CHEMISTRY LETTERS, pp. 2105-2108, 1991.

Calix[4]arene-5,11,17,23-tetrasulfonate as an Analytical Reagent for Cerium(III) Ion

Isao YOSHIDA,* Nobuhiro YAMAMOTO, Fumio SAGARA, Keihei UENO,
Daido ISHII, and Seiji SHINKAI†
Department of Industrial Chemistry, Kumamoto Institute of
Technology, 4-22-1 Ikeda, Kumamoto 860
†Chemirecognics Project, ERATO, Research Development Corporation of Japan, 332-1 Kamikoga, Chikushino, Fukuoka 818

Calix[4]arene-5,11,17,23-tetrasulfonate(1) reacts with cerium(III) ion in alkaline solution to form a colored complex(λ_{max}=417 nm, ε=1.09 x 10^4 1 mol^{-1} cm^{-1}). The coloration reaction is specific for cerium among rare-earth elements. The coloration mechanism was discussed on the basis of the stability constants.

Calix[n]arenes are a new class of macrocyclic ligand with phenolate oxygens as the coordination site. The coordinating behavior of calix[n]-arenes can be easily modified by changing "n" or by introducing appropriate substituents on aromatic rings. Thus, several calix[n]arene have been investigated as the novel analytical reagents for certain metal ions.

For example, p-t-butylcalix[6]arene, which is insoluble in water but soluble in organic solvents, has been used as an extraction reagent for copper(II) ion, whereas, p-t-butylcalix[4]arene does not extract copper(II) ion under the similar conditions.[1,2] The extractability of copper(II) ion has increased when more hydrophobic homolog, p-n-hexylcalix[6]arene is used as an extraction reagent.[2]

On the other hand, the sulfonate derivatives of calix[n]arenes are water soluble,[3] and calix[6]arene-5,11,17,23,29,35-hexasulfonate is highly selective toward uranyl ion in aqueous solution.[4] While we are investigating the reaction of **1** with rare-earth ions, we unexpectedly found an intense coloration on the reaction of **1** with cerium(III) ion in an alkaline aqueous solution. None of the other rare-earth ions gave any coloration with **1**. The finding reported in this paper indicates that **1** acts as a specific chromogenic reagent for cerium(III) ion.

Figure 1 shows absorption spectra of **1** and its cerium(III) complex in a solution of pH 11.7(NH_3-NH_4Cl). The aqueous solution of **1** is colorless while the cerium(III) complex is red-brown(λ_{max}=417 nm, ε=1.09 x 10^4 l mol^{-1} cm^{-1}). The color intensity increased with the increase of pH, reaching the absorption maximum at pH 11.7.

None of the other rare-earth ions, however, gave any enhanced color reaction with **1**. Thus, it is clear that the coloration of **1** is very specific to cerium(III) ion in the series of the rare-earth ions. Many colorimetric reagents are suggested for the analysis of rare-earth ions, however, none of them gave any color reaction with a particular member of rare-earth ions including cerium(III) ion. Therefore, **1** is a very useful colorimetric reagent for cerium(III) ion even in the presence of other rare-earth ions.

Although, the coloration decreased slightly, in fact, in the presence of a small amount of other rare-earth ions, the color intensity became constant when their concentrations were larger than 20 ppm. Therefore, cerium(III) ion was determined with **1** in the presence of excess amount of lanthanum(III) ion as follows.

Into a 25 ml of measuring flask, each 5 ml of the sample solutions containing 0 to 400 μg of cerium(III) and 500 μg of lanthanum(III) ions was taken, then 5 ml of 0.025 M(1 M=1 mol dm^{-3}) of **1** was added. After 1 M NH_3-NH_4Cl buffer solution was added to the mixture, it was diluted to the mark with water. The optical absorbance at 417 nm was measured in a 1 cm cell, using the reagent blank as a reference.

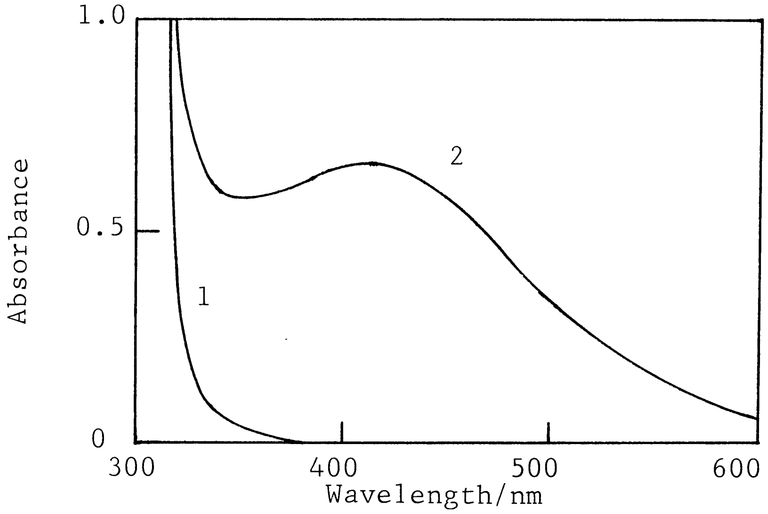

Fig. 1. Absorption spectra of 0.005 M **1** in the absence(1) and the presence of 8.0 ppm Ce(III) ion(2) at pH=11.7. light-path length=1 cm, reference=water

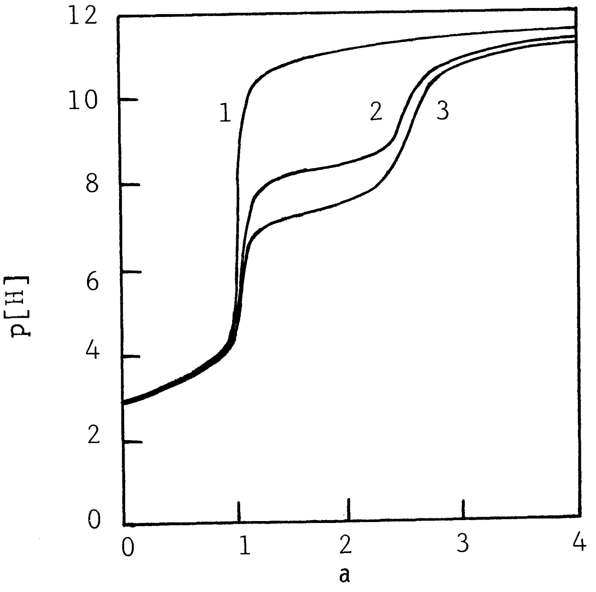

Fig. 2. pH titration curves for 0.1101 mmol 1(1), (1)+0.04993 mmol $La(NO_3)_3$(2), and (1)+0.05301 mmol $Ho(NO_3)_3$(3) with 0.09961 M KOH at 25 °C. $\mu=0.1$ with KNO_3, initial volume=40.0 ml, a=molar ratio of KOH to 1.

Table 2. Overall stability constants, log β_{ML2OH}, at 25 °C and at $\mu=0.1$

M^{3+}	log β_{ML2OH}	M^{3+}	log β_{ML2OH}
Y	21.88		
La	19.26	Tb	21.33
Ce	20.25	Dy	21.47
Pr	20.51	Ho	21.56
Nd	20.57	Er	21.66
Sm	20.90	Tm	22.01
Eu	21.02	Yb	22.76
Gd	20.93	Lu	22.42

A linear calibration line for cerium(III) ion was obtained($\varepsilon=9.00 \times 10^3$ l mol^{-1} cm^{-1}). The recovery of cerium(III) ion was satisfactory in the presence of various amounts of other rare-earth ions. These results indicate that 1 is a useful colorimetric reagent for cerium(III) ion in the presence of other rare-earth ions.

The stability constants of rare-earth ion complexes with 1 were studied by the pH-titration method to elucidate the specific coloration reaction of 1 with cerium(III) ion. The aqueous solution of 1 was titrated at 25 °C with 0.1 M potassium hydroxide in the absence or presence of metal ion in a ratio of 2:1 or 3:1, as described in the previous paper.5)

Titration curves for 1 alone and those of the mixtures with lanthanum(III) or holumium(III) ions are shown in Fig. 2. At an initial stage of titration, the pH values are same for these three curves. However, in a range of a=1 - 2.5, the pH values of the titration curve for the metal ligand mixture become lower than those for the ligand alone, indicating the metal complex formation. The similar titration curves were observed for other members of rare-earth metal ions.

The complex formation constants were calculated by analyzing the titration curves using the computer program BEST.[6)] The result indicates that 1 reacts with rare-earth ions according to the following equation(1) except scandium(III) ion.

$$2\ LH_2 + M^{3+} + H_2O \rightleftarrows ML_2OH^{2-} + 5\ H^+ \qquad (1)$$

where the electric charges on sulfonate groups was neglected.

Overall stability constants, $\beta_{ML2OH}=[ML_2OH^{2-}]/[M^{3+}][L^{2-}]^2[OH^-]$, are summarized in Table 1. In this equation, 1 was treated as a di-protonic acid($pK_{a1}=3.26$, $pK_{a2}=12.38$),[7)] releasing two protons on the complex formation with a metal ion. The dissociations of the third and the fourth protons of 1 were not considered because of their high basicity.[7)]

The stability constants(in Table 1) increase with the increase of the atomic number of the element showing the slight decrease at gadollinium and at lutetium. The value for yttrium complex is found in between those for erbium and tullium complexes. Such a trend of stability constants has been often observed for other common rare-earth ion complexes.[8)] Thus, it is clear that the complex formation of 1 is not specific for cerium(III) ion, but the coloration reaction accompanied by the complex formation is characteristic of cerium(III) ion among the rare-earth ions.

References

1) I. Yoshida, S. Fujii, K. Ueno, S. Shinkai, and T. Matsuda, *Chem. Lett.*, 1989, 1535.
2) I. Yoshida and S. Shinkai, unpublished data.
3) S. Shinkai, K. Araki, H. Koreishi, T. Tsubaki, and O. Manabe, *Chem. Lett.*, 1986, 1351.
4) S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, and O. Manabe, *J. Am. Chem. Soc.*, 109, 6371(1987).
5) I. Yoshida, F. Sagara, and K. Ueno, *Bull. Chem. Soc. Jpn.*, 62, 2296 (1989).
6) A. E. Martell and R. J. Motekaitis, "*Determination and Use of Stability Constants*," VCH publishers Weinheim, Germany(1988), p.171.
7) I. Yoshida and S. Shinkai, to be published.
8) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, 65, 1(1965).

(Received August 22, 1991)