

## Highly Selective Chromogenic Ionophores for the Recognition of Cerium (IV) Based on a Water-soluble Azocalixarene Derivative

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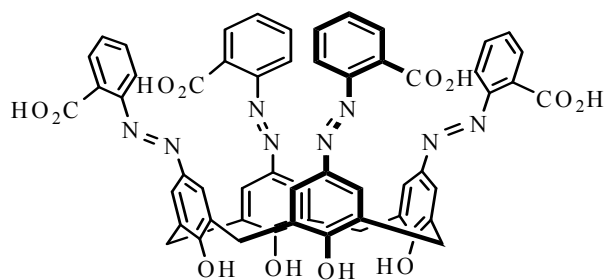
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**Abstract.** A new water-soluble cerium-selective chromogenic azocalix[4]arene had been synthesized from diazo coupling reaction between calix[4]arene and diazonium salts, and characterized by <sup>1</sup>HNMR, IR, UV and element analysis. It possesses a maximum absorbance at 365 nm in buffered aqueous environment, but addition of cerium(IV) ion induced a shift to 370 nm and a new absorption peak at 515 nm (bathochromic shift of 150 nm), exhibited an isosbestic point at 465 nm. It is more noticeable that the absorbance at 515 nm increases along with the augment of the concentration of cerium(IV) ion. Based on this complexation, a simple and selective spectrophotometric method was developed for the determination of cerium(IV) in the range of  $8.0 \times 10^{-6}$  to  $3.0 \times 10^{-5}$  mol.L<sup>-1</sup> of cerium(IV), the linear regression equation was determined to be: absorbance (A) =  $0.701 \times C(10^{-5} \text{ mol L}^{-1} \text{ cerium(IV)}) + 0.021$ ,  $r = 0.997$ ,  $n = 5$ .

**Keywords:** Cerium; Azocalix[4]arene; Chromogenic; Spectrophotometry

### 1. Introduction

There has been much recent interest in the design of new stimuli responsive host systems. Of these, the developments of chromogenic or fluorogenic ionophores have been a very active research area in supramolecular chemistry, since these can be applied to useful and important chemical sensor technology. Calixarenes, which are accessible by the base-catalyzed condensation of para-substituted phenols with formaldehyde, are ideal frameworks for the development of chromogenic ionophores in the molecular recognition of ionic species of chemical and biological interest since the incorporation of a suitable sensory group into the calixarene result in a tailored chromogenic receptor. A variety of compounds based upon calixarene having nitrophenylazophenol, nitrophenol, indoaniline, indophenol, and azophenol functional groups have been successfully designed and exhibit a pronounced chromogenic behavior towards Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Ca<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, and even chiral amines. Shinkai et al. had synthesized calix[4]arene with a 4-(4-nitrophenyl)azophenol unit and three ethyl ester residues on the lower rim and observed the lithium sensitivity of the ionophore. Toth et al. also reported the sodium selectivity of related azophenol derivatives [1]. Some recent authors have also reported selectivity of reagent ions with Th<sup>4+</sup>, Pb<sup>2+</sup> [2, 3] However, there has been no reports on calixarene-based selective chromoionophores for detecting cerium(IV) ion up to now.



**1**

Scheme 1

Cerium is a rare earth metal, used as a getter in the metal industry, blurring and polished in glass industry, in the Welsbach gas, in carbon arc and as agents extracted liquid - liquid to separation of fission products from uranium fuel has consumed all. Cerium levels in the crust is 66 ppm ( $6.10^{-3}\%$ ), usually in the form xerit. So development of a simple, sensitive and reliable method for the determination of cerium(IV) is essential, it is even more interesting and significant to develop a new type of calixarene-based chromogenic reagent for selective detection of cerium(IV). Generally, the most chromogenic reagents based on the supramolecular calixarene were prepared by attaching a chromogenic moiety for the optical reading-out to the platform of calixarene, their ability to recognize and discriminate metal ions is one of the most remarkable features in previous reports, which makes them suitable as specific receptors. Similarly the target reagents 5,11,17,23-tetrakis[(o-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (**1**) (Scheme 1) in this paper were synthesized through a diazocoupling reaction between the calix[4]arene and diazonium salts, and it displayed excellent chromogenic behavior towards cerium(IV). This motivated us to study it deeply, the following experiment did validate that the reagent exhibit good selectivity for cerium(IV).

## 2. Experimental

### 2.1. Reagents and materials

All chemicals and solvents used were of analytical grade and used without further purification unless otherwise mentioned. Double distilled and degasified water was used throughout.

### 2.2. Apparatus

Uv/Vis Lamda 25 (Perkin Elmer), FT-IR: Bomen DA 8 spectrometer as KBr pellets (Canada) and  $^1\text{H}$ NMR spectroscopy: AVANCE- 600FT-MNR 600 MHz. (Germany). Fourier-transform Raman spectroscopy was carried out in the macroscopic mode with a specimen footprint of about 100 microns using a Bruker IFS 66 instrument with a FRA 106 Raman module.

The pH values were determined at room temperature with 211 Microprocessor pH Meter (Portugal) calibrated to standard buffer solutions of pH 6.96 and 4.00.

### 2.3. Synthesis of 5,11,17,23-tetrakis[(o-carboxyphenyl)azo]-25,26,27,28-tetrahydroxycalix[4]arene (**1**)

Le Van Tan author and colleagues have published synthesis of reagents (**1**) and analytical ability of their complexes [4].

### 2.4. UV absorption spectra research general procedure

A stock solution of reagent **1** was prepared in double water.  $\text{Ce}^{4+}$  stock solution were prepared by dissolving  $\text{Ce}(\text{NO}_3)_4$  with doubly distilled water. In various experiments, a diverse amount of  $\text{Ce}(\text{NO}_3)_4$  crystal was added to a stock solution of reagent **1**, respectively, the final volume of the solution was adjusted to same volume with HAc–NaAc buffer solution after crystal being dissolved. Two minutes later the absorbance was measured at 515 nm in 1 cm quartz cell against water blank and the reagent blank, respectively, at room temperature.

## 3. Results and discussion

### 3.1. Absorption spectra

Preparatory experiments for determining the optimum testing conditions have been done, the absorption spectra of the reagent **1** and its **1**-cerium(IV) complex under the optimum conditions are shown in Fig. 1. In the figure, curve 'a' and 'b' are the spectra of **1** and **1**-cerium(IV) complex against water blank, respectively. In the UV spectra of reagent **1**, the only absorption peak at 365 nm arises from  $\pi \rightarrow \pi^*$  transition of the N - N bond (Fig. 1a), but in the spectra of **1**-cerium, the change was marked by shift to 370 nm and a decrease in intensity, with the concurrent appearance of a new conspicuous absorption peak at 515 nm (Fig. 1b), along with the incremental addition of cerium in a certain range the peak at 370 nm trailed off and the peak at 515 nm boosted up (not shown). Curve 'c' is the absorption spectra of **1**-chromium(III) complex against the corresponding reagent **1** blank (Fig. 1c). As can be seen, the maximum absorption peak of the reagent **1** lies at 365 nm, whereas the absorption peak of the **1**-cerium(IV) complex is dissimilar to it.

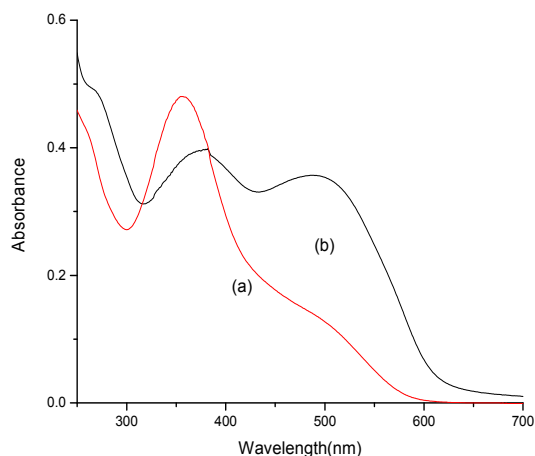


Fig. 1. Absorption spectra of **1** and its cerium complex at pH 6.0 conditions:

- (a)  $2.0 \times 10^{-5}$  mol L<sup>-1</sup> of **1** solution against water blank;
- (b) the solution containing  $2.0 \times 10^{-5}$  mol L<sup>-1</sup> of **1** and  $2.0 \times 10^{-5}$  mol L<sup>-1</sup> of Ce<sup>4+</sup> against water blank;

The remarkable thing to note is the fact that the addition of cerium(IV) induced a weak red shift and a new absorption peak at 515 nm, exhibited an isosbestic point at 470 nm. This feature was expected to be utilized to detect the important ion cerium(IV), and our experiment in this work approved this point well. Similar observation can be found in literatures [13–16]. The UV absorption spectra of the reagent **1** and cerium mixture was measured periodically, we found that the absorption peak at 515 nm of **1**-cerium(IV) appeared only 10 s after addition of cerium(IV) to the stock solution of the reagent **1**, the equilibrium was attained in ca. 2 min. From these characteristics, it is proposed that the topic water-soluble reagent **1** could be a significant chromogenic ionophores for the recognition of ion cerium(IV), this is very advantageous in the practical application of it.

### 3.2. Effect of pH on absorbance of complex

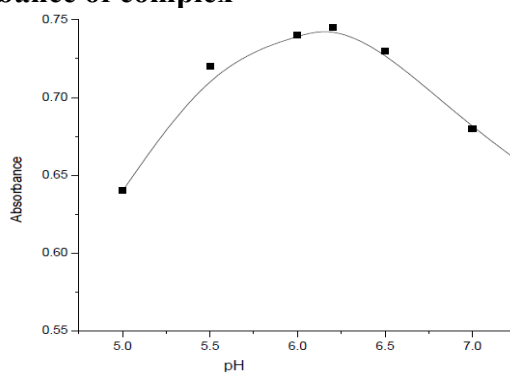


Fig. 2. Effect of pH conditions on absorbance of complex at 515 nm

( $3.0 \times 10^{-5} \text{ mol L}^{-1}$  of **1** and  $2.5 \times 10^{-5} \text{ mol L}^{-1}$  of  $\text{Ce}^{4+}$ ).

Since cerium(IV) tends to form precipitate in weak acidic environments, the absorption spectra of **1**-cerium(IV) complex was obtained in the pH range 5.0–7.0. To keep the other conditions optimum, appropriate concentration ( $3.0 \times 10^{-5} \text{ mol L}^{-1}$ ) of reagent **1** and mezzo cerium(IV) ion concentration ( $2.5 \times 10^{-3} \text{ mol L}^{-1}$ ) were chosen. The effect of pH on the absorbance of **1**-cerium(IV) complex at 515 nm is shown in Fig. 2. Different pH values were obtained by varying the relative amounts of NaAc and HAc, and confirmed by a digital pH-meter. As can be seen from Fig. 2, in the pH range 5.0–7.0, different acidities display prominent affect on the absorption peak intensity, the absorbance at 515 nm increase with acidity increment first, then reach the peak point and decrease last. The maximum absorbance of the complex is obtained in the pH range 6.0–6.5, so pH condition of 6.0 was assumed as the best and chosen for the following experiments.

### 3.3. Effect of cerium(IV) concentration on absorbance of complex

Under the optimum acidic condition (pH 6.0, the concentration of **1** is  $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ), the effect of the concentration of cerium(IV) on absorbance at 515 nm was checked. As can be seen from Fig. 3, the absorption of **1**-cerium(IV) complex at 515 nm show a continuous increase in intensity along with the augment of the cerium(IV) concentration in the range of  $8. \times 10^{-6}$  to  $3.0 \times 10^{-5} \text{ mol L}^{-1}$ , a plateau is reached until the cerium(IV) ion concentration increase to  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ , and linear regression equation was determined to be: absorbance (A) =  $0.701 \times C(10^{-5} \text{ mol L}^{-1} \text{ cerium(IV)}) + 0.021$ ,  $r = 0.997$ ,  $n = 5$ , the insert in the Fig. 3 shows the linearity of them.

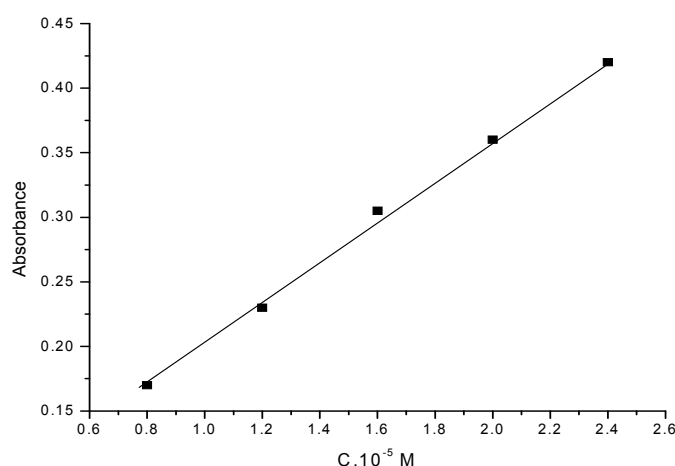


Fig. 3. Effect of  $\text{Ce}^{4+}$  concentration (pH 6.0,  $3.0 \times 10^{-5} \text{ mol L}^{-1}$  of **1**).

The insert shows the linear relation in the range of  $0.8$ – $2.5 \times 10^{-5} \text{ mol L}^{-1}$  of cerium: absorbance (A) =  $0.701 \times C(10^{-5} \text{ mol L}^{-1} \text{ cerium(IV)}) + 0.021$ ,  $r = 0.997$ ,  $n = 5$ .

### 3.4. Selectivity towards cerium(IV) against other metal ions

For the sake of studying the anti-jamming ability of reagent **1** selectivity towards cerium(IV), many metal ion were added to the reagent **1** aqueous solution and their UV spectra were measured, the UV absorption of the reagent **1** and **1**- $M^{n+}$  complex were showed in Fig. 4. Upon interaction with aqueous  $\text{Ce}(\text{NO}_3)_4$  solution, the reagent **1** experienced a marked absorption peak at 515 nm and the absorption peak at 365 nm experienced minor red shift, whereas addition of other metal ions to the solution of reagent **1** did not cause any conspicuous change, although their absorption intensities at 365 nm increased or decreased a little compared to the metal ion free reagent **1**. This phenomenon is very important, and showed that reagent **1** possess good selectivity towards cerium(IV) even  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  are present.

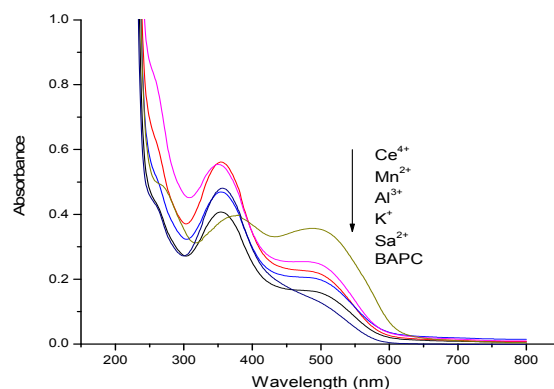


Fig. 4. The absorption spectra of reagent **1** and **1**- $M^{n+}$

### Compared with other methods.

The figures compare reagents Cerium determined by traditional optical methods with reagents BAPC is given in Table 1. These data indicate that highly selective BAPC reagents for ion Cerium and BAPC reagents can be used for analysis.

Table 1. Comparison of analytical methods Cerium

Reagent	$\epsilon_{\lambda}(\text{l.mol}^{-1}\text{cm}^{-1})$	Conditions
Cupferron – Ce(IV)	440 $9.3 \cdot 10^{-3}$	pH = 4,5;
$\beta$ -Diketone – Ce(IV)	440	
Oxine–5–sulfonic Acid-Ce(IV)	480	pH = 1,5;
Ferroin-Ce(IV)	520	
3,3'-Diaminobenzidine-Ce(IV)	355	pH = 2.0-3.0;
BAPC-Ce(IV)	515 $7.8 \cdot 10^{-4}$	pH = 5.0-7.0, $2.5 \cdot 10^{-6}$ - $3 \cdot 10^{-5}$ mol $\text{l}^{-1}$

## 4. Conclusion

Based on the complexation of  $\text{Ce}^{4+}$  with BAPC, we have investigated the optimum conditions of the complex. The results show that complex formed in acidic environment with a pH of 5.0-7.0, a 1:1 ratio. Beer's law is obeyed in the range of  $5.0 \cdot 10^{-6}$ - $2.5 \cdot 10^{-5}$  mol $\text{l}^{-1}$  of  $\text{Ce}^{4+}$ , molar absorptivity of complex ( $\epsilon$ ) is  $7.81 \cdot 10^4$  Lmol $^{-1}\text{cm}^{-1}$  at wavelength of 515 nm and detection limit is  $2.5 \cdot 10^{-6}$  mol $\text{l}^{-1}$ . The original signal can be shown that a new spectrophotometric analytical method of Cerium in the real sample will be proposed in optimal conditions.

## 5. References

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