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Europium(III)-triflate interactions in water and aqueous methanol studied by UV–vis and luminescence

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Abstract

The use of perchlorates as non-complexing rare-earth ligands has been common. However, the possibility of perchlorate explosions in the presence of organic materials led many workers to substitute lanthanide triflates (lanthanides bound to the anion of trifluoromethanesulfonic acid) as the source of rare-earths for studies with other ligands. Using UV–visible and fluorescence emission measurements in water and 50% aqueous methanol, we have shown that triflate does not form complexes with 0.200 M Eu(III) in the absence and presence of perchlorate.

Keywords: Luminescence; Europium complexes; Triflate; Perchlorate; Inner sphere complexes; Outer sphere complexes

1. Introduction

The lanthanides are characterized as being hard acids, which tend to react with hard bases, especially those with oxygen donor atoms. In studies of lanthanide complexation, researchers commonly use perchloric acid to dissolve lanthanide oxides, assuming that the perchlorate anion does not form complexes. In the solid state, X-ray diffraction and luminescence studies have showed the existence of both inner and outer sphere perchlorates [1]. Ultrasonic relaxation measurements on Er(III) [2], Gd(III) [3] and Nd(III) [3] perchlorates in aqueous solution demonstrated the absence of any measurable complexes. Aqueous methanol solutions of the rare-earth perchlorates showed the existence of both inner and outer sphere complexes, which increase in relative amounts as the methanol content increases [2,3]. Bunzli and Kasparek [4] studied complex formation between lanthanides and perchlorate in acetonitrile using FT-IR, and found an average of more than one perchlorate binding per lanthanide ion. Complex formation constants were also determined and were larger for the heavier lanthanides than for the lighter ones [4]. In methanol with less than 40 ppm water, both perchlorate and $CF_3SO_3^-$, triflate ion (abbreviated as OTf), formed weak complexes as determined by ^{139}La NMR. In anhydrous acetonitrile the formation constant for the first complex was found to be 390 ± 60 for perchlorate and 450 ± 60 for triflate with La(III) [5]. Choppin and co-workers also investigated lanthanide triflate complexes in anhydrous acetonitrile by FT-IR [6]. In acetonitrile, both $Ln(OTf)_2^+$ and $Ln(OTf)_3$ species were found to be dominant, but the binding of triflate is very dependent upon the small amount of water present [6]. An earlier study had found that triflate forms a 1:3 electrolyte in acetonitrile [7], but this may indicate the presence of more water than in the Choppin study [6]. Choppin found that the triflates form stronger bonds than perchlorates in acetonitrile and determined the formation constants of mixed complexes [6]. As in the case of perchlorate, crystal studies have been carried out, with three tridentate triflates bound per europium or lutetium ion [8].

Our interests are in the quantitative determination of stability constants for lanthanide complexes in aqueous organic solvents and we had been using perchloric acid to dissolve the lanthanide oxides. Because perchlorate solutions can explode when heated to dryness in the presence of organic species, the use of perchlorates has been declining, with triflic acid being used to dissolve the oxides. This study in water and 50% aqueous methanol by volume was initiated to determine if measurable quantities of $EuOTf^{2+}$ complexes can be detected.

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2. Experimental

The experimental procedures are similar to those used in previous complexation studies [9]. After drying Eu_2O_3 (Molycorp), two separate stock solutions of europium oxide were made with slight excess of trifluoromethanesulfonic acid (Alfa Aesar) to produce $Eu(OTf)_3$, and slight excess of perchloric acid to produce $Eu(ClO_4)_3$. These stock solutions were standardized by EDTA titrations and were used in subsequent UV–vis and luminescence emission acquisitions with different counter ions. The UV–vis measurements were made on a Varian Cary 3 spectrophotometer and the luminescence measurements were made on a SPEX Fluorolog instrument. Both were thermostated with Neslab refrigerated/heated baths. Initially, absorbance measurements were carried out in water and in 50% aqueous methanol. Separate Beer's Law experiments were carried out on the Eu(III) triflate and perchlorate solutions. In the second set of experiments, constant Eu(III) triflate or perchlorate solutions were used and sodium trifluoromethanesulfonate (Alfa Aesar) or sodium perchlorate (Aldrich) were added, respectively, to determine if added ligand changed the absorbance at constant Eu(III) concentration. In the third set of experiments NaOTf was added to the $Eu(ClO_4)_3$ solutions and $NaClO_4$ to the $Eu(OTf)_3$ solutions, each at a constant Eu(III) concentration. Similarly, the luminescence emission experiments involved the same three types of experiments with the $Eu(ClO_4)_3$ and $Eu(OTf)_3$ solutions, but at lower Eu(III) concentrations for the luminescence studies. In water data were obtained at 25°C and in aqueous methanol the measurements were carried out at 15°C, 20°C, 25°C and 37°C. Excitation was performed at 394 nm, and emission peaks were observed between 525 and 725 nm for these solutions.

3. Results and discussion

In our previous studies we have shown that the addition of a complexing ligand, such as nitrate [10], glutamine [9] or serine [9] results in deviations from Beer's Law that increased as the ratio of ligand to lanthanide(III) ion increases. In water and in 50% aqueous methanol, the absorbance was measured as a function of concentration and temperature. In Fig. 1 at 25°C, the Beer's Law results for both $Eu(ClO_4)_3$ and $Eu(OTf)_3$ are linear throughout the concentration range under investigation, even when the absorbance exceeds one. This same result was obtained at 15°C, 20°C, 25°C and 37°C and is consistent with either the absence of complexation or the possible existence of a very weak complex below the sensitivity threshold of the Cary 3 spectrophotometer. For both glutamine [9] or serine [9] the complexation constant was near to or less than unity and if inner sphere complexation was occurring to a measurable extent, it would have been detected. The addition of excess $NaClO_4$ or NaOtf to 0.200 M $Eu(ClO_4)_3$ results in the absence of any systematic deviation from the free Eu(III) absorbance shown in Fig. 2, again indicating no measurable complexation.

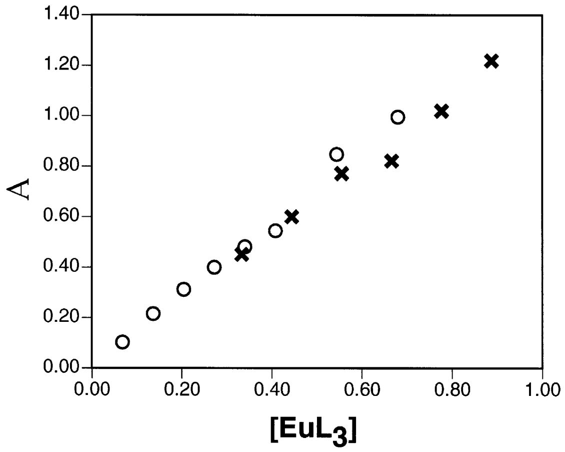

Fig. 1. The absorbance for $Eu(ClO_4)_3$ (○) and $Eu(OTf)_3$ (**X**) at 394 nm in 50% aqueous methanol at 25°C.

Eu(III) luminescence measurements are extremely sensitive to the existence of inner sphere complexes and they have the advantage of using lower concentrations of europium ions compared to UV–vis measurements. The intensity of the emission of a europium inner sphere species, such as solvated Eu(III) ion or a complex with a ligand other than water is proportional to the concentration of the species. Thus, we could expect Beer's Law type of behavior if no complex other than the solvated cation species is present. Emission data were obtained at 554, 590, 615, 649 and 696 nm and except for the solutions at high ligand to Eu(III) ratios, similar results were obtained at each wavelength. In Figs. 3 and 4 a linear relationship was indeed found for $Eu(ClO_4)_3$ and for $Eu(OTf)_3$ as a function of concentration in water and in 50% aqueous methanol even though we exceeded one million counts, which is not recommended by SPEX for their fluorimeter. The concentration used was much below that used in the UV–vis absorbance experiments. If significant inner sphere complexes would have been present, the emission intensity would have likely been different for each species and deviations from linearity would have been expected. In Fig. 5, the data at each of the five wavelengths are shown for $Eu(OTf)_3$ and within experimental error, the emission intensity at each wavelength varies linearly with $Eu(OTf)_3$ concentration.

Experimentally, the solubility of $Eu(ClO_4)_3$ exceeds that of $Eu(OTf)_3$ in either solvent studied, and we were able to achieve higher ligand to Eu(III) ion concentration ratios ([L]/[Eu(III)]) for perchlorate relative to that

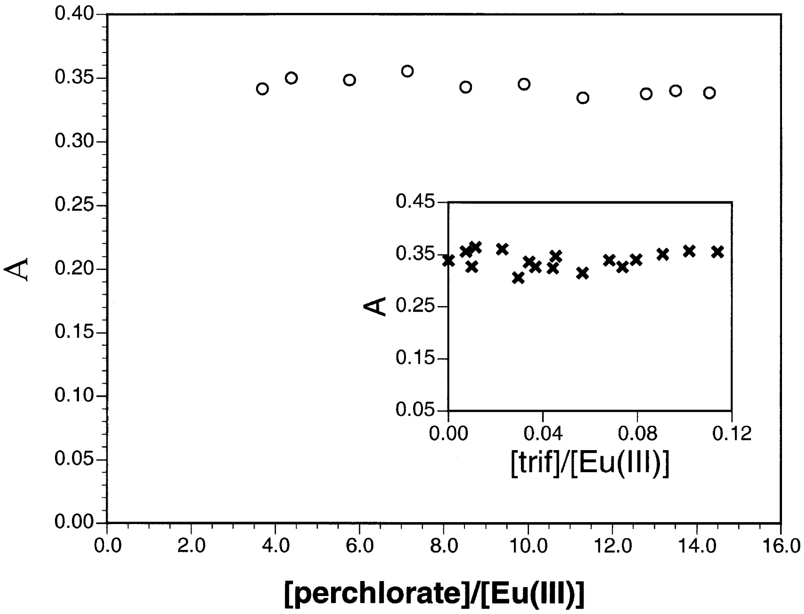

Fig. 2. The absorbance for 0.200 M $Eu(ClO_4)_3$ with added $NaClO_4$(○) or NaOTf (**X**) at 394 nm in 50% aqueous methanol at 25°C.

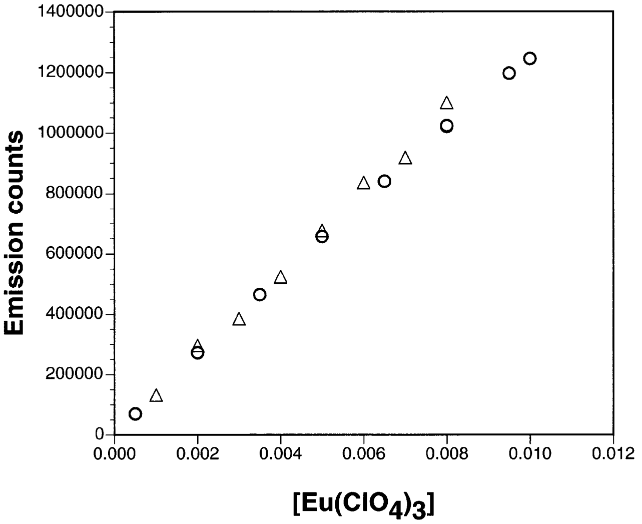

Fig. 3. Luminescence emission for $Eu(ClO_4)_3$ at 590 nm as a function of concentration in water (○) and in 50% aqueous methanol (△).

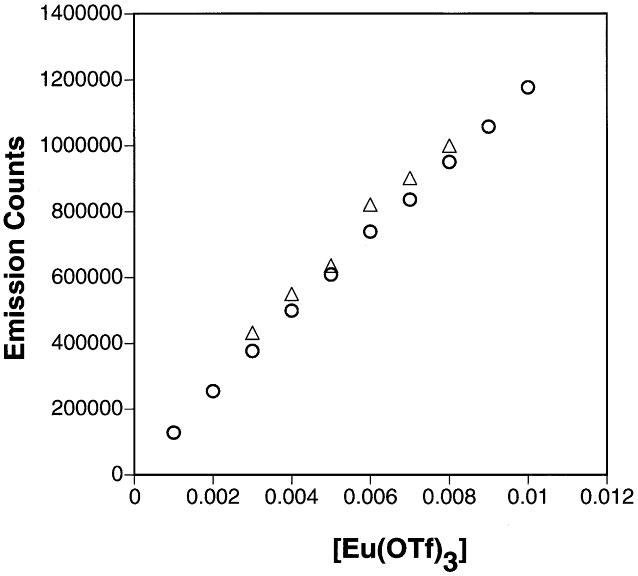

Fig. 4. Luminescence emission for $Eu(CF_3SO_3)_3$ at 590 nm as a function of concentration in water (○) and in 50% aqueous methanol (△).

of triflate. Starting with 0.005 M $Eu(ClO_4)_3$, the addition of either $NaClO_4$ or NaOTf , resulted in no systematic change in the emission intensity in water or 50% aqueous methanol, as shown in Fig. 6. Similarly starting with the perchlorate salt of europium and adding triflate gave equivalent results to that starting with the triflate salt of europium and adding perchlorate, as shown in Fig. 7. The conclusion reached is that Eu(III) neither forms inner sphere complexes with perchlorate or triflate ions, no matter which europium salt is initially used. This has the effect of allowing Eu_2O_3 to be dissolved in triflic acid, followed by the addition of $NaClO_4$ to control the ionic strength, a procedure often used.

Using the hypersensitive peak at 615 nm results in the suggestion of a small amount of complex between Eu(III) and triflate in aqueous methanol, which is absent in water. Examining Fig. 8, starting with $Eu(ClO_4)_3$ we find an increase in intensity when NaOTf is added, consistent with the increased intensity of the triflate solutions compared to the perchlorate ones. In water no further increase in intensity is observed as the NaOTf is added to a ratio of about 40:1. However, in 50%

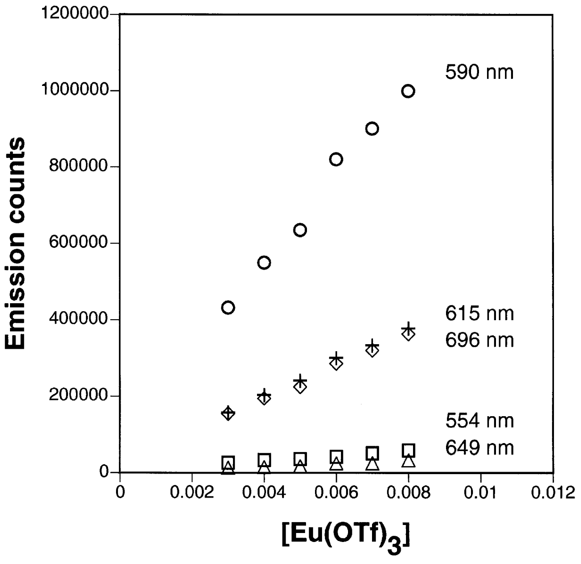

Fig. 5. Luminescence emission for $Eu(OTf)_3$ at different wavelengths as a function of concentration in 50% aqueous methanol at 25°C.

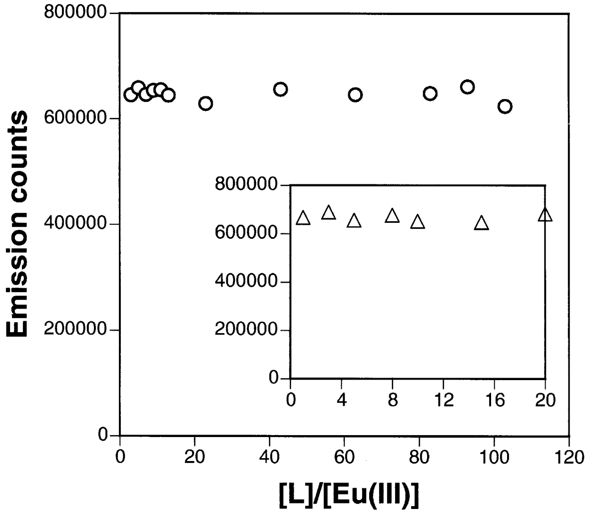

Fig. 6. Luminescence emission for 0.005 M $Eu(ClO_4)_3$ with added $NaClO_4$ (○) or NaOTf (△) at 590 nm in 50% aqueous methanol at 25°C. *L* represents total perchlorate or triflate.

aqueous methanol, the intensity appears to increase as more NaOTf is added, suggesting the formation of a small amount of measurable complex. However, by dissolving the Eu_2O_3 in triflic acid and then adding $NaClO_4$ it is possible to work in a region where the weak triflate complexation is negligible. This study suggests that as the solvent mixtures progress toward anhydrous methanol, it may be possible to detect inner sphere Eu(III) complexes in the absence of significant amounts of water, consistent with the results of Bunzli [4,5] and Choppin [6].

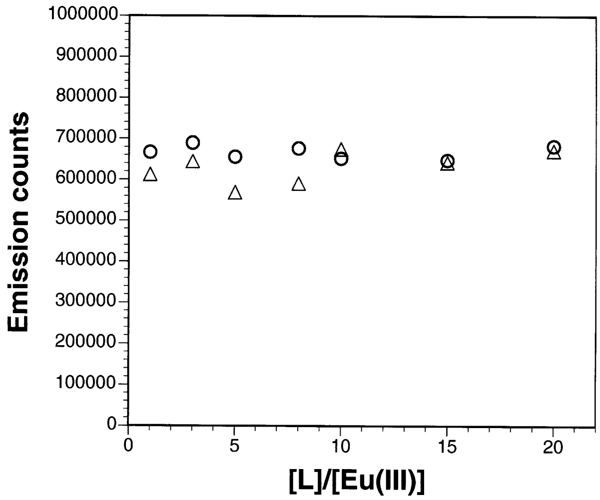

Fig. 7. Luminescence emission for $Eu(ClO_4)_3$ with NaOTf (○) and for $Eu(OTf)_3$ with $NaClO_4$ (△) at 590 nm and 25°C in 50% aqueous methanol.

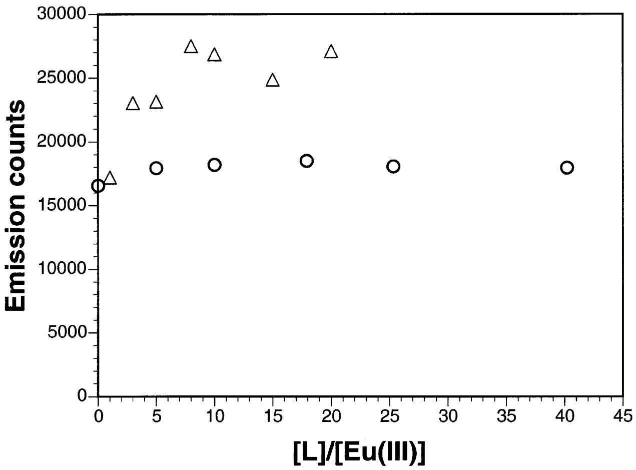

Fig. 8. Luminescence emission data at the 615 nm hypersensitive peak for 0.005 M $Eu(ClO_4)_3$ with added NaOTf in water (○) and in 50% aqueous methanol (△).

Acknowledgments

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