

Ternary Complexes of Lanthanide–Calix[4]Arene with Sulphophthalein Dyes

I. NĚMCOVÁ*, V. VONDRKOVÁ, and K. NESMĚRÁK,

Department of Analytical Chemistry, Faculty of Science, Charles University of Prague, Albertov 6, CZ-128 43, Prague 2, Czech Republic

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Abstract

The formation of ternary complexes of lanthanide–calix[4]arene with sulphophthalein dyes was studied. The extraction of model system Gd(III)–calix[4]arene–bromothymol blue was characterized and the distribution, extraction, and stability constants were determined. The applicability of studied system for spectrophotometric determination of lanthanides was demonstrated and parameters of calibration dependences were calculated.

Introduction

Lanthanides act as hard acids with a high affinity for hard bases (oxygen, nitrogen) and for negatively charged groups. Therefore, they are able to form complexes with various organic compounds including calixarenes [1–3]. A number of papers has been reported in literature dealing with the theoretical study of complexation of lanthanides with calixarenes [e.g. 4–11]. It has also been demonstrated that the carboxylic acids and esters of calixarenes are very active complexing agents [12, 13] with the analytical applicability for the construction of ion selective electrodes [14, 15].

The spectrophotometric determinations of lanthanides are mostly based on the formation of complexes with organic dyes [16–19]. The extraction of ternary complexes (ion associates), in which the metal is bonded with 1,10-phenanthroline yielding a complex cation interacting in the organic phase with an anion of suitable dye (Chromazurol S), was also proposed [20].

The aim of this work was to test the possibility of the use of calixarenes for the spectrophotometric determination of lanthanides. A 5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(ethoxycarbonylmethoxy)-28-carboxymethoxy-calix[4]arene (CA; for structure see Figure 1), that, on the basis of its structure, is a suitable reagent for interaction with lanthanides, was employed. In the analogy with extraction of crown-ethers complexes [21], sulphophthalein dyes were used for conversion of the positively charged lanthanide–calixarene (Ln(III)–CA) complexes to a product capable of extraction into an organic solvent. Bromophenol blue (BPB), bromocresol green (BCG) and bromothymol blue (BTB) (Figure 2),

differing in the hydrophobicity of the molecule, were compared. The work was carried out to determine the optimum experimental conditions for the complexation reaction, characterization of the extraction system, and use of the information obtained to propose new procedure for determining the ions of interest

Experimental

Chemicals

5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(ethoxycarbonylmethoxy)-28-carboxymethoxy-calix[4]arene C₅₈H₇₆O₁₂, CASN [125379-27-3], $M_r = 965.23$, was synthesized according literature data [22]. Stock solution with a concentration of 4×10^{-3} M was prepared in chloroform.

Bromophenol blue C₁₉H₁₀O₅Br₄S (Schering, Germany), CASN [115-39-9], $M_r = 699.96$; bromocresol green C₂₁H₁₄O₅Br₄S (Lachema, Czech Republic), CASN [76-60-8], $M_r = 698.015$; bromothymol blue C₂₇H₂₈O₅Br₂S (Lachema, Czech Republic), CASN [76-59-5], $M_r = 624.38$; were employed. Stock solutions with a concentration of 4×10^{-3} M were prepared in 96% ethanol.

The La(III), Gd(III) and Tm(III) stock solutions with a concentration of 1×10^{-3} M were prepared from corresponding nitrates by dissolving in distilled water. All other chemicals were of analytical grade.

Instrumentation

The absorption spectra were measured using a HP 8453 (Hewlett Packard, Great Britain) diode-array spectrophotometer with a glass cuvette with an absorption layer

* Author for correspondence. E-mail: inemcova@natur.cuni.cz

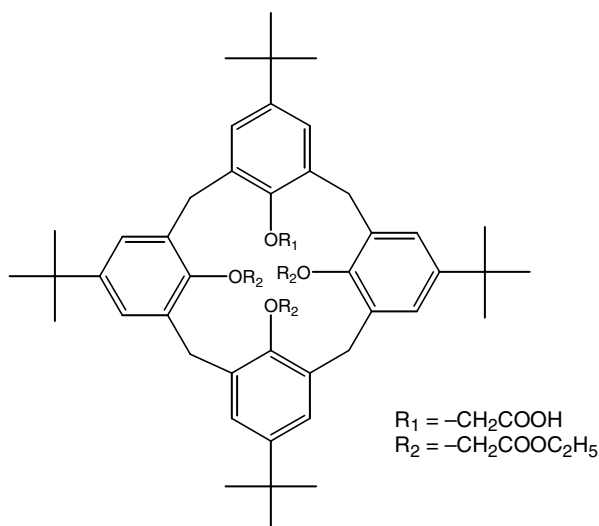


Figure 1. The structure of 5, 11, 17, 23-tetra-*tert*-butyl-25, 26, 27-tris(ethoxycarbonylmethoxy)-28-carboxymethoxy-calix[4]arene (CA).

thickness of 1 cm. The pH was measured on a 3320 pH-meter (Jenway, Great Britain).

Extraction procedure

The aqueous solution of reaction mixture (appropriate volumes of stock solution of $\text{Ln}(\text{NO}_3)_3$ and stock solution of dye, $\text{pH} = 3.5$) was transferred to a separating funnel and extracted by 5 ml of chloroform solution of calixarene for 3 min. Reducing the volume of the chloroform phase leads to increased absorbance, but the phases are separated only after 30 min. The 3 min of extraction was optimal. The repeated extraction leads to only a slight increase in the efficiency. All the absorption spectra measurements were carried out against an extracted dye.

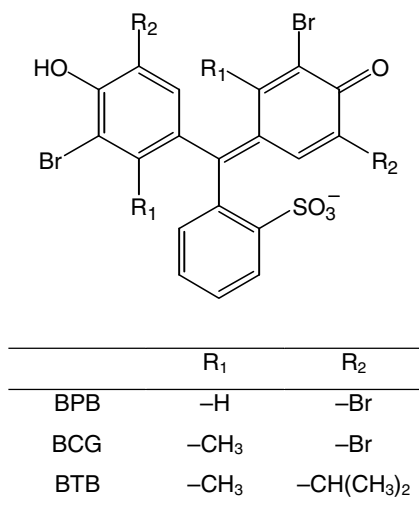


Figure 2. The structures of used sulphophthalein dyes: bromophenol blue (BPB), bromocresol green (BCG), and bromothymol blue (BTB).

Distribution ratio

For the evaluation of the extraction (K_{ex}), distribution (K_{D}) and the stability constants (K_{A}), the distribution ratios D were determined using relationship [23]

$$D = \frac{c_{\text{org}}}{c_{\text{aq}}} = \frac{A}{A_{\text{max}} - A} \quad (1)$$

where c_{org} (c_{aq}) is the concentration of ion associate in organic (aqueous) phase; A is the absorbance of solution obtained after extraction of 5 ml of aqueous reaction mixture by a volume of 5 ml of the chloroform solution of calixarene and diluting the extract with chloroform to a volume of 25 ml; A_{max} is the absorbance of the solution obtained by triplicate extraction of 5 ml of reaction mixture by volumes of 5 ml of the chloroform solution and diluting with chloroform to a volume of 25 ml (it was confirmed by the dependence of the absorbance of the extracts on the number of extractions that the complex is quantitatively transferred to the chloroform phase after the third extraction).

Results and discussion

Interactions with sulphophthalein dyes

According to the literature [21], chlorinated solvents are suitable for extraction of ternary complexes; as the monitored reaction occurred similarly in all common solvents of this type, chloroform was used for practical reasons (lowest toxicity, reasonable price). We have found that the CA alone and the chloroform extracts of its complexes with Ln(III) exhibit a very weak absorption maximum in the UV range of the spectrum ($\lambda_{\text{max}} = 280 \text{ nm}$).

Bromophenol blue

A very poorly extractable product (small increase in absorbance against the blank) is formed in the reaction of Ln(III) with CA and this dye, probably because of its low hydrophobicity.

Bromocresol green

It was found on the basis of a series of experiments that the absorbance of the extract corresponds to the sum of the absorbances of the ternary complexes Ln(III)-CA-BCG and the binary complexes Ln(III)-BCG. The concentration dependences of the three lanthanides with gradually increasing atomic number (La(III), Gd(III) and Tm(III)) were thus measured orientatively (without the statistical evaluation). From Figure 3 it is obvious that the greatest complexation occurred for the lightest lanthanide. The complexation ability should theoretically increase towards the heavier lanthanides (the lanthanoid contraction leads to the increase of charge density and decrease in the hydration number, resulting in easier accessibility of heavier lanthanides for ligands).

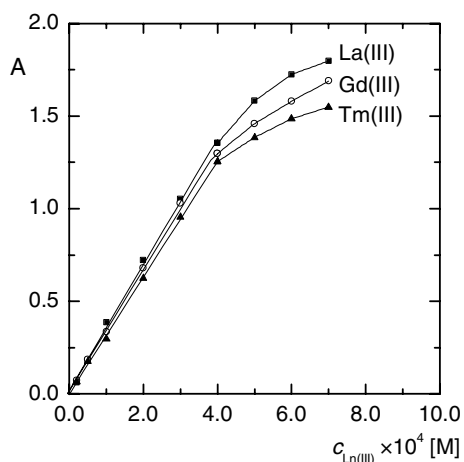


Figure 3. Concentration dependences for ternary complexes Ln(III)–CA–BCG. ($c_{CA} = 4 \times 10^{-4}$ M, $c_{BCG} = 8 \times 10^{-4}$ M, $\lambda_{max} = 406$ nm, pH = 3.5; measured against extracted BCG).

However, the various strength of complexation was found in the cited literature, depending on the specific structural properties of calixarenes. The dependences obtained are linear in all three cases to a ratio of Ln(III):CA = 1:1.

Bromothymol blue

From Figure 4 which depicts the spectra for the individual extracted component of system Gd(III)–CA–BTB it is apparent that there is only a small increase in the absorbance at $\lambda_{max} = 412$ nm for extraction of the Gd(III)–BTB binary complex compared to the extracted dye alone, while there is a substantial increase in absorbance on formation of the ternary complex Gd(III)–CA–BTB.

Figure 5 gives the effect of the pH on the extractability of the complex (curve a) and the dye (curve b). From a value of pH = 3.5, the difference in their absorbances (curve c) is practically constant and this pH was considered optimal. Hence, the acidity of solutions was adjusted to this value by diluted HCl.

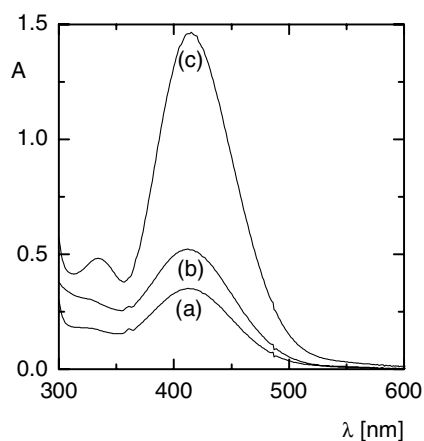


Figure 4. Absorption spectra of individual extracted components of system Gd(III)–CA–BTB. (a) BTB, (b) Gd(III)–BTB, (c) Gd(III)–CA–BTB. ($c_{Gd(III)} = 1 \times 10^{-4}$ M, $c_{BTB} = 8 \times 10^{-4}$ M, $c_{CA} = 4 \times 10^{-4}$ M, pH = 3.5).

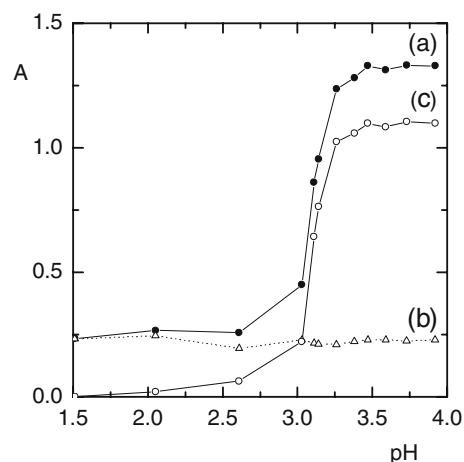


Figure 5. The dependence of the absorbance of chloroform extracts on the pH of the aqueous phase (a) Gd(III)–CA–BTB, (b) BTB, (c) difference curve ($c_{Gd(III)} = 1 \times 10^{-4}$ mol dm⁻³, $c_{CA} = 4 \times 10^{-4}$ mol dm⁻³, $c_{BTB} = 8 \times 10^{-4}$ mol dm⁻³, $\lambda_{max} = 412$ nm).

The concentration dependences of Ln(III)–CA–BTB were measured for La(III), Gd(III) and Tm(III) under optimal reaction conditions (Figure 6). The greatest absorbance was again observed for complexes of La(III) and the lowest for complexes of Tm(III). The dependences are linear to a ratio of Ln(III):CA = 2:1, i.e. the formation of binuclear complexes could be also supposed. A further gradual increase in absorbance on an increase in the metal concentration above the ratio Ln(III):CA = 2:1 could be caused by the formation of weak complexes of metals with unbonded dye present in excess.

To compare the reactivities of the individual lanthanides towards CA and BTB, the concentration dependences were also measured for the binary Ln(III)–BTB complexes, see Figure 6. In this case, the reactivity increases slightly from lanthanum to thulium. This effect could be caused by better steric conditions for the for-

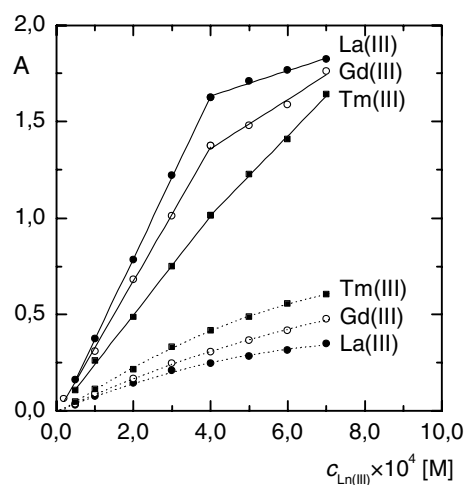


Figure 6. Concentration dependences for the ternary complexes Ln(III)–CA–BTB (full lines), and binary complexes Ln(III)–BTB (dashed lines). ($c_{CA} = 2 \times 10^{-4}$ M, $c_{BTB} = 8 \times 10^{-4}$ M, $\lambda_{max} = 412$ nm, pH = 3.5; measured against extracted BTB).

mation of complex of the Tm(III) ion having a smaller ionic radius and hydration number with bromothymol blue with a large $-\text{CH}(\text{CH}_3)_2$ substituent. In all cases, formation of the complex with calixarene predominates over the weak interaction of Ln(III) with BTB.

Characterization of the extraction system

The Gd(III)–CA–BTB complex was studied as a model system. The extraction (K_{ex}), distribution (K_{D}) and the stability constants (K_{A}) of the complexes were determined in analogy to [23, 24].

The distribution ratios D were determined for the expected complexes 1:1 and 2:1 (Gd(III):CA) at various BTB concentrations (a ratio of Gd(III):CA = 1:4 was maintained for the formation of 1:1 complex to ensure an excess of calixarene). The values of D increase in both cases with increasing BTB concentration. At low BTB concentrations, the D values are higher for a complex with ratio of 1:1; at higher BTB concentrations, the D values are higher for a complex with ratio of 2:1.

The distribution ratio D of the cationic Ln(III)–CA extracted in the form of the ternary complex Ln(III)–CA–BTB is given by the relationship

$$D = \frac{[\text{Ln(III)–CA–BTB}]_{\text{org}}}{[\text{Ln(III)–CA}]_{\text{aq}} + [\text{Ln(III)–CA–BTB}]_{\text{aq}}} \quad (2)$$

At low concentrations of [BTB] the concentration of $[\text{Ln(III)–CA}]_{\text{aq}} \gg [\text{Ln(III)–CA–BTB}]_{\text{aq}}$ and the distribution ratio is then given by the relationship

$$D = \frac{[\text{Ln(III)–CA–BTB}]_{\text{org}}}{[\text{Ln(III)–CA}]_{\text{aq}}} \quad (3)$$

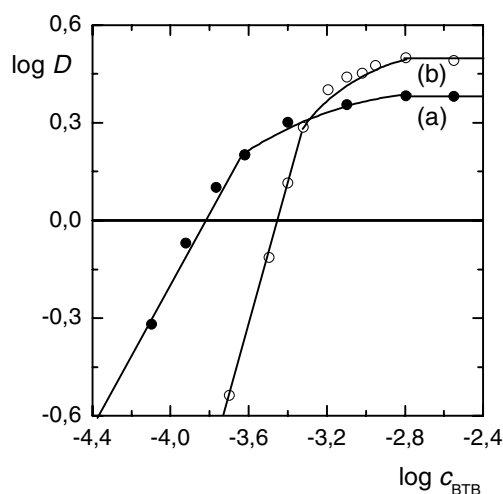


Figure 7. Dependence of $\log D$ on $\log c_{\text{BTB}}$ for (a) Gd(III):CA = 1:1 complex ($c_{\text{Gd(III)}} = 1 \times 10^{-4}$ M, $c_{\text{CA}} = 4 \times 10^{-4}$ M, pH = 3.5), and (b) Gd(III):CA = 2:1 complex ($c_{\text{Gd(III)}} = 2 \times 10^{-4}$ M, $c_{\text{CA}} = 1 \times 10^{-4}$ M, pH = 3.5).

The extraction constant K_{ex} is given by

$$K_{\text{ex}} = \frac{[\text{Ln(III)–CA–BTB}]_{\text{org}}}{[\text{Ln(III)–CA}]_{\text{aq}}[\text{BTB}]_{\text{aq}}} = K_{\text{A}}K_{\text{D}} \quad (4)$$

where K_{A} is the stability constant and K_{D} is the distribution constant.

Combination of equation (3), (4), and rearrangement yields an equation that in our case has the form

$$\log D = \log c_{\text{BTB}} + \log K_{\text{ex}} \quad (5)$$

Therefore, in this dependence the intercept on the y -axis corresponds to the logarithm of the value of the extraction constant K_{ex} .

At high concentrations of [BTB] the concentration of $[\text{Ln(III)–CA}]_{\text{aq}} \ll [\text{Ln(III)–CA–BTB}]_{\text{aq}}$, and the distribution ratio is given by the relationship

$$D = \frac{[\text{Ln(III)–CA–BTB}]_{\text{org}}}{[\text{Ln(III)–CA–BTB}]_{\text{aq}}} = K_{\text{D}} \quad (6)$$

The value of the distribution ratio D then yields the value of the distribution constant K_{D} .

Figure 7 depicts the dependences of $\log D$ on $\log c_{\text{BTB}}$ for the supposed complexes Gd(III):CA = 1:1 (curve (a)) and Gd(III):CA = 2:1 (curve (b)). It is apparent that the dependences are linear at low concentrations. The slope of the linear part of dependence corresponds to the number of ligands [23] (number of BTB molecules at a constant Ln(III):CA ratio). In our case, a slope value of 1.08 was found for the complex Gd(III):CA = 1:1; thus, the complex with the ratio of components 1:1:1 is formed. For the Gd(III):CA = 2:1 complex, a slope value of 2.16 was obtained; thus, a complex with component ratio 2:1:2 is formed. The remaining positive charges of lanthanide cations can be balanced by nitrate anions in both cases.

At higher dye concentrations, the dependence approaches the value $\log D$, which corresponds to the $\log K_{\text{D}}$. The values of the extraction constant (K_{ex}) were obtained from the Equation (5) and the values of the stability constant of the system (K_{A}) were calculated from the Equation (4). Table 1 gives the determined values of constants K_{ex} , K_{D} and K_{A} for both complexes. It is apparent from comparison of values in Table 1 that higher values were obtained for the binuclear complexes for all the determined constants.

Table 1. The values of extraction (K_{ex}), distribution (K_{D}), and stability (K_{A}) constants for Gd(III)–CA–BTB mononuclear and binuclear complexes

Gd(III)–CA–BTB	K_{ex}	K_{D}	K_{A}
1:1:1	14.1×10^3	2.41	5.8×10^3
2:1:2	28.4×10^6	3.15	9.0×10^6

Table 2. Parameters of calibration dependences ($A = b \times c_{\text{Ln(III)}} + a$) for determination of lanthanides in linear dynamic range of $2 \times 10^{-5} - 4 \times 10^{-4}$ M ($c_{\text{CA}} = 2 \times 10^{-4}$ M, $c_{\text{BTB}} = 8 \times 10^{-4}$ M, $\lambda_{\text{max}} = 412$ nm, pH = 3.5)

	$b \times 10^2$ $\mu\text{g}^{-1} \text{ ml}$	$a \times 10^2$	r^2	LOD $\mu\text{g ml}^{-1}$	LOQ $\mu\text{g ml}^{-1}$
La(III)	3.02	4.26	0.9998	2.23	3.88
Gd(III)	2.20	1.85	0.9994	1.80	4.05
Tm(III)	1.51	1.38	0.9990	2.30	5.57

LOD – limit of detection, LOQ – limit of quantification.

Spectrophotometric determination of lanthanides using Ln(III)–CA–BTB complexes

In spite of the described complexity of the system, it is apparent that there is a linear dependence between the absorbance of the solution and the metal concentrations in a certain concentration range for all the studied lanthanides. Bromothymol blue is most useful as a reagent for this system, of the studied sulphophthalein dyes. The parameters of the calibration dependences ($A = b \times c_{\text{Ln(III)}} + a$) for determination of lanthanides are given in Table 2.

Conclusions

The work was carried out to characterize the extraction of ternary complexes of lanthanides with 5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(ethoxycarbonylmethoxy)-28-carboxymethoxy-calix[4]arene and sulphophthalein dyes bromophenol blue, bromocresol green and bromothymol blue. Differences in the reactivities of the individual dyes can be explained on the basis of their different hydrophobic properties.

For the model system Gd(III)–CA–BTB (the other lanthanides react with this dye analogously) the relationships derived in the literature were employed and the complexes Ln(III):CA:BTB were characterized. The extraction constants K_{ex} , the distribution constants K_{D} , and stability constants K_{A} were determined for both the 1:1 and the 2:1:2 complexes.

The use of studied system for spectrophotometric determination of lanthanides was demonstrated and parameters of calibration dependences were calculated.

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