

Luminescence study on determination of the hydration number of Cm(III)

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Abstract

A luminescence study of Cm(III) has shown a linear correlation between the decay constant k_{obs} (the reciprocal of the excited-state lifetime) and the number of water molecules $n_{\text{H}_2\text{O}}$ in the first coordination sphere of complexes. From measurements of k_{obs} of Cm^{3+} in D_2O – H_2O solutions and of Cm(III) doped lanthanum compounds, the following correlation for k_{obs} (ms^{-1}) vs. $n_{\text{H}_2\text{O}}$ was established: $n_{\text{H}_2\text{O}} = 0.65k_{\text{obs}} - 0.88$. This relationship was applied to study of the residual hydration of Cm(III) complexes of polyaminopolycarboxylate ligands. The hydration number of Cm(III) in these complexes is apparently larger than that of Eu(III).

1. Introduction

The hydration of a metal ion is an important factor in the structural and chemical behavior of complexes. The techniques for studying the size and/or structure of the hydration sphere can be classified as direct or indirect methods. The direct methods include X-ray and neutron diffraction, luminescence decay and nuclear magnetic resonance (NMR) relaxation measurements, while the indirect methods involve compressibility, NMR exchange and absorption spectroscopy measurements. Because of the high sensitivity and selectivity of laser-induced luminescence spectroscopy, the luminescence measurement is the most promising direct method for study of the hydration of radioactive actinide ions such as Cm(III) and Am(III).

For Eu(III) and Tb(III), a linear correlation has been found between the reciprocal of the excited-state lifetime (*i.e.* the decay constant k_{obs}) and the number of water molecules in the first coordination sphere $n_{\text{H}_2\text{O}}$ of their complexes [1]. A similar correlation is expected for Cm(III) from the analogy between spectroscopic properties of trivalent lanthanide and actinide ions. Beitz and Hessler [2] reported the first study of aqueous Cm^{3+} photophysics, including measurement of the emission spectrum and lifetime of aqueous Cm^{3+} in H_2O and D_2O . Research on the spectroscopic and luminescence studies of Cm(III) in solution has been re-

viewed recently [3–5]. The lifetimes of various Cm(III) complexes were measured and the number of coordinated water molecules was calculated by Beitz [3]. From the assumption that aqueous Cm^{3+} has 8 or 9 water molecules in the first coordination sphere, he calculated 2.5–2.8 water molecules for Cm^{3+} complexed by carbonate in 1 M Na_2CO_3 , 3.4–3.8 for the Cm–CDTA complex and 1.3–1.5 for the DTPA complex. These values are chemically reasonable but the method remained suspect without validation from studies of crystalline solids of known hydration.

A luminescence study of Cm(III) and of Eu(III) (as a reference ion) was performed to assess the relationship between the lifetime and the hydration number of Cm(III) in liquid and solid phases. The lifetimes of Cm^{3+} in D_2O – H_2O mixtures and in crystalline lanthanum compounds were measured for the calibration of k_{obs} vs. $n_{\text{H}_2\text{O}}$. As an application of the relationship obtained, the hydration state of Cm(III) complexed with polyaminopolycarboxylate ligands was measured.

2. Experimental details

2.1. Reagents

^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ y, >96 at.%) was purified by passage through cation exchange resin (Dowex 50wX4) with elution by ethanol–HCl solution [6]. The Cm fraction in effluent was evaporated to dryness and redissolved in dilute HClO_4 . The concentration of the Cm(III) stock solution (0.01 M HClO_4) was determined by liquid scintillation counting (LSC) with discrimination of the spontaneous fission and fission product regions.

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Eu(III) stock solution was prepared by dissolving an appropriate amount of Eu_2O_3 (Aldrich) in perchloric acid. D_2O (99.8 at.% D) was obtained from Aldrich and used to prepare the D_2O – H_2O solutions. Samples of the Cm(III) or the Eu(III) stock solutions were evaporated to dryness and the residues dissolved in a fixed amount of the D_2O – H_2O solution followed by a second evaporation to dryness. The sample solutions for measurement were prepared by redissolving the residues in the $\text{D}_2\text{O}/\text{H}_2\text{O}$ solution.

Nitrilotriacetic acid (NTA), *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA) and triethylenetetraamine-*N,N,N',N'',N''',N'''*-hexaacetic acid (TTHA) were used in this study as received from commercial sources (Aldrich). Solutions of the polyaminopolycarboxylate complexes were prepared by mixing stoichiometric amounts of Cm^{3+} or Eu^{3+} and ligand stock solutions of known concentration. Variation of the solution pH of each solution was effected by the addition of small amounts of standard NaOH or HClO_4 directly to the cuvette and was checked before and after measurement of the luminescence lifetime. The concentrations of Cm(III) and Eu(III) were 10^{-7} – 10^{-6} M and 10^{-2} M respectively, in the samples.

Crystalline lanthanum compounds doped with Cm(III) and Eu(III) were prepared according to the procedures of the references listed in Table 1. Thiodiacetic acid (Aldrich), oxalic acid (Mallinckrodt), nicotinic acid (Matheson) and dipicolinic acid (Aldrich), all reagent grade, were used without further purification. The values reported in the figures or tables are the average of four to six measurements of the luminescence lifetimes.

2.2. Method

The Cm(III) in the samples was excited to the F-state ${}^6\text{I}_{17/2, 11/2}$ [13] by a pulsed laser beam at 397 ± 1 nm with subsequent emission from the A-state ${}^6\text{D}_{7/2}$ to the groundstate Z ${}^8\text{S}_{7/2}$ [2], 594–605 nm, which was measured to obtain the luminescence lifetime. The

Eu(III) was excited to the lowest excited state ${}^5\text{D}_0$ by a pulsed laser beam at 579 ± 1 nm and the emission from the ${}^5\text{D}_0$ state to the groundstate ${}^7\text{F}$ manifold (${}^7\text{F}_2$), 615 nm, was measured. The 397 nm pulsed laser beam was obtained with a pulsed (10 Hz) 532 nm output of a Quanta Ray DCR 2A Nd-YAG laser pumping DCM (Exciton Chemical) in methanolic solution in a Quanta Ray PDL2 dye laser head. The beam from the dye laser was converted to 397 nm by frequency doubling and mixing with the 1064 nm fundamental in a Quanta Ray WEX-1 wavelength extender. The 579 nm pulsed laser beam was obtained with a 532 nm output of the Nd-YAG laser pumping rhodamine 590/610 (Exciton Chemical) in the dye laser head. The pulse power was typically 2–3 mJ for 397 nm and 10–15 mJ for 579 nm, and the pulse width was in the nanosecond range.

The solution sample was contained in a standard 1 cm fluorimetry cell and the solid samples were placed between quartz plates for the luminescence measurement. The experiments were conducted at room temperature. The emission light was collected at 90° into a monochromator after passing through a low-cut filter (cut-off 580 nm) and detected by a Hamamatsu R928 photomultiplier tube. The whole emission wavelength range was observed. After amplification in a Lecroy 6130 amplifier, the signal was fed into a Lecroy TR8288C transient recorder which was connected to an IBM PC computer through a Lecroy 8901A GPIB interface for signal averaging with the program catalyst (Lecroy). Most of the luminescence decays observed in this work were single-exponential curves.

3. Results and discussion

3.1. Calibration of k_{obs} vs. $n_{\text{H}_2\text{O}}$ for Cm(III)

The hydration number of Eu(III) and Tb(III) has been obtained by using the difference in the decay rate constants in H_2O and D_2O solutions [1]. In general, $k_{\text{H}_2\text{O}} \gg k_{\text{D}_2\text{O}}$, $k_{\text{D}_2\text{O}} \approx \text{constant}$, and ligands are not as effective in causing non-radiative de-excitation of the excited state. For Eu(III), a relationship has been proposed in which the hydration number is related directly to the decay rate constant in H_2O [7].

TABLE 1. Calibration data for Cm(III) or Eu(III) doped lanthanum compounds with H_2O hydration

Anion (reference)	$n_{\text{H}_2\text{O}}^a$	Decay constant k_{obs} (ms^{-1})			
		La(Cm) ^b	La(Eu) ^c	Eu (ref. 1)	Eu (ref. 7)
Dipicolinate[8]	0	2.11	0.64	0.77	0.73
Nicotinate[9]	2	3.76	2.31	2.49	2.40
Oxalate[10]	3	6.16	3.03	3.53	3.58
Thiodiacetate[11]	4	7.03	4.98	5.35	4.42
Bromate[12]	9	15.41	8.80	8.69	8.83

^aNumber of H_2O molecules in the primary coordination sphere of La(III) and Eu(III); ^bCm:La = $1.6.9 \times 10^3$; ^cEu:La = 1.50.

The luminescence decay constants k_{obs} (m s^{-1}) of Cm^{3+} and Eu^{3+} were measured in D_2O – H_2O solutions of various volume percentage, $X_{\text{H}_2\text{O}}$, of H_2O . The results are shown in Fig. 1, and eqns. (1) and (2) express the relations obtained for Cm^{3+} and Eu^{3+} :

$$k_{\text{obs}}(\text{Cm}) = 0.147X_{\text{H}_2\text{O}} + 0.786 \quad r = 0.9999 \quad (1)$$

$$k_{\text{obs}}(\text{Eu}) = 0.0859X_{\text{H}_2\text{O}} + 0.430 \quad r = 0.9997 \quad (2)$$

where r is a correlation coefficient. The results show that the quenching behavior of Cm^{3+} and Eu^{3+} in the D_2O – H_2O system is similar and is due mainly to energy transfer from the excited state to OH vibrators of the H_2O molecules bound to the metal. From eqn. (1), the lifetimes of Cm^{3+} in H_2O and D_2O are calculated to be $64.6 \pm 0.7 \mu\text{s}$ and $1270 \pm 20 \mu\text{s}$ respectively. Our data in H_2O agreed with those of Beitz *et al.* ($65 \pm 2 \mu\text{s}$ [2], $68 \pm 3 \mu\text{s}$ [14]) and Wimmer *et al.* ($65 \pm 2 \mu\text{s}$ [15]). However, our data in D_2O are appreciably longer than that of Beitz and Hessler ($940 \pm 20 \mu\text{s}$ [2]) and close to the radiative lifetime of $1300 \mu\text{s}$ computed by Carnall and Crosswhite [16]. The lifetimes of Eu^{3+} in H_2O and D_2O are calculated to be $111 \pm 2 \mu\text{s}$ and $2330 \pm 40 \mu\text{s}$ respectively, from eqn. (2), in agreement with the literature [17, 18].

The electron configuration of Cm^{3+} , $[\text{Rn}]5f^7$, and that of Gd^{3+} , $[\text{Xe}]4f^7$, are similar. However, the emissive properties of Cm^{3+} are quite different from those of Gd^{3+} and are more similar to those of Eu^{3+} and Tb^{3+} . This is due to the energy gap of Cm^{3+} (1.68×10^3

cm^{-1}) (defined as the energy difference between the lowest emissive level and the highest level of the ground-state manifold), which is smaller than that of Gd^{3+} ($3.2 \times 10^3 \text{ cm}^{-1}$) but close to those of Eu^{3+} ($1.215 \times 10^3 \text{ cm}^{-1}$) and Tb^{3+} ($1.48 \times 10^3 \text{ cm}^{-1}$) [19].

The hydration number of Eu^{3+} in H_2O has been reported to be between 9.0 and 9.6 from luminescence studies of perchlorate [1, 7], while it is 8.3 (from X-ray studies) in 3.23 M chloride solution [20]. The luminescence studies have an inherent uncertainty of about ± 0.5 water molecules. We have measured the k_{obs} of Cm(III) and Eu(III) doped lanthanum compounds with the results summarized in Table 1. For each compound of the La(Cm) and La(Eu) systems, at least two different samples were prepared. The errors of the k_{obs} measured were estimated to be within ± 0.1 for each compound. Although the chemical structure of the compounds was not analyzed by X-ray diffraction, the compounds prepared were indicated to be the expected composition from the k_{obs} value of the La(Eu) compounds which was very similar to that of the Eu(III) compounds in the literature [1, 7]. The following correlations were derived for the hydration numbers of Cm(III) and Eu(III) under our experimental conditions:

$$n_{\text{H}_2\text{O}} = 0.65k_{\text{obs}}(\text{Cm}) - 0.88 \quad r = 0.9938 \quad (3)$$

$$n_{\text{H}_2\text{O}} = 1.07k_{\text{obs}}(\text{Eu}) - 0.62 \quad r = 0.9921 \quad (4)$$

If there is no contribution from the ligand to the de-excitation of the luminescent excited state, the hydration of Cm(III) and Eu(III) in the different complexes can be obtained directly from the values of k_{obs} measured in H_2O . Equation (4) for Eu(III) agrees with that reported by Barthelemy and Choppin [7] and should give results consistent with those obtained by the procedure of Horrocks and Sudnick [1] within the uncertainty of the luminescence method. By using eqns. (1)–(4), the $n_{\text{H}_2\text{O}}$ of Cm^{3+} and Eu^{3+} in H_2O were calculated to be 9.2 ± 0.5 and 9.0 ± 0.5 respectively.

3.2. Hydration states of Cm(III) complexes of polyaminopolycarboxylate ligands

The residual hydration of lanthanide complexes of polyaminopolycarboxylate ligands were determined by luminescence measurements as a function of the pH for Eu(III) and Tb(III) by Brittain and coworkers [21–23]. Table 2 shows the results of our measurements of k_{obs} for Cm(III) and Eu(III) for a number of such complexes. The solution pH was kept constant at 4.6 by acetate buffer for Cm(III) and at 5.5, without buffer, for Eu(III). For the Eu(III) complexes, the calculated hydration numbers agreed well with the literature values [21–23], within ± 0.2 water molecules. This suggests that eqn. (4) is reliable for determination of the hydration number of Eu(III) in the complexes and, pre-

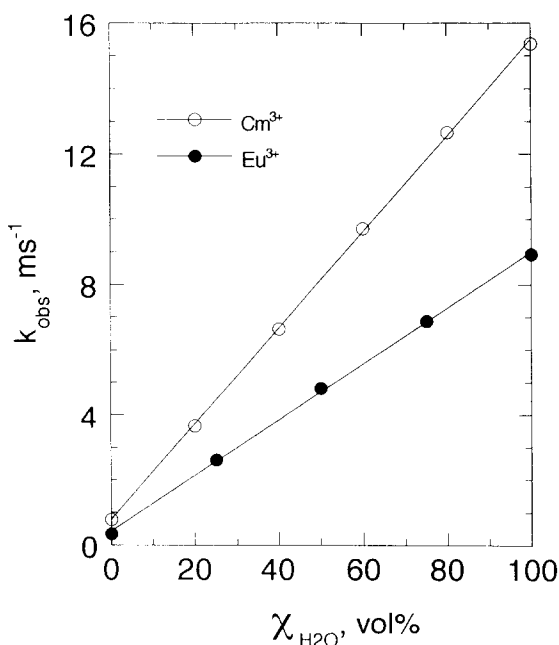


Fig. 1. Luminescence decay constants for Cm^{3+} and Eu^{3+} as a function of volume percentage $X_{\text{H}_2\text{O}}$ of H_2O in D_2O – H_2O solutions: \circ 3.0×10^{-7} M Cm^{3+} , \bullet 1.0×10^{-2} M Eu^{3+} .

TABLE 2. Hydration state of Cm(III) and Eu(III) complexes of polyaminopolycarboxylate ligands

Ligand	Cm ^a		Eu ^b		
	k_{obs} (ms ⁻¹)	$n_{\text{H}_2\text{O}}^c$	k_{obs} (ms ⁻¹)	$n_{\text{H}_2\text{O}}^d$	$n_{\text{H}_2\text{O}}$ (reference)
NTA	11.01 ± 0.14	6.28	4.78 ± 0.04	4.49	4.5 21
HEDTA	7.78 ± 0.10	4.18	3.56 ± 0.13	3.19	3.1 22
EDTA	7.09 ± 0.03	3.73	3.06 ± 0.10	2.65	2.6 22
CDTA	7.20 ± 0.23	3.80	2.90 ± 0.07	2.48	2.3 22
DTPA	3.89 ± 0.02	1.65	1.47 ± 0.02	0.95	1.1 22
TTHA	2.25 ± 0.02	0.58	0.74 ± 0.01	0.17	0.2 23

^a[Cm(III)] = 5.3×10^{-6} M, [ligand] = 5.7×10^{-6} M, [acetate] = 3.6×10^{-2} M, pH 4.6. ^b[Eu(III)] = 1.0×10^{-2} M, [ligand] = 1.0×10^{-2} M, pH 5.5. ^cCalculated using eqn. (3); ^dcalculated using eqn. (4).

sumably, eqn. (3) for Cm(III). The residual hydration number of Cm(III) is consistently larger than that of Eu(III) for the same complex, despite the similar thermodynamic parameters of complexation for both the complexes [24]. To clarify the differences in $n_{\text{H}_2\text{O}}$ between the Cm(III) and Eu(III) complexes, the [ligand]/[Cm(III)] ratio and dependences on pH of the hydration state in the Cm(III)-polyaminopolycarboxylate complexes were then studied.

The decay constants k_{obs} of the Cm(III) complexes were measured by varying the [ligand]/[Cm(III)] ratio R at pH 4.6 using acetate buffer. Figure 2 shows the results of hydration number calculated from k_{obs} vs. R . The hydration numbers for R were almost independent of R , except for the Cm + NTA complex. This is consistent with formation of the 1:1 complex with HEDTA, EDTA, CDTA, DTPA and TTHA under these conditions, which agreed with speciation calculations using stability constants [25]. In the case of NTA complexation, the speciation calculation was con-

sistent with a decrease in net hydration number as the formation of Cm(NTA)₂ increased.

The dependence on pH of the hydration of Cm(III) in the presence of these ligands was studied over the pH range 1–13 in 0.1 M NaClO₄ solution without buffer. The results are shown in Fig. 3 and are similar to the pH dependence of the hydration of the Eu(III) and Tb(III) complexes [21, 22]. There are three buffer regions: the first is at low pH in which the hydration number of the cations is equivalent to that of the free ions; a second is in the pH range 4–8 in which the hydration number is that of the metal ion in the 1:1 complex; the third is at high pH (*ca.* 9–12) associated with the formation of ternary hydroxo complexes. This pattern is not followed by the NTA system. The speciation calculation shows that a first plateau at pH 2.5–5.0 is caused by the formation of a Cm(NTA) complex and that a second plateau at pH 7.5–11.5 is due to the formation of Cm(NTA)₂ and Cm(OH)₂⁺ complexes.

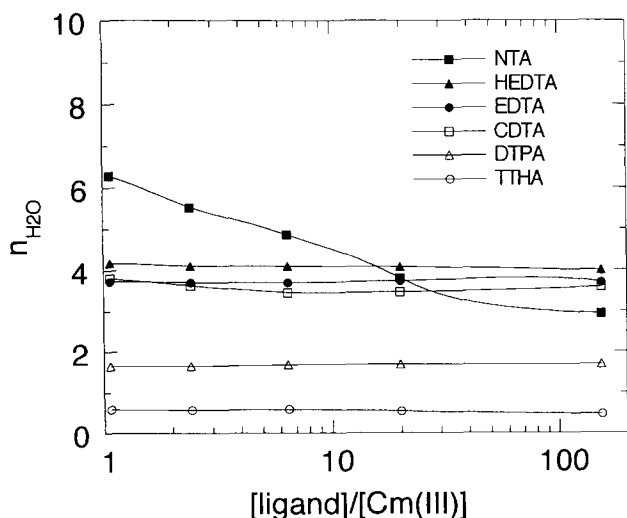


Fig. 2. Dependence on the [ligand]/[Cm(III)] ratio of the hydration state in Cm(III) complexes of polyaminopolycarboxylate ligands; [Cm(III)] = 5.3×10^{-6} M, [acetate] = 3.6×10^{-2} M, pH 4.6.

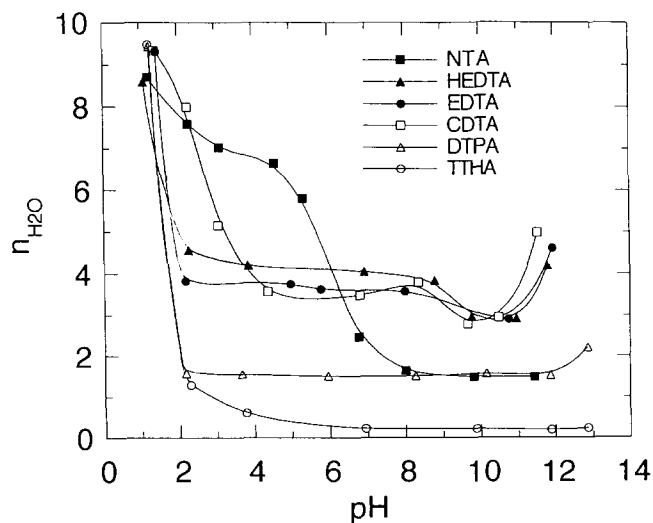


Fig. 3. Dependence on pH of the hydration state in Cm(III) complexes of polyaminopolycarboxylate ligands; $I = 0.1$ M NaClO₄, [Cm(III)] = 7.3×10^{-6} M, [ligand] = 8.0×10^{-6} M.

In all these systems, the total coordination number, *i.e.* the sum of the number of ligand donor groups and the number of primary water molecules, was 8.8 ± 0.5 for Eu(III) and 8.5 ± 0.5 for Tb(III) complexes [21–23], where $n(\text{NTA})=4$, $n(\text{HEDTA})=5.5$, $n(\text{EDTA})=n(\text{CDTA})=6$, $n(\text{DTPA})=7.5$ and $n(\text{TTHA})=8.5$ [26] were used as the numbers of the ligand donor groups. If the value for the Cm(NTA) complex is omitted, the total coordination number of the Cm(III) complexes is calculated to be 9.3 ± 0.4 , which is consistent with the value 9.2 ± 0.5 in H_2O .

In summary, our results indicate that the total coordination number of Cm(III) is possibly 0.5 larger than that of Eu(III) in polyaminopolycarboxylate complexes.

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