Solvent Extraction and Transport of Rare Earth Metal Ions Using 5,11,17,23-Tetra-*tert*-butyl-25,27-bis (diethylcarbamoylmethoxy)-26,28-dihydroxy Calix[4]arene

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ABSTRACT: *The solvent extraction of rare earth metal ions from nitrate solutions by 5,11,17,23-tetra-tert-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-dihydroxycalix[4]arene (**L**) in 1,2-dichloroethane has been investigated. The analysis of the extraction equilibrium obtained from a mixture of* La^{3+}, Eu^{3+}, Er^{3+} *and* Y^{3+} *revealed that the extracted species have a 1:1 metal/ligand ratio. The intra-group separation efficiencies of the ligand have been evaluated in a competitive extraction and transport of 11 rare earth metal ions (*La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+} *and* Y^{3+} *). The transport experiment has been performed through a supported liquid membrane containing the ligand in o-nitrophenyl hexyl ether (NPHE). The distribution ratio and the flux of the ions generally increases as the atomic radii decrease.*

KEY WORDS: *Calix[4]arene, Extraction, Transport, Rare earth, Metal ions*

INTRODUCTION

Calixarenes [1] are a family of synthetic macrocyclic receptors consisting of cyclic arrays of phenol moieties linked by methylene groups (Fig. 1). This class of macrocyclic compounds offers an interesting platform for the arrangement of various ligating functions [2,3]. The highly lipophilic nature of metal-

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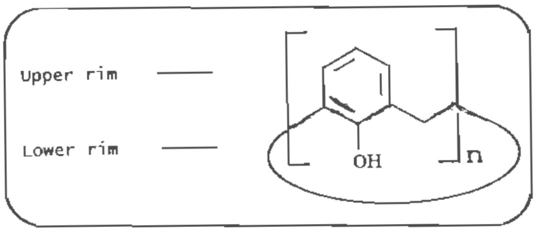

Fig. 1: Calix[n]arene (in general n= 4-8)

ion complexes of many modified calixarenes indicates a potential for use in solvent extraction and transport processes [4].

Solvent extraction have been widely used to intragroup separation of the rare earth metal ions [5]. Molecules which contains amide and/or phosphoryl functionalities are well established in lanthanide and actinide extraction [5-7]. The extraction and complexation of lanthanides with calixarenes substituted by amide and phosphoryl groups is investigated recently [8-12].

Following to our studies on the extractive and mobile carrier properties of multifunctional calix[4]arenes [13-17], these properties for diamide-calix[4]arene (L) (Fig. 2) towards rare earth metal ions in nitrate media is reported in this paper.

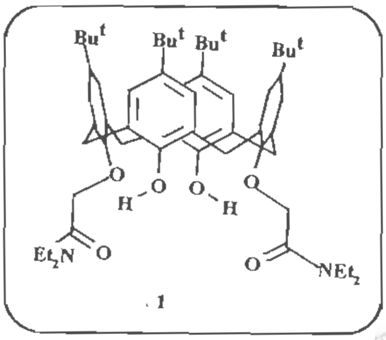

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Fig. 2: Chemical structure of the ligand studied

EXPERIMENTAL

Materials

The ligand 5,11,17,23-tetra-*tert*-butyl-25,27-bis (diethylcarbamoylmethoxy)- 26,28 -dihydroxycalix[4]-arene (L) was synthesized according to the procedure described previously [18]. 1,2-Dichloroethane and nitrobenzene (sds) were washed several times with distilled water before they were used in solvent extraction experiments. The rare earth nitrate solutions were prepared from a weighted amount of the corresponding oxides (Fluka) by dissolution in hot concentrated nitric acid and dilution to a known volume. Aluminum nitrate (Fluka) was analytical reagent. The polymeric film Accurel® PP1E was a gift from *Ak=o Nobel* (Germany). This film was a 92.5 μm thick microporous polypropylene film with a nominal porosity of 64% and an effective pore size of 0.1 μm. *o*-Nitrophenyl hexyl ether (NPHE) was donated by the *Commissariat a l'Energie Atomique* (CEA), Cadarache (France).

Extraction procedure

The solvent extraction experiments were carried out in a stoppered glass tube immersed in a thermostated water bath (25±0.1°C) using equal volumes (10 mL) of aqueous and organic phases. The extraction equilibrium was reached after 30 min. under continuous stirring. The organic phase was centrifuged to complete the separation of the phases before the organic phase was stripped with a 0.025 M aqueous solution of nitric acid. X-ray fluorescence analysis on the evaporated stripped organic phase showed that the stripping is quantitative at this condition. Rare earth metal ion concentrations were analyzed using a Varian (Liberty 220) ICP/AES instrument.

Transport experiment

The supported liquid membrane was prepared by soaking for 10 h the support in a 0.002 M solution of L in *o*-nitrophenyl hexyl ether and then blotting it with filter paper. The transport experiment was carried out in a set-up presented elsewhere [17]. Any other particular experimental details are mentioned in the footnote of the corresponding figure. A transport experiment of europium (initial concentration: 0.001 M) in the presence of aluminum nitrate (0.9 M) through the polymeric support containing NPHE without carrier, after 10 h showed no detectable value of europium in the receiving phase (0.025 M HNO_3).

RESULTS AND DISCUSSION

Characterization of the extracted species

The extraction of rare earth metal ions (M^{3+}) from aqueous nitrate media to an organic solution containing a neutral ligand (L) can be described by the following extraction equilibrium:

$$M^{3+}_{aq} + 3NO^-_{3\,aq} + nL_{org} \rightleftharpoons ML_n(NO_3)_{3\,org}$$

the corresponding extraction equilibrium constant, K_{ex}, is:

$$K_{ex} = \frac{[ML_n(NO_3)_3]_{org}}{[M^{3+}]_{aq}[NO^-_3]^3_{aq}[L]^n_{org}} \qquad (1)$$

If we introduced the distribution coefficient (D),

$$D = \frac{[M]_{org}}{[M]_{aq}} \qquad (2)$$

we obtain equation (3):

$$\log D = \log (K_{ex}[NO^-_3]^3_{aq}) + n \log[L]_{org} \qquad (3)$$

As the metal organic concentrations are much lower than the initial ligand concentrations, the equilibrium ligand concentration can be considered as equal to initial ligand concentrations ($[L]_{0,org} = [L]_{org}$). With these assumptions, a plot of log D *vs.* log $[L]_{org}$ provides the metal/ligand ratio of the extracted species. This method was applied to the extraction of four rare earth metal ions (La^{3+}, Eu^{3+}, Er^{3+} and Y^{3+}) in the presence of aluminum nitrate (0.9 M) by diamide-calix[4]arene (L). The slopes were in agreement with a metal/ligand ratio of 1:1 (Fig. 3). Aluminum nitrate was chosen as the salting out agent. We checked that extraction of this salt by L was very weak under the conditions used.

These stoichiometries are in agreement with those reported recently by *Beer et al.* [10,11] based on the determination of the structure of some lanthanide-L complexes in the solid state by the X-ray diffraction.

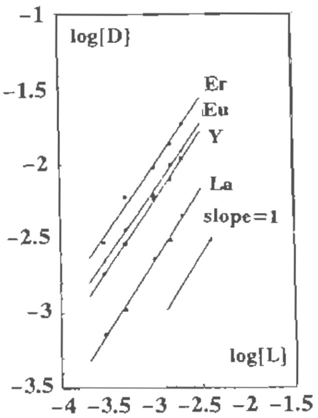

Fig. 3: Variation of the log D vs log [L] for the extraction of four rare earth ions ($[Y^{3+}] = [La^{3+}] = [Eu^{3+}] = [Er^{3+}] =$ 0.001 M) in the presence of $Al(NO_3)_3$ (0.9 M) by 1 (3×10^{-4}, 2×10^{-3} M) in 1,2-dichloroethane.

Intra-group separation

The competitive extraction of 11 rare earth ions (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+} and Y^{3+}) in the presence of aluminum nitrate (0.9 M) was performed to evaluate the intra-group separation potential of the ligand (Fig. 4). This lignad exhibits a regular increase in distribution coefficient of the ions as the ionic radii decrease. It should be noted that yttrium is not placed in its real place (Table 1). We used this element as a reference for comparing the selectivity factors. The observed in the case of the gadolinium is a general phenomenon [19]. This phenomenon, called generally *gadolinium rupture,* is also observed for the extraction of the rare earths by trioctylphosphine oxide [17] and some carbamoylmethylphosphine oxides [6].

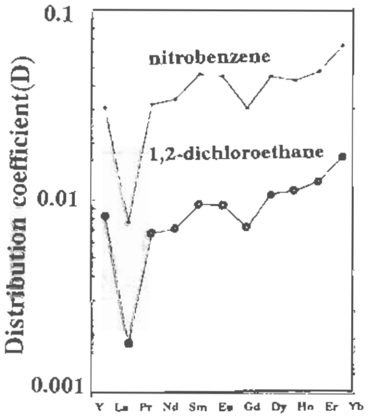

Fig. 4: Influence of the diluent on the distribution coefficients in the competitive extraction of 11 rare earth metal ions ($[Y^{3+}] = [La^{3+}] = [Pr^{3+}] = [Nd^{3+}] = [Sm^{3+}] = [Eu^{3+}] = [Gd^{3+}] = [Dy^{3+}] = [Ho^{3+}] = [Er^{3+}] = [Yb^{3+}] =$ 0.001 M) in the presence of $Al(NO_3)_3$ (0.9 M) by 1 (0.002 M) at 25°C.

The use of nitrobenzene instead of 1,2-dichloroethane as diluent for calixarene L caused an enhancement of the distribution ratio of the ions due to the higher polarity of the former favoring anion transfer between phases (Fig. 4). The order of selectivity presented by L in these solvents is different in some extent (see Table 1).

***Table 1: Separation factors (relative to Y, $\alpha_{M/Y}=D_M/D_Y$) obtained from the competitive extraction of rare earths by L*[a]**

M^{3+}	Ionic radius (Å)[b]	$\alpha_{M/Y}$ (1,2-dichloroethane)	$\alpha_{M/Y}$ (nitrobenzene)
La^{3+}	1.061	0.22	0.25
Pr^{3+}	1.013	0.81	1.04
Nd^{3+}	0.995	0.86	1.11
Sm^{3+}	0.964	1.15	1.51
Eu^{3+}	0.950	1.14	1.47
Gd^{3+}	0.938	0.87	1.00
Dy^{3+}	0.908	1.31	1.48
Ho^{3+}	0.894	1.37	1.41
Y^{3+}	0.892	1.00	1.00
Er^{3+}	0.881	1.53	1.57
Yb^{3+}	0.858	2.08	2.14

a : Calculated from data presented in the figure 4

b : Reference 5.

Competitive transport

It is now well established that the facilitated transport of metal ions through a thin organic liquid layers immobilized on a polymeric support (supported liquid membrane, SLM) is an interesting method for the separation and concentration of metals [20]. The possibility to employ highly lipophilic calixarenes in supported liquid membranes has been illustrated recently [17,21,22].

In order to compare the selectivity and the efficiency of calixarene (L) in both extraction and transport experiments, a competitive transport of 11 rare earth ions through a supported liquid membrane containing this ligand was carried out. In this study *o*-nitrophenyl hexyl ether (NPHE) as diluent was used. This compound is particularly interesting because of its low solubility in water, low volatility and high dielectric constant (25.7). These properties ensure a proper stability of the membrane and a good solvation of the ions which favors the ion extraction into the organic phase. Since the diluent used in this system differs from those used in the extraction experiments, this experiment provides a complementary information for the diluent effect on the selectivity presented by the ligand. It was observed that for the ligand **L** the flux parallels that of the distribution coefficient in 1,2-dichloroethane or nitrobenzene (Fig. 5). The results show that there is no particular diluent effect by using NPHE which has some chemical similarities with nitrobenzene.

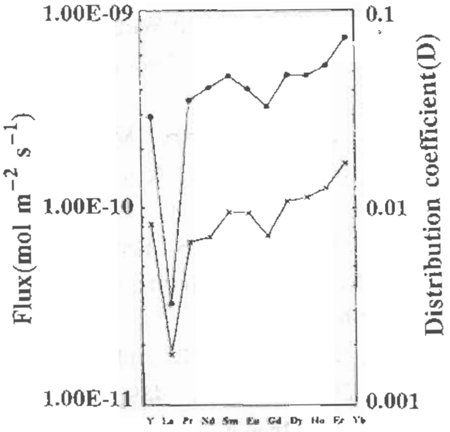

***Fig. 5:** Comparison between the selectivity obtained in a competitive transport (●) and a competitive extraction (x) of 11 rare earth metal ions. Extraction: see foot note of the Fig. 5: Transport; Feed phase: $[Y^{3+}]=[La^{3+}]=[Pr^{3+}]=[Nd^{3+}]=[Sm^{3+}]=[Eu^{3+}]=[Gd^{3+}]=[Dy^{3+}]=[Ho^{3+}]=[Er^{3+}]=[Yb^{3+}]=0.001$ M in the presence of $Al(NO_3)_3$ (0.9 M), Receiving phase: 0.0025 M HNO_3 , Support: Accurel LPPE, Diluent: o-nitrophenyl hexyl ether; T= 25°C; ligand concentration: 0.002 M, stirring rate: 260 rpm.*

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