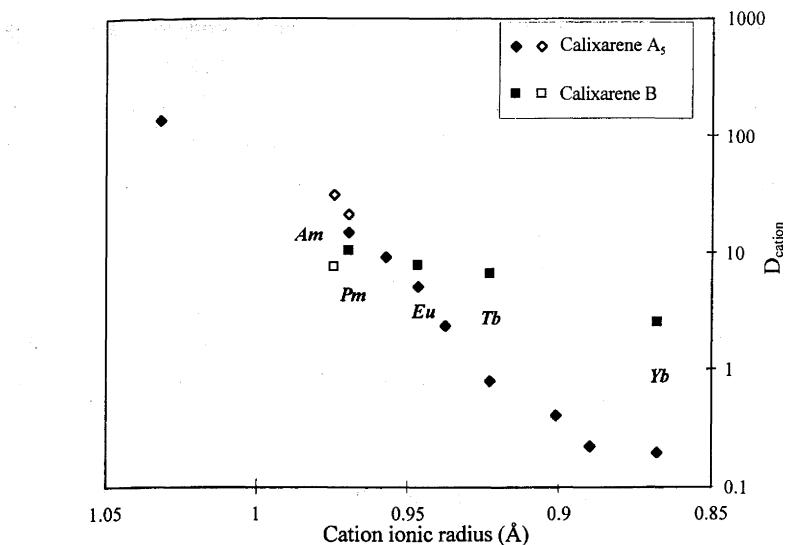


FIGURE 7. Comparison of extraction efficiencies of calixarenes A₅ and B. Organic phase: chloroform containing either [A₅]_{init} = 10⁻³ M or [B]_{init} = 10⁻³ M; aqueous phase: 4 M sodium nitrate, 10⁻² M nitric acid, 10⁻⁶ M metallic cation nitrate (except for promethium, americium, and curium used at trace level); T = 25°C. Filled symbols: lanthanides; open symbols: actinides.

CONCLUSIONS

The present study demonstrates that a calix[4]arene bearing CMPO moieties exhibits extraction efficiencies far higher than those obtained with CMPO alone. Moreover, these "CMPO-like" calixarenes show very interesting selective extraction properties toward light trivalent lanthanides with about three orders of magnitude separation between lanthanum and ytterbium distribution coefficients, thus permitting a separation among the lanthanides (19). This discrimination is most likely due to a size recognition effect. For the same cation radius, actinides are more efficiently extracted than lanthanides, which may reflect more covalent interactions between the ligand and the actinides. It may be interesting to look further in this direction, using types of functionalities that are more selective toward the actinides.

The nature of the substituent present on the phosphorus atom was shown to strongly influence the metal-ion selectivity. Results showed that phenyl groups were required in order to have a good selectivity.

It was found that the extracted metal ions could be stripped quantitatively from these extractants by nitric acid aqueous solutions of low concentration. Favorable stripping results led us to the next part of our study, which entails an application of the results: development of lanthanide and actinide extraction by membrane transport (20,21).

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