Journal of Alloys and Compounds, 213/214 (1994) 333–340
JALCOM 4095

A study of the carbonate complexation of Cm^{III} and Eu^{III} by time-resolved laser fluorescence spectroscopy

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Abstract

Carbonate complexation of Cm^{III} and Eu^{III} is studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). The carbonato species $M(CO_3)^+$, $M(CO_3)_2^-$ and $M(CO_3)_3^{3-}$ ($M = Cm^{III}$ and Eu^{III}) are characterized by measuring excitation and emission spectra, and lifetime. Stability constants for the first carbonato complex in 0.1 M $NaClO_4$ are found to be $\log \beta_{11} = 6.65 \pm 0.07$ for $Cm(CO_3)^+$ and $\log \beta_{11} = 6.57 \pm 0.08$ for $Eu(CO_3)^+$. The constant for Cm^{III} compares well with the values for Am^{III} derived spectroscopically and by solubility measurement. No difference is found for the stability constant of $Eu(CO_3)^+$ in the excited state as determined by TRLFS and in the ground state as determined by solubility measurement.

1. Introduction

Carbonate complexation is one of the most important geochemical reactions of actinides in any natural groundwater. For the trivalent actinides, thermodynamic data for carbonate complexation in aqueous solution are available only for Am^{III}; these have been determined by solvent extraction [1–3], solubility measurement [4–8] and spectroscopic methods [7–9]. The spectroscopic methods offer the advantage that the species in thermodynamic equilibrium are characterized directly. The limited sensitivity of UV-absorption spectroscopy allows only the first carbonato complex $Am(CO_3)^+$ to be studied [7–9], whereas laser-induced photoacoustic spectroscopy (detection limit of 7×10^{-9} mol/l for the Am^{3+} aquo ion [10]) allows the stability constant for $Am(CO_3)_2^-$ [7,8] to be determined. The high sensitivity of time-resolved laser fluorescence spectroscopy (TRLFS) for the detection of Cm^{III} (detection limit 5×10^{-12} mol/l for the Cm^{3+} aquo ion [11]) allows the study of carbonate complexation in the nanomole range far below the solubility limit. This method has been applied to study Cm^{III} hydrolysis [12] and its complexation with fulvic and humic acid [13–17], and for the speciation of Cm^{III} in groundwaters [18,19].

Although the luminescence of Eu^{III} has been studied extensively and is being applied in various areas, such as biochemistry [20], little work has been devoted to the study of complexation in aqueous solutions [20], e.g. the complexation with humic/fulvic acid [21,22]. The chemical properties of the excited actinide or lanthanide ion may be different from the ground state properties. As the lifetime of the excited state is in the range of some tenths of milliseconds or longer, the excited state will reach thermodynamic equilibrium [23]. It was claimed that the excited Gd^{3+} ion is coordinated by six water molecules, whereas in the ground state the coordination number is 8 or 9 [24]. If there were really a significant change in chemical properties from the excited state to the ground state, this would devalue the TRLFS method for the determination of thermodynamic data. Therefore, comparison of stability constants derived by TRLFS with data obtained by other methods is an important aspect.

In this paper, we present the fluorescence spectroscopic characteristics of the carbonato complexes $M(CO_3)^+$, $M(CO_3)_2^-$ and $M(CO_3)_3^{3-}$ for $M = Cm^{III}$ and Eu^{III}. Based on this information, the stability constants of the monocarbonato complexes are determined. The results are compared to literature data on Am^{III} and Eu^{III}.

2. Experimental details

A stock solution of ^{244}Cm in 0.01 M $HClO_4$ with an initial concentration of 6.07×10^{-6} mol/l and a solution of 6×10^{-2} mol/l Eu^{III}, prepared by dissolving Eu_2O_3 in 0.1 M $HClO_4$, were used for the experiments. The 10% contamination of the Cm^{III} solution with ^{241}Am, found by spectrophotometry and α-spectrometry [12], did not influence the TRLFS measurement, because

0925-8388/94/$07.00
SSDI 0925-8388(94)04095-L

the Am^{III} fluorescence was easily filtered out by wavelength and time discrimination. The experimental solutions were prepared by dilution of the stock solutions with 1 M $NaClO_4$, adjusting the ionic strength to 0.1 M. The pH was adjusted with 0.1 M $HClO_4$ or 0.1 M NaOH and measured by a combination glass electrode (Type Ross, model 8103 SC). Experiments under 100% CO_2 atmosphere were performed by bubbling CO_2 through the solution in a titration cell. Equilibrium at each pH was attained after 2–4 days. The concentration of Cm was assayed quantitatively by liquid scintillation counting (Beckman LS 6800) with corrections for Am activity. The Eu concentration was determined by ICP-AES (Plasma 40, Perkin Elmer).

The instrumentation used for TRLFS is described elsewhere [10]. It consists, briefly, of an excimer pumped dye laser (EMG 201 and FL2002, Lambda Physics) and an optical multichannel analyzer (polychromator: HR320, Jobin Yvon; intensified detector: IRY 700G, Spectroscopy Instr.). Using a 1200 mm^{-1} grating, a spectral range of 40 nm at a resolution of 0.2 nm was detected simultaneously. Time resolution down to 5 ns was achieved by a variable delay generator (DG535, Standford Research).

To record the excitation spectra of Cm^{III}, the total emission from 580 to 620 nm in the time window from 1 to 800 ms was detected. Emission spectra were obtained in the same time window exciting at 375 nm. Relaxation of the excited Cm^{III} was studied using the same excitation wavelength and integrating the emission in the range from 580 to 620 nm. In the same manner, appropriate parameters have been used to record the Eu^{III} fluorescence spectra.

3. Results and discussion

3.1. Spectroscopic characterization of Cm^{III} carbonato complexes

According to the energy level of the $5f^7$ configuration of Cm^{III} [25], the fluorescence emission is observed only from the lowest excited electronic state A ($^6D_{7/2}$) to the ground state Z ($^8S_{7/2}$). Due to the large energy gap between these states (16 920 cm^{-1} in Cm^{3+}:$LaCl_3$ [26]), the quantum yield for the radiative decay is much higher than for any other 5f-element. Both states involved in the transition will split by the crystal field of lower symmetry into four crystal field levels. Ground state splitting of several wavenumbers is not resolved in room temperature emission spectra, whereas the A-state splitting is higher than kT (304 cm^{-1} in Cm^{3+}:$LaCl_3$ [26]) and emission occurs from the lowest thermally populated crystal field states. The observed shift and splitting of the emission bands caused by change in coordination of the Cm^{III} ion, together with excitation spectra and lifetime, are the source of information used to quantify the chemical species of Cm^{III}.

The Cm^{III} species present in carbonate solution are spectroscopically characterized by their excitation and emission spectra as well as by their lifetimes. The characteristic spectroscopic properties of the Cm^{III} carbonate species are determined in the following three solutions: (a) 5.21×10^{-8} mol/l Cm^{III} at pH 6.19 in equilibrium with 100% CO_2 atmosphere, (b) 7.61×10^{-8} mol/l Cm^{III} in 0.1 M $NaHCO_3$ at pH 9.2 and (c) 1.60×10^{-9} mol/l Cm^{III} in 1 M Na_2CO_3 solution. The Cm^{3+} aquo ion was studied in 0.1 M $HClO_4$ at a concentration of 1.42×10^{-7} mol/l. Based on thermodynamic data derived below ($\log\beta_{11}=6.65$) and from the solubility experiment for Am^{III} carbonates ($\log\beta_{12}=9.60$ and $\log\beta_{13}=10.70$ [8]), the species distribution for Cm^{III} in these carbonate solution can be estimated. Under 100% CO_2 atmosphere at pH 6.2, 96.2% of $Cm(CO_3)^+$, 2.0% Cm^{3+} and 1.6% $Cm(CO_3)_2^-$ are to be expected. Under the same conditions, the influence of hydrolysis is negligible. In 0.1 M $NaHCO_3$ at pH 9.2, 81% $Cm(CO_3)_2^-$, 9.5% $Cm(CO_3)^+$, 9.5% $Cm(CO_3)_3^{3-}$ and less than 0.1 % $Cm(OH)_2$ are expected. The third carbonato complex is formed in solution with $I=0.1$ M in minor amounts only, while in 1 M Na_2CO_3, this complex should be the dominating species (>90%).

Excitation spectra of the Cm^{3+} aquo ion and of the carbonato complexes ranging from 370 to 405 nm are shown in Fig. 1. For the purpose of comparison, the

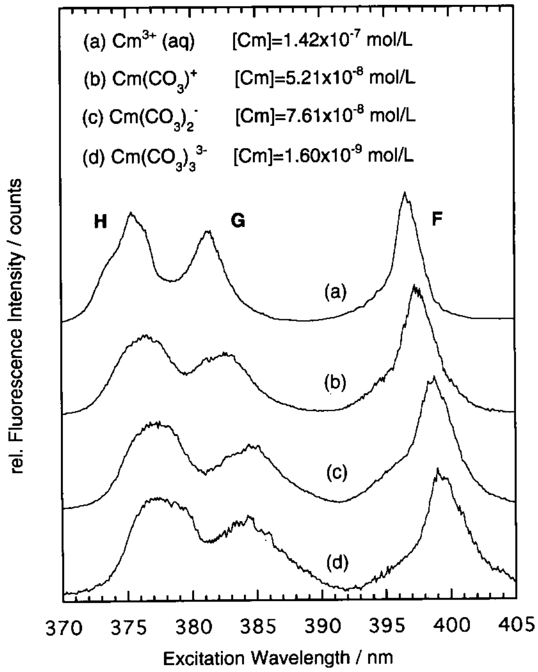

Fig. 1. Excitation spectra of the Cm^{3+} aquo ion and Cm^{III} carbonato complexes, normalized to the same peak intensity of the F band.

TABLE 1. Spectroscopic characteristics of the Cm^{3+} aquoion and Cm(III)-carbonatocomplexes

	Cm^{3+}_{aq}	$Cm(CO_3)^+$	$Cm(CO_3)_{2-}$	$Cm(CO_3)_3^{3-}$
Excitation (nm)				
Z→H	375.4 (2.5)[a]	376.5 (5.4)	377.5 (5.2)	377.5 (2.9)
Z→G	381.3 (2.3)	382.5 (6.0)	384.5 (5.7)	384.1 (3.0)
Z→F	396.5 (1.8)	397.5 (5.7)	398.9 (5.1)	399.9 (3.5)
Emission (nm)				
Z→H	593.8 (7.7)[a]	598 (10.0)	605.9 (8.6)	607.6 (9.1)
Lifetime (μs) in H_2O	65 ± 2	85 ± 4	105 ± 5	215 ± 6
in D_2O	1130 ± 15			605 ± 10
Rel. intensity[b]	1	1.57 ± 0.27	2.33 ± 0.15	7.51 ± 0.16

[a] Full width at half maximum (FWHM) in nm.

[b] Ratio of emission intensity relative to Cm^{3+} aquoion, excitation at peak maximum of the absorption band Z→H.

spectra are scaled to the same height. The spectral range covers the most intensive absorption bands of Cm^{III}, exciting the F state ($^6I_{17/2}$,$^6I_{11/2}$), the G state ($^6D_{9/2}$, $^6I_{13/2}$) and the H state ($^6I_{15/2}$) [26]. With stepwise coordination of CO_3^{2-}, the excitation bands show a bathochromic shift, which is pronounced for the F-band being shifted by about 1 nm for each CO_3^{2-} group added. The characteristic data of the excitation spectra of the Cm^{3+} aquo ion and the Cm^{III} carbonate species are listed in Table 1 together with other spectroscopic properties.

The observed relaxation of a given Cm^{III} species in the different carbonate solutions shows a monoexponential time dependence up to five times the lifetime τ, indicating that a single Cm^{III} species is predominant in each solution investigated. The lifetime of the Cm^{3+} aquo ion ($\tau = 65 \pm 2$ μs) is increased to $\tau = 85 \pm 4$ μs in $Cm(CO_3)^+$, to $\tau = 105 \pm 5$ μs in $Cm(CO_3)_2^-$ and in 1 M Na_2CO_3, a value of $\tau = 215 \pm 6$ μs is found. The latter value can be compared to the lifetime $\tau = 160$ μs determined by Beitz [25] in 1 M Na_2CO_3 and to $\tau = 240$ μs by Decambox *et al.* [27] in 3 M Na_2CO_3. The increase in lifetime upon complexation reflects the stepwise exclusion of water molecules from the metal ion coordination sphere. In 1 M Na_2CO_3 dissolved in deuterium oxide (99% D_2O), the lifetime is found to be $\tau = 605 \pm 10$ μs, compared to 1130 ± 15 μs for the Cm^{3+} aquo ion in 0.1 M DCl. The number of coordinated water molecules obtained from these data using the method of Horrocks [28] is found to be 1.7 ± 0.5 in $Cm(CO_3)_3^{3-}$. This result compares well with the estimate by Beitz of 2.5–2.8 based on the same method [25] and is in accordance with the coordination of Cm^{III} by three bidentate carbonate groups. In parallel with the lifetime, the fluorescence emission intensity is increased. Normalized to the intensity of the Cm^{3+} aquo ion, the values found are 1.57 ± 0.27 in $Cm(CO_3)^+$, 2.33 ± 0.15 in $Cm(CO_3)_2^-$ and 7.51 ± 0.16 in $Cm(CO_3)_3^{3-}$. These values correspond to the excitation at the peak maximum of the H band. The relative increase in fluorescence intensity of all carbonato complexes is higher than the corresponding increase in the lifetime of the fluorescence emission. This not only indicates a change in quantum yield but also in absorptivity of the species at the excitation wavelength.

Figure 2 shows the emission spectra of the Cm^{3+} aquo ion and the carbonato complexes, using excitation at 375 nm, in the range from 580 to 618 nm. The spectrum of $Cm(CO_3)^+$ is derived by peak deconvolution of mixed spectra in the pH range from 4.26 to 6.19 under 100% CO_2 atmosphere. The emission maximum shifts from 593.8 nm of the Cm^{3+} aquo ion to 598.0, 605.9 and 607.6 nm of $Cm(CO_3)^+$, $Cm(CO_3)_2^-$ and

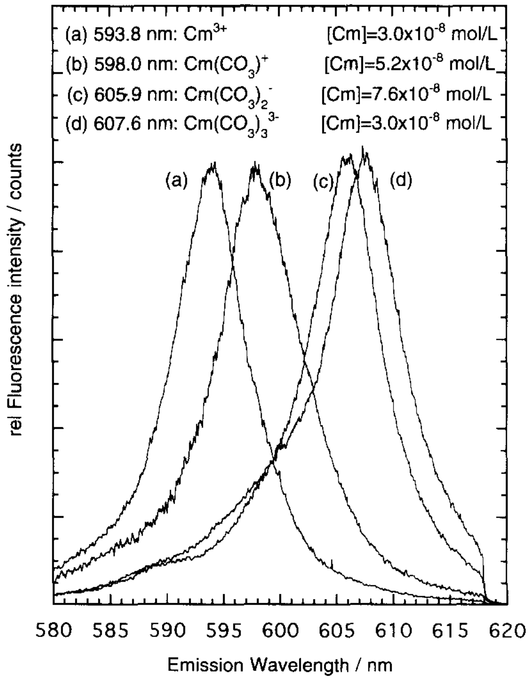

Fig. 2. Emission spectra of the Cm^{3+} aquo ion and Cm^{III} carbonato complexes, normalized to the same peak intensity.

$Cm(CO_3)_3^{3-}$, respectively. The FWHMs determined for these four species are 7.7, 10.0, 8.6 and 9.1 nm, respectively. In 1 M Na_2CO_3, Beitz [25] reports a peak maximum at 607.1 nm with a FWHM of 9.7 nm; Moulin *et al.* [27] found a peak maximum in 3 M Na_2CO_3 solution at 608 nm. The emission spectrum of $Cm(CO_3)_{2-}$ shows a weak shoulder at 595 nm, whereas in 1 M Na_2CO_3, shoulders are observed at 590 and 595.5 nm, which are due to thermally populated excited crystal field states of the $^6D_{7/2}$ [11].

3.2. Cm^{III} carbonate complexation

The quantification of the Cm^{III} species present at various CO_3^{2-} concentrations is based on the peak deconvolution of the emission spectra. Figure 3 shows the emission spectra of Cm^{III} in 0.1 M $NaClO_4$ under 100% CO_2 in the pH range from 4.26 to 5.89. The Cm concentration varies between 1.01×10^{-7} and 5.44×10^{-8} mol/l. With increasing pH, the emission band of the Cm^{3+} aquo ion ($\lambda_{max}=593.8$ nm), which is predominant at pH 4.26, will decrease and a new peak with a maximum at 598.0 nm will appear. This peak is assigned to the $Cm(CO_3)^+$ ion. The spectrum of the $Cm(CO_3)^+$ ion shown in Fig. 2 is deduced from the composed emission spectra by peak deconvolution. The presence of small amounts of $Cm(OH)^{2+}$ is corrected numerically taking into account the first hydrolysis constant $\beta_{11}=6.67\pm0.18$ [12]. The deconvolution of the emission spectra is demonstrated in Fig. 4 for the spectrum of the pH 5.40 solution. As is apparent from the small residues, fitting appears satisfactory; the derived error is 2% related to the total peak area.

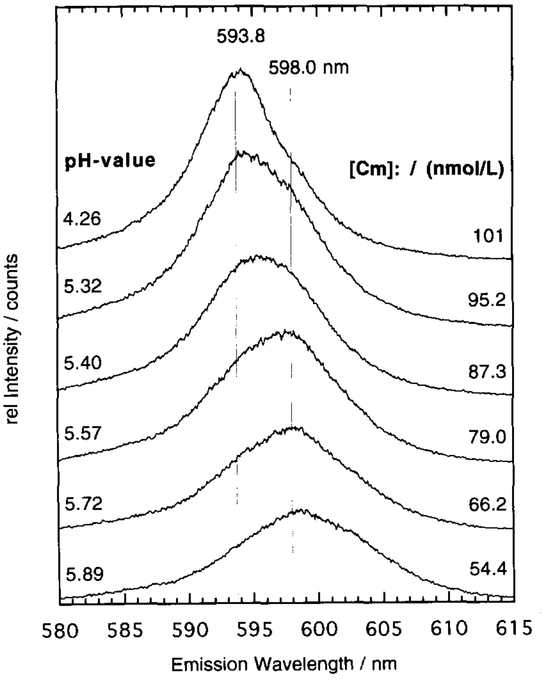

Fig. 3. Emission spectra of Cm^{III} in carbonate solutions under 100% CO_2 atmosphere in the pH range from 4 to 6.

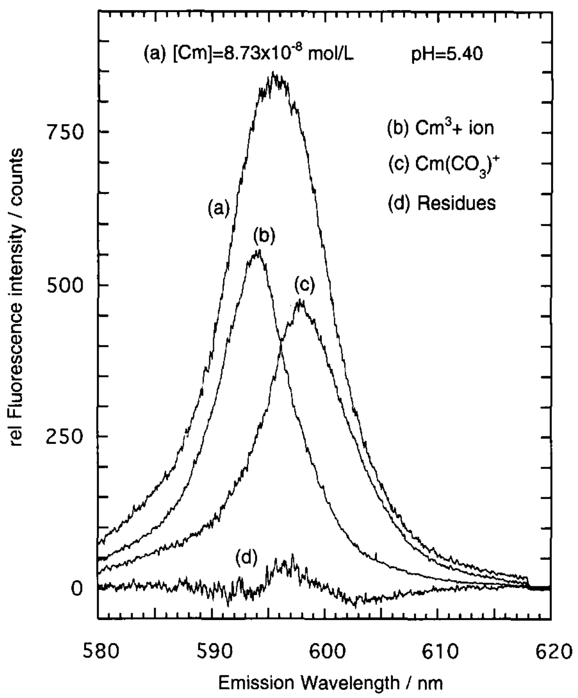

Fig. 4. Peak deconvolution of emission spectrum of Cm^{III} under 100% CO_2 atmosphere at pH 5.4. The original spectrum (a) is decomposed into the components of the Cm^{3+}aquo ion (b) and $CmCO_3^+$ (c). The residue is shown in (d).

The quantification of the spectroscopic results allows the formation constant to be determined for the monocarbonato complex:

$$\log\frac{[Cm(CO_3)^+]}{[Cm^{+3}]}=\log\beta_{11}+\log[CO_3^{2-}] \qquad (1)$$

The ratios $[Cm(CO_3)^+]/[Cm^{3+}]$ are derived by peak deconvolution taking into account the different quantum efficiencies of the Cm^{3+} and $Cm(CO_3)^+$ species. Absolute concentrations of the Cm species are calculated from the mole fraction given by spectroscopic quantification and the total Cm concentration determined by liquid scintillation counting. According to the carbonate equilibria

$$CO_2(g) \overset{K_H}{\longleftrightarrow} CO_2(aq) \overset{K_1'}{\longleftrightarrow} H^+ + HCO_3^- \overset{K_2}{\longleftrightarrow} 2H^+ + CO_3^{2-} \qquad (2)$$

the CO_3^{2-} concentration is related to the CO_2 partial pressure and the pH value by

$$\log[CO_3^{2-}]=\log(K_HK_1'K_2)+\log p_{CO_2}+2pH \qquad (3)$$

with the previously determined constant $\log(K_HK_1'K_2)=-17.62\pm0.07$ [7].

The analysed data and the spectroscopically derived species concentrations are listed in Table 2. According to eqn. (1), the correlation of the Cm species ratio as

TABLE 2. Carbonate complexation of Cm(III) in 0.1 M $NaClO_4$ under 100% CO_2 atmosphere: analyzed data and values calculated from peak deconvolution of emission spectra and first stability constant β_{11}

pH	$[Cm]_{tot}$ (nmol l^{-1})	$[CO_3^{2-}]$ (mol l^{-1})	$[Cm^{3+}]$ (nmol l^{-1})	$[Cm(CO_3)^+]$ (nmol l^{-1})	log β_{11}
5.32	95.2	1.05×10^{-7}	65.3	29.9	6.64
5.34	60.6	1.15×10^{-7}	38.1	22.5	6.71
5.40	87.3	1.51×10^{-7}	50.3	37.0	6.71
5.57	79.0	3.31×10^{-7}	28.4	50.6	6.69
5.72	66.2	6.61×10^{-7}	17.4	48.8	6.63
5.89	54.4	1.45×10^{-6}	9.32	45.1	6.53

a function of $[CO_3^{2-}]$ is expected to give a slope of 1 on a logarithmic scale. In Fig. 5, the experimental data are shown together with the analog data for the Eu carbonate complexation. The data for Cm follow a linear relationship with a slope of 0.97 ± 0.07 which is in accordance with eqn. (1). Excluding the possibility of polynuclear species $Cm_x(CO_3)_y^{3x-y}$, which are unlikely to exist at these low concentrations, the assumed formation of a monocarbonato complex of Cm^{III} is justified. The stability constants β_{11}, derived by eqn. (1), are listed in Table 2. The average of the logarithmic values is $\log\beta_{11}=6.65\pm0.07$ for $Cm(CO_3)^+$. No data on the carbonate complexation of Cm^{III} are available in the literature which could be used for direct comparison. A comparison with stability constants of Am^{III} and Eu^{III} is given below.

3.3. *Eu^{III} carbonate complexation*

By analogy with the Cm^{III} complexation study, the Eu^{III} carbonato complexes are spectroscopically characterized in different carbonate media. The $Eu(CO_3)^+$ complex is studied under 100% CO_2 atmosphere at pH 6.24. Under these conditions, the CO_3^{2-} concentration is calculated to be 7.24×10^{-6} mol/l. According to the first stability constant derived from the solubility experiment [30], it is calculated that 96% of Eu^{III} will be present in this solution as a monocarbonato complex and 4% as a dicarbonato complex. Solutions of Eu in 0.1 M $NaHCO_3$ at pH 9.2 and in 1 M Na_2CO_3 contain predominantly the species $Eu(CO_3)_2^-$ and $Eu(CO_3)_3^{3-}$ [30]. The spectroscopic characteristics of the carbonato complexes as well as of the Eu^{3+} aquo ion in 0.1 M $HClO_4$ are summarized in Table 3.

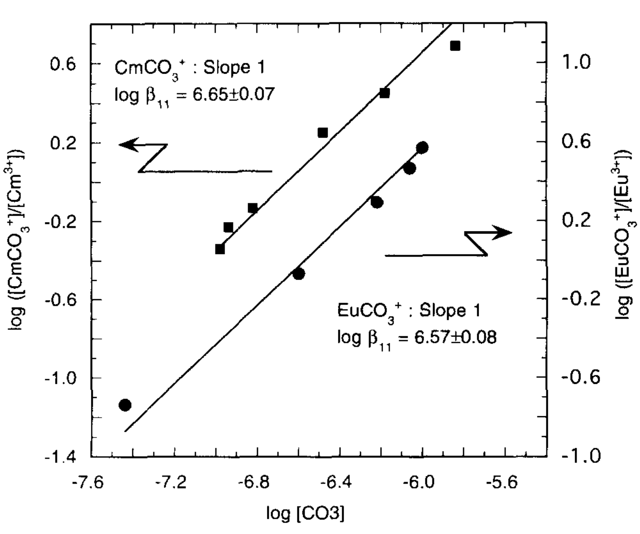

Fig. 5. Correlation of $\log([MCO_3^+]/[M^{3+}])$ as determined by TRLFS with $\log[CO_3^{2-}]$ according to eqn. (1) for M = Cm^{III} and Eu^{III}.

The excitation spectra of the most intensive transition $^7F_0\rightarrow{}^5L_6$ ($\lambda_{max}=393.4$ nm, $\epsilon=2.77$ l/(mol cm) for the Eu^{3+} aquo ion [20]) for the different Eu^{III} species are shown in Fig. 6. The maximum of the excitation band is shifted on complexation with carbonate from 393.5 nm to 394.3 nm in $Eu(CO_3)^+$. In addition, the peak is broadened and satellites on the red side appear at 398 and 400 nm. Upon further complexation, only a small shift of the peak maximum and changes in position and intensity of the satellites are observed. The lifetime of the transition $^5D_0\rightarrow{}^7F$ increases from $\tau=110\pm4$ μs of the Eu^{3+} aquo ion in 0.1 M $HClO_4$ to $\tau=170\pm10$ μs in $Eu(CO_3)^+$, to $\tau=230\pm15$ μs in $Eu(CO_3)_2^-$ and to $\tau=385\pm20$ μs in $Eu(CO_3)_3^{3-}$. Thus, for Eu^{III}, the same trend is observed as in Cm^{III}, indicating the substitution of water molecules in the inner coordination sphere by bidentate carbonate ligands.

Emission spectra of the Eu^{3+} aquo ion and the carbonato species in the range from 535 to 745 nm are shown in Fig. 7. In this spectral range, the dominating transitions $^5D_0\rightarrow{}^7F_J$ ($J=0$–4) are observed [29]. Compared with Cm^{III}, the shift of the emission bands upon complexation is rather small (see Table 3), while the change in intensity of the hypersensitive $^5D_0\rightarrow{}^7F_2$ transition is much more pronounced. The latter transition has highest intensity in the complexed species, whereas in the Eu^{3+} aquo ion, the magnetically allowed transition $^5D_0\rightarrow{}^7F_1$ is the most intensive. The branching ratios of the $^5D_0\rightarrow{}^7F_J$ ($J=0$–4) transition are listed in Table 3 together with the emission intensity relative to the Eu^{3+} aquo ion.

For the quantification of the formation of the monocarbonato complex, the emission spectra of Eu^{III} in

TABLE 3. Spectroscopic characteistics of the Eu^{3+} aquoion and Eu(III)-carbonatocomplexes

	$Eu^{3+}{}_{aq}$	$Eu(CO_3)^+$	$Eu(CO_3)_2{}^-$	$Eu(CO_3)_3{}^{3-}$
Excitation (nm)				
$^7F_0 \rightarrow {}^5L_6$	393.5 (1.53)[a]	394.3 (2.3)	394.7 (3.2)	394.9 (3.7)
Emission (nm)[b]				
$^5D_0 \rightarrow {}^7F_0$	–	578.5 (4.9)	579.6 (1.4)	–
$^5D_0 \rightarrow {}^7F_1$	591.5 (41.6)	592.0 (18.2)	592.4 (10.3)	592.1 (9.1)
$^5D_0 \rightarrow {}^7F_2$	616.6 (26.9)	616.9 (56.6)	617.2 (74.6)	615.3 (81.8)
$^5D_0 \rightarrow {}^7F_3$	652 (3.2)	651 (3.9)	649.9 (4.0)	650.6 (3.2)
$^5D_0 \rightarrow {}^7F_4$	696.7 (28.3)	694 (16.4)	693.2 (9.7)	692.5 (5.9)
Lifetime (μs)	110 ± 4	170 ± 10	230 ± 15	385 ± 20
Rel. intensity[c]	1.00	2.35	12.7	19.1

[a] Full width at half maximum (FWHM) in nm.

[b] In brackets, branching ratio in per centage of the total emission intensity, not corrected for detector sensitivity.

[c] Ratio of emission intensity relative to the Eu^{3+} aquoion, excitation at peak maximum of the absorption band $^7F_0 \rightarrow {}^5L_6$.

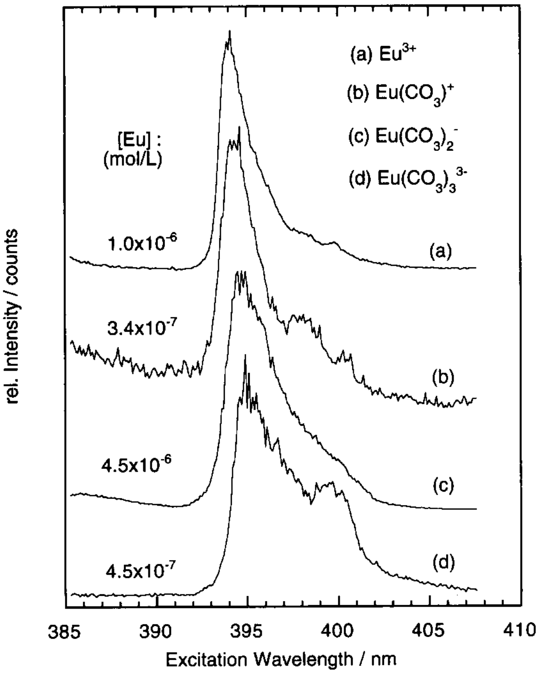

Fig. 6. Excitation spectra of the Eu^{3+} aquo ion and Eu^{III} carbonato complexes, scaled to the same peak intensity.

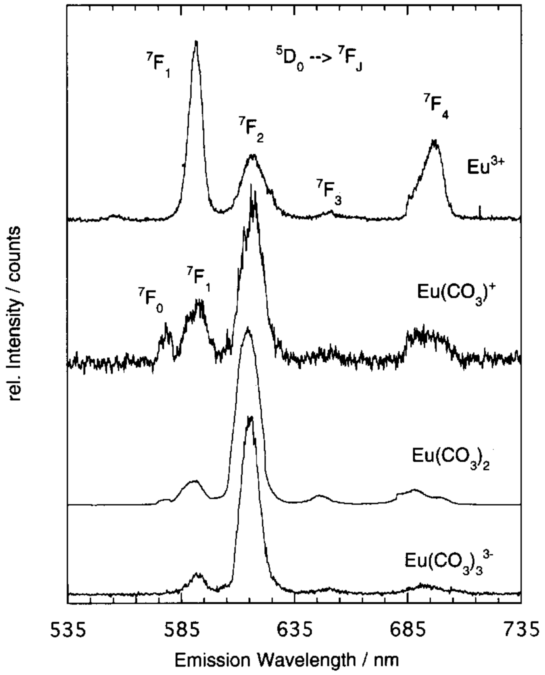

Fig. 7. Emission spectra of the Eu^{3+} aquo ion and Eu^{III} carbonato complexes

0.1 M $NaClO_4$ under 100% CO_2 atmosphere are determined between pH 5.08 and 5.81, using 394.0 nm for excitation. As the position and the shape of the emission bands are influenced only insignificantly by complexation, the quantification of the Eu^{III} species is based on changes in the intensities of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. This restricts the applicability of the spectroscopic study on systems with no more than two different Eu^{III} species present in the solution.

The results of peak analysis together with the analyzed data of the studied solutions are listed in Table 4. As in the case of $CmCO_3{}^+$, a linear correlation is found between the ratios $[Eu(CO_3)^+]/[Eu^{3+}]$ and $[CO_3{}^{2-}]$ on a logarithmic scale with a slope near to 1 (see Fig. 5). By averaging the calculated $\log \beta_{11}$ values for each single experiment, a mean value for the stability constant is found: $\log \beta_{11} = 6.57 \pm 0.08$ for $Eu(CO_3)^+$ This value is nearly identical to the stability constant derived from solubility measurements which were performed under the same conditions in parallel to the TRLFS study, i.e. $\log \beta_{11} = 6.51 \pm 0.21$ [30].

3.4. Discussion of thermodynamic results

In Table 5, the present results are compared with the corresponding constants of Am^{III} and Eu^{III} in the

TABLE 4. Carbonate complexation of Eu(III) in 0.1 M $NaClO_4$ under 100 CO_2 % atmosphere: analyzed data and calculated values from peak deconvolution of emission spectra and first stability constant β_{11}

$[Eu]_{tot}$ (mol l^{-1})	pH	$[CO_3^{2-}]$ (mol l^{-1})	$[Eu^{3+}]$ (mol l^{-1})	$[Eu(CO_3)^+]$ (mol l^{-1})	log β_{11}
2.02×10^{-5}	5.09	3.63×10^{-8}	1.71×10^{-5}	3.14×10^{-6}	6.71
1.16×10^{-6}	5.51	2.51×10^{-7}	6.25×10^{-7}	5.35×10^{-7}	6.53
7.97×10^{-7}	5.70	6.03×10^{-7}	2.68×10^{-7}	5.29×10^{-7}	6.52
5.59×10^{-7}	5.78	8.71×10^{-7}	1.42×10^{-7}	4.18×10^{-7}	6.53
4.28×10^{-7}	5.81	1.00×10^{-6}	9.04×10^{-8}	3.38×10^{-7}	6.57

TABLE 5. Comparison of stability constant β_{11} of the carbonato complexes $M(CO_3)^+$ for Cm(III), Am(III) and Eu(III)

Element	Method	Conditiofns	log β_{11}	Reference
Cm	TRLFS	0.1 M $NaClO_4$, RT	6.65 ± 0.07	this work
Am	Extr.	1.0 M $NaClO_4$, 25 °C	5.81 ± 0.04	2
Am	UV	0.1 M $NaClO_4$, 25 °C	6.69 ± 0.15	9
Am	Sol.	0.1 M $NaClO_4$, 1% CO_2, 25 °C	5.97 ± 0.15	7
Am	UV	0.1 M $NaClO_4$, 1% CO_2, 25 °C	6.48 ± 0.03	7
Am	Sol.	0.1 M $NaClO_4$, 100% CO_2, 25 °C	6.32 ± 0.10	8
Am	UV	0.1 M $NaClO_4$, 100% CO_2, 25 °C	6.33 ± 0.06	8
Eu	TRLFS	0.1 M $NaClO_4$, RT	6.57 ± 0.08	this work
Eu	Sol.	0.1 M $NaClO_4$, 25 °C	6.51 ± 0.21	30
Eu	Extr.	1.0 M $NaClO_4$, 25 °C	5.93 ± 0.05	2
Eu	Extr.	1.0 M $NaClO_4$, 25 °C	5.88 ± 0.05	31
Eu	Extr.	0.68 M $NaClO_4$, 25 °C	5.86	32
Eu	Sol.	$I=0$, 25 °C	7.11	33

Extr., solvent extraction; Sol., solubility; TRLFS, time resolved laser fluorescence spectroscopy; UV, absorption spectroscopy.

literature. The β_{11} values of Am^{III} determined in 0.1 M $NaClO_4$ [7–9] corroborate well the value of Cm^{III}, except for the value $\log\beta_{11}=5.97\pm0.15$ [7] which is subject to re-examination. The value of Am^{III} $\log\beta_{11}=5.81\pm0.04$ [2] determined in 1.0 M $NaClO_4$ appears substantially lower than the values in 0.1 M $NaClO_4$. This difference is certainly ascribed to the effect of ionic strength. The quantification of this effect is being examined spectroscopically in our laboratory. As for Eu^{III}, the TRLFS value agrees quite well with the value determined by the solubility experiment [30] at the same ionic strength. The literature values determined either in 0.68 M [32] or 1.0 M $NaClO_4$ [2, 31] are in good agreement with one another, but distinctively lower than the present value in 0.1 M $NaClO_4$, probably because of the ionic strength effect as is observed in the case of Cm^{III}. The $\log\beta_{11}=7.11$ value at $I=0$ [33] is larger than the present value, possibly also due to the effect of ionic strength. The good agreement observed between the constants of β_{11} from the TRLFS and solubility experiments infers that the thermodynamic properties of the electronic excited and ground states of the 4f or 5f elements do not show any differences, particularly for the carbonate complexation, as opposed to the claim made for hydration [24].

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