'CMPO-substituted' calix[4]arenes, extractants with selectivity among trivalent lanthanides and between trivalent actinides and lanthanides

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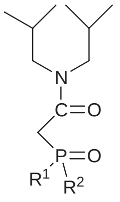
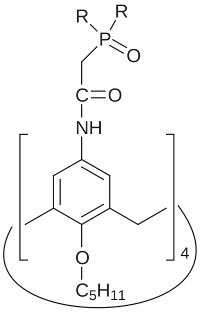
Calix[4]arenes substituted by acetamidophosphine oxide groups at their wider (upper) rim not only exhibit excellent extraction efficiency towards trivalent cations but also show pronounced selectivity for the light lanthanides and actinides in their extraction from highly saline or acidic media.

Calixarenes[1] are readily available molecular platforms, on which various functional groups may be assembled in a well defined mutual arrangement. Numerous cation extractants derived from calixarenes have been developed in the past decade, in which the preorganization of ligating functions adds favorably to their specificity.[2] Crown ethers derived from calix[4]arenes fixed in the 1,3-alternate conformation may be cited as one of the most typical examples, showing the highest potassium over sodium (crown-5)[3] and caesium over sodium (crown-6)[4] selectivities ever reported.

Carbamoylphosphine oxides **1** (CMPOs) are known to extract trivalent cations from highly acidic and highly saline media,[5] and **1a** is industrially used in the TRUEX process.[6] The extracted complex requires three molecules of **1a** per cation,[7] thus attachment of CMPO-like functions to the calixarene scaffold in the cone conformation should achieve cooperativity. Indeed, calix[4]arenes such as **2a** bearing four diphenyl acetamidophosphine oxide functions on the wider rim[8] are powerful extractants for europium and tri- and tetravalent actinides with an efficiency highly superior to that of **1a**. Here we compare the two ligands **1a** and **2a**[8] with respect to their extraction efficiencies towards nine lanthanides (La, Pm, Sm, Eu, Gd, Tb, Ho, Er, Yb) and two actinides (Am, Cm).



1a $R^1 = C_6H_5$, $R^2 = C_8H_{17}$
1b $R^1 = R^2 = C_6H_5$
1c $R^1 = R^2 = C_4H_9$



2a $R = C_6H_5$
2b $R = C_6H_{13}$

Extractions were followed by radiotracers and were quantified by the distribution coefficient of the metallic cation M ($D_M = \Sigma[M]_{org,eq}/\Sigma[M]_{aq,eq}$). The concentrations of **1a** and **2a** were chosen to obtain comparable distribution coefficients. Preliminary experiments showed that the extraction kinetics are rapid; all reported distribution coefficients are at equilibrium.

The behavior of CMPO **1a** is in agreement with literature data,[5] while we observe for **2a** a marked decrease of the distribution coefficients along the lanthanide series, from 140 for lanthanum to 0.19 for ytterbium (Fig. 1). This corresponds to a separation factor (ratio of the distribution coefficients) of nearly three orders of magnitude. It is important to point out that distribution coefficients are independent of the equilibrium aqueous metal ion concentration. This eliminates any influence of cation concentrations on the selectivity.

In order to determine one of the possible origins of the selectivity, we modified the functional groups present on the phosphorus. The observed size selectivity nearly disappears for **2b**,[9] in which the phenyl groups of **2a** have been replaced by *n*-hexyl groups (Fig. 2). This observation is in agreement with the results obtained for the two CMPO type molecules **1b** and **1c**.[10] While the diarylphosphine oxide **1b** shows a small selectivity (separation factor $D_{La}/D_{Lu} \approx 10$), no selectivity is found for the dialkylphosphine oxide **1c**. We can conclude, therefore, that the attachment of four CMPO functions with diphenylphosphine oxide groups to the calixarene skeleton leads to a significant increase of their discriminating properties towards lanthanides and actinides.

The selectivity discussed so far is related to the extraction of trivalent cations from a highly saline but moderately acidic medium. A topic of current interest is actinide–lanthanide group mixtures separation at high acidity, which, at low acid

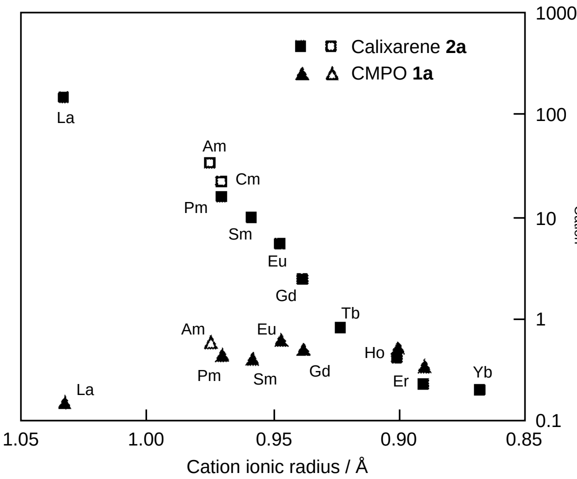


Fig. 1 Comparison of the extraction efficiencies of CMPO **1a** and calixarene **2a**. Organic phase: chloroform containing either $[\mathbf{1a}]_{init} = 0.2$ M or $[\mathbf{2a}]_{init} = 10^{-3}$ M. Aqueous phase: $[NaNO_3] = 4$ M, $[HNO_3] = 10^{-2}$ M, $[Ln^{3+}] = 10^{-6}$ M. Promethium and actinides were used at trace levels. Phase ratio 1:1. $T = 25$ °C. Filled symbols: lanthanides; open symbols: actinides.

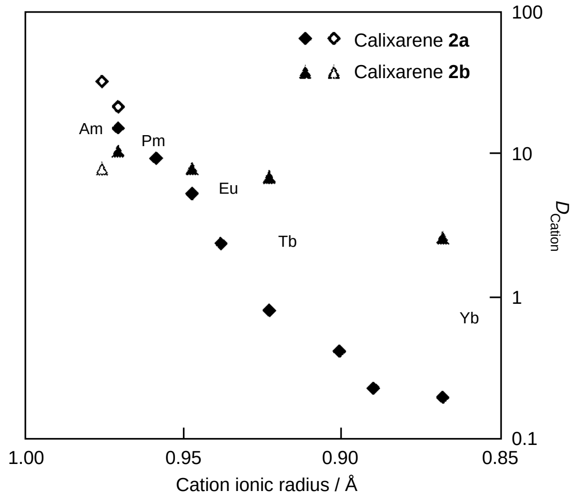


Fig. 2 Comparison of extraction efficiencies of calixarenes **2a** and **2b**. Organic phase: chloroform containing either $[\mathbf{2a}]_{init} = 10^{-3}$ M or $[\mathbf{2b}]_{init} = 10^{-3}$ M. Aqueous phase: $[NaNO_3] = 4$ M, $[HNO_3] = 10^{-2}$ M, $[Ln^{3+}]_{init} = 10^{-6}$ M. Promethium and actinides were used at trace levels. Phase ratio 1:1. $T = 25$ °C. Filled symbols: lanthanides; open symbols: actinides.

concentrations (pH $>$ 1) can usually be achieved by extractants containing soft donors (sulfur or nitrogen).[11] Although a recent publication shows that calix[6]arene derivatives bearing acid and amide functions can be used for this group separation, the same pH limitations (pH $>$ 2.5) apply.[12]

We have repeated some of our experiments with **2a** extracting the trivalent cations from 3 M nitric acid (Fig. 3). We observe essentially the same trend for both media (4 M sodium nitrate or 3 M nitric acid), which suggests the selectivity is not caused by a constituent of the aqueous phase. In particular, the potential interaction between nitric acid and the ligand has no effect on the selectivity. The separation factor D_{Am}/D_{Eu} for 3 M nitric acid (10.2) is slightly better than that for 4 M sodium nitrate (7.5), and is probably one of the best ever obtained at this acidity and this ionic strength.

In conclusion, calixarene **2a**, and more general calix[4]arenes bearing four CMPO moieties on their upper rim where the phosphorus atoms are substituted with phenyl groups, are not only excellent extractants for trivalent lanthanides and actinides, they also exhibit remarkable selectivity based mainly on the size of the cations. This selectivity can reach nearly three orders of magnitude and remains even under strongly acidic conditions. It does not yet allow complete actinide–lanthanide group mixtures separation but the separation factors could be useful for the selective extraction of actinides (or light lanthanides) from heavy lanthanides.

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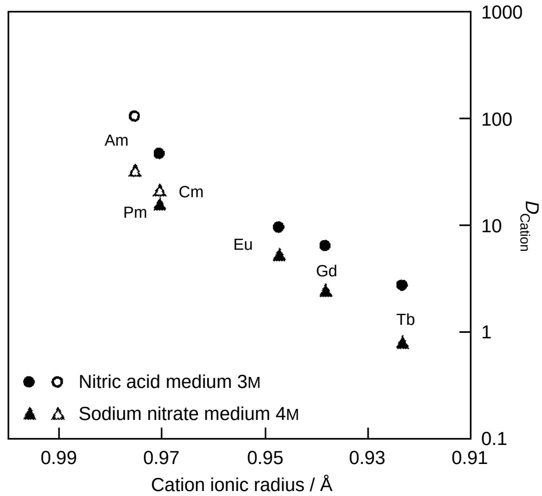

Fig. 3 Extraction of trivalent lanthanides and actinides by calixarene **2a** from two different media, $[NaNO_3] = 4$ M/$[HNO_3] = 0.01$ M or $[HNO_3] = 3$ M. Organic phase: chloroform containing $[\mathbf{2a}]_{init} = 10^{-3}$ M. Aqueous phase: $[Ln^{3+}]_{init} = 10^{-6}$ M. Promethium and actinides were used at trace levels. Phase ratio 1:1. $T = 25$ °C. Filled symbols: lanthanides; open symbols: actinides.

Notes and References

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