A complexation study of Cm(III) and Tb(III) with chelating aromatic ligands by time-resolved laser fluorescence spectroscopy

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Abstract

Complexation of Tb(III) and Cm(III) with 5-sulfo-salicylic acid (SSA) is studied by time-resolved laser fluorescence spectroscopy (TRLFS). The chelating aromatic ligand is supposed to represent a dominating complexing entity of humic substances for the interaction with metal ions. The free ligand concentration is varied by changing the total ligand concentration or pH. By peak deconvolution of emission spectra the pure spectral components of complex species are analyzed and their mole fraction in the mixture are ascertained. The stability constants derived are: $\log \beta_{101}(\text{Cm}) = 6.44 \pm 0.03$, $\log \beta_{102}(\text{Cm}) = 11.99 \pm 0.04$, $\log \beta_{101}(\text{Tb}) = 7.32 \pm 0.04$, $\log \beta_{102}(\text{Tb}) = 12.85 \pm 0.05$. © 1998 Elsevier Science S.A.

1. Introduction

In recent years much effort has been made to describe the complexation behavior of trivalent actinide ions with humic acids [1–3]. The complexation behaviour of Cm(III) with organic ligands [4], which are considered as representative complexing functional groups of humic substances [5,6], are studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). Excitation and emission spectra, lifetime and energy transfer from a ligand to the complexed Cm(III) are compared for humic and fulvic acids with model ligands like 5-sulfosalicylic and phthalic acid [6]. This study shows that chelating complexes with *o*-hydroxo-benzoate (salicylate) are found to contain similar spectroscopic features as complexes with humic substances. This is in accordance with earlier results on complexes of copper with humic acid derived by EPR [7].

A study of model complexes provides information that can be applied to less known complexation systems with humic acids. Because of its analytical importance the complex formation of 5-sulfosalicylate with trivalent lanthanides as well as Am(III) and Pu(III) has been studied by various experimental methods [8–11]. However, no study of Cm(III) is available in the literature. In this paper the complexation of 5-sulfosalicylate with Cm(III) and Tb(III) by TRLFS is presented. This method provides a selective fluorescence measurement of metal ion species discriminating background of organic ligand by wavelength selection and time-gating and is highly sensitive to work at trace concentrations [12,13]. The determination of stability constants is made by quantification of different metal ion species through peak deconvolution of emission spectra under parameter variation.

2. Experimental

[244]Cm (half-life: 18.1 a) used for the present investigation is purified from the daughter nuclide [240]Pu by anion exchange (Dowex 1×4) in 7 M HNO$_3$. The remaining 10% contamination with [241]Am does not influence the Cm(III) fluorescence measurement because of low fluorescence yield of Am(III) and its very short lifetime in the ns-range. The Cm(III) concentration is assayed by liquid scintillation counting (Beckmann LS 6800). Samples for the spectroscopic investigation are prepared under 100% Ar atmosphere in a glove box to avoid carbonate contamination. pH is adjusted by addition of NaOH or HClO$_4$. Complexation of Cm(III) is studied with 5-sulfosalicylic acid concentrations of 0.05 and 0.10 M in the pH-range 6.20–6.55, while the Cm(III)-concentration is kept con-

stant at about 9×10^{-8} mol l^{-1}. For the complexation of Tb(III), concentrations of Tb(III) and 5-sulfosalicylic acid are kept constant at 10^{-5} mol/l and 0.1 M, respectively, while changing pH from 1.1 to 9.0.

The time-resolved laser fluorescence spectroscopy consists of an excimer (XeCl, 308 nm) pumped dye laser system (Lambda Physik, EMG 201E and LPD 3002), a polychromator (HR 320, Jobin Yvon), and an optical multichannel analyzer (OSMA IRY 700 GR) as a fluorescence detector. Using a 1200 mm^{-1} grating, the emission spectra are detected simultaneously within a spectral range of 41 nm at the spectral resolution of 0.2 nm. Further details of the TRLFS instrumentation are given elsewhere [12].

3. Results and discussion

3.1. Complexation of Cm(III) with 5-sulfosalicylic acid

A detailed spectroscopic characterization of Cm(III) salicylate complexes by their excitation and emission spectra and their lifetimes is presented in the previous paper [6]. The Cm(III) is excited at the absorption maximum of the H-band at 375.4 nm, the fluorescence emission is detected in the wavelength range 580–620 nm.

In Fig. 1 the emission spectra of Cm(III) at various ligand concentrations and pH are shown in comparison to the emission of the Cm^{3+} aquo ion (in 0.1 M $HClO_4$) The emission maximum of Cm^{3+}aq at 593.8 nm is shifted to 597.8 nm in 5×10^{-2} mol l^{-1} of SSA at pH 6.2. The shoulder observed at 603.5 nm evolves to another peak on further addition of ligand or increase of pH. By peak deconvolution of emission spectra, spectral components of each Cm(III) species are derived. It is found that besides Cm^{3+}aq two Cm(III) complexes with 5-sulfosalicylic acid corresponding to 1:1 and 1:2 complexes are formed, which are denoted by Cm(SSA) and $Cm(SSA)_2^{3-}$. The contribution of hydrolyzed species, namely $Cm(OH)^{2+}$ at pH < 6.58, to the emission spectrum cannot be derived by peak deconvolution, because of spectral overlap, and is calculated from the known emission spectrum and thermodynamic data (log $\beta_{101} = 6.67 \pm 0.18$) determined in the previous study [14].

As a typical example, the peak deconvolution of Cm(III) spectra in 0.1 M 5-sulfosalicylic acid at pH 6.20 is shown in Fig. 2 together with the spectral contributions of individual components: Cm^{3+}aq, Cm(SSA) and $Cm(SSA)_2^{3-}$ and $Cm(OH)^{2+}$. Under these conditions, the mixed emission spectrum is dominated by the first three Cm(III) species: 15.9% Cm^{3+}aq, 55.6% Cm(SSA) and 27.0% $Cm(SSA)_2^{3-}$. The hydrolyzed species appears to be negligible at pH 6.2. The residual part reflects only the noise and gives no indication for the presence of another spectral component.

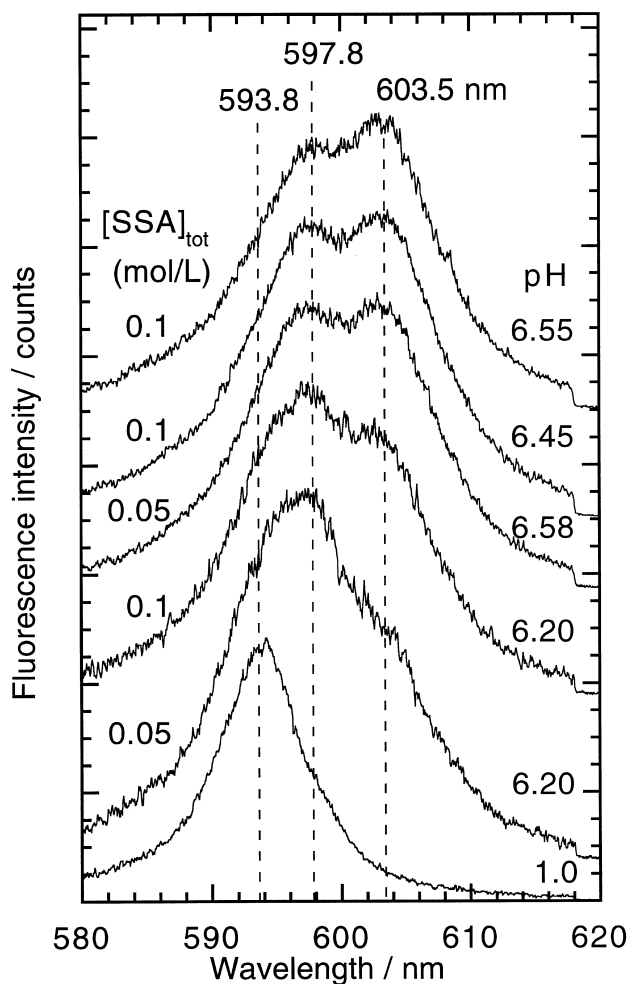The total fluorescence intensity integrated over the peak

Fig. 1. Emission spectra of Cm(III) in 5-salicylate solution (0.05 and 0.1 M Na_2HSSA) at various pH and in 0.1 M $HClO_4$. Spectra are normalized to same area and baseline shifted.

area is considerably increased for the 1:1 complex ($FI = 1.65 \pm 0.05$) and the 1:2 complex ($FI = 2.85 \pm 0.1$) as compared to Cm^{3+}aq. This effect is caused by the energy transfer from the photo-excited ligand to Cm(III) [6]. Using these factors, the mole fractions of Cm(III) species are calculated from the individual peak areas as derived by multivariant analysis. The concentration ratios [Cm(SSA)]/[Cm^{3+}aq] and [$Cm(SSA)_23^{-}$]/[Cm(SSA)] are given together with analytical data in Table 1.

The complexation is described by the following general reaction:

$$p M^{3+} + n H_q SSA^{q-3} \rightleftharpoons M_p(H_q SSA)_n^{3p-(3-q)n}, \qquad (1)$$

where the concentration of the complexing salicylate anion is related to the reaction:

$$H_3 SSA \rightleftharpoons (3 - q)H^+ + H_q SSA^{q-3} \qquad (2)$$

The proton dissociation constants of 5-sulfosalicylic acid are $pK_{a2} = 2.32 \pm 0.02$ for the carboxylic group and $pK_{a3} =$

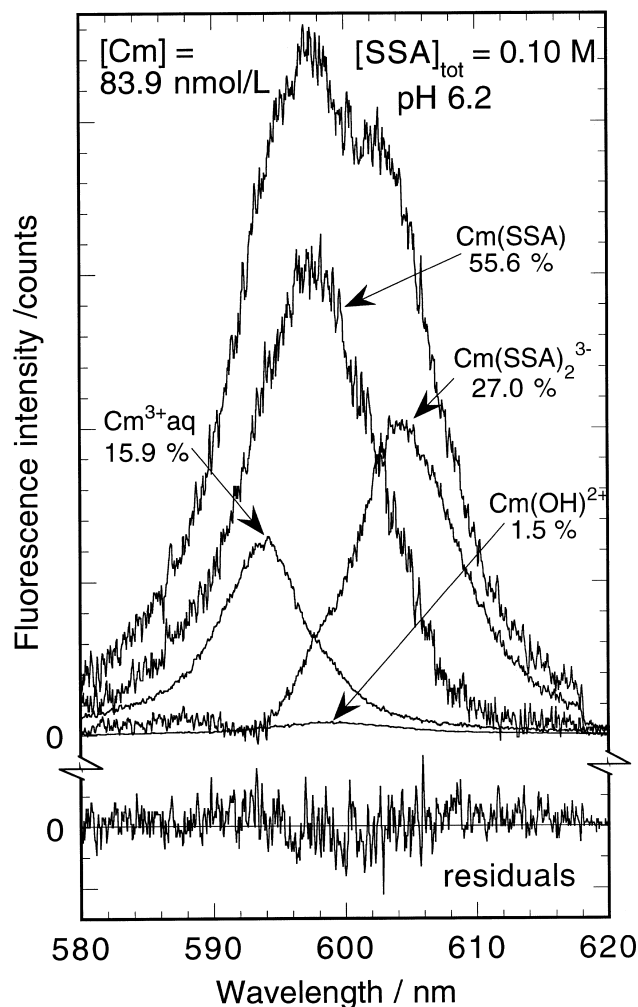Fig. 2. Peak deconvolution of Cm(III) emission spectrum in 0.1 M Na$_2$HSSA at pH 6.20 by spectra of individual species Cm^{3+}aq, Cm(OH)$^{2+}$, Cm(SSA) and Cm(SSA)$_2^{3-}$. The contribution of the pure species to the total emission intensity fractions is given in %. The Cm(OH)$^{2+}$ contribution is calculated from thermodynamic data (see text).

11.3±0.02 for the phenolic group [9]. In the pH range under study the sulfonic group is dissociated completely ($pK_{a1} = 1.52$ [15]) and the phenolic group is mostly protonated. Thus, the total ligand concentration corresponds to [HSSA^{2-}] and the concentration of [SSA^{3-}] is given by [SSA^{3-}] = Ka$_3$ [HSSA^{2-}]/[H$^+$] neglecting trace amounts of ligand complexed to Cm(III).
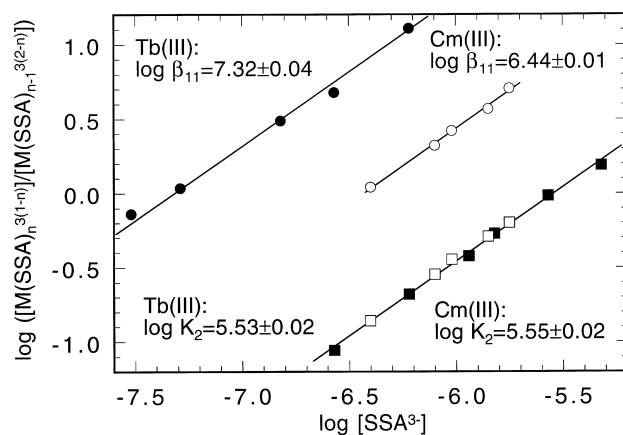

Fig. 3. Linear regression of concentration ratios [M(SSA)]/[M^{3+}] (circles) and [M(SSA)$_2^{3-}$]/[M(SSA)] (square dots) against free ligand concentration [SSA^{3-}] on a double logarithmic scale. Open symbols: M = Cm(III); closed symbols: M = Tb(III). The slope of the fitted regression line is fixed to 1.0.

Complexation constants β_{10n} for the formation of mononuclear chelate complexes ($p = 1$, $q = 0$ and $n = 1, 2$) are defined by:

$$\beta_{10n} = \frac{[M(SSA)_n^{3(1-n)}]}{[M^{3+}][SSA^{3-}]^n} \quad (3)$$

Rearranging into a linear correlation:

$$\log \frac{[M(SSA)_n^{3(1-n)}]}{[M^{3+}]} = \log \beta_{10n} + n\log[SSA^{3-}] \quad (4)$$

Alternatively, a stepwise stability constant $K_{102} = \beta_{102}/\beta_{101}$ may be defined by the following relation:

$$\log \frac{[M(SSA)_2^{3-}]}{[M(SSA)]} = \log K_{102} + \log[SSA^{3-}] \quad (5)$$

The ratios [Cm(SSA)]/[Cm^{3+}aq] and [Cm(SSA)$_2$3$^-$]/ [Cm(SSA)] determined experimentally are plotted in Fig. 3 as a function of the free ligand concentration [SSA^{3-}] on a double logarithmic scale. The data fit well to a slope of 1 according to Eqs. (4) and (5) and thus the postulated complexes are validated. The stability constants are given in Table 1 for each measured point. The average values are found to be:

Table 1
Analytical data, concentration ratios of Cm(III) species determined by spectroscopy and stability constants for the complexation of Cm with 5-sulfosalicylic acid.

pH	[SSA]$_t$ (mol/l)	log[SSA^{3-}] (mol/l)	[Cm(SSA)]/ [Cm^{3+}]	[Cm(SSA)$_2$]/ [Cm(SSA)]	log β_{101}	log K_{102}	log β_{102}
6.20	0.05	−6.40	1.10	0.14	6.44	5.55	11.99
6.20	0.1	−6.10	2.10	0.28	6.42	5.55	11.97
6.58	0.05	−6.02	2.58	0.36	6.43	5.58	12.01
6.45	0.1	−5.85	3.71	0.51	6.42	5.56	11.98
6.55	0.1	−5.75	5.11	0.63	6.46	5.55	12.01

$\log \beta_{101} = 6.44 \pm 0.03$,

$\log K_{102} = 5.55 \pm 0.04$,

$\log \beta_{102} = 11.99 \pm 0.07$.

It should be noted that the stability constant derived at ionic strength 0.15 and 0.30 (0.05 and 0.1 M Na$_2$HSSA, respectively) are identical within the error limit. From the extended Debye-Hückel theory

$$\log \beta(I) = \log \beta^0 - \Delta z^2 \frac{a\sqrt{I}}{1 + b\sqrt{I}} \qquad (6)$$

using $a = 0.509$ and $b = 1.5$ [16], it is expected that log β_{101} should be higher about 0.51 log units at 0.15 than at 0.30 ionic strength. As $\Delta z^2 = 0$ for the stepwise formation of Cm(SSA)$_2^{3-}$, no ionic strength effect on K_{102} is to be expected. These results indicate that the extended Debye-Hückel theory overestimates the influence of ionic strength on activity coefficient of the largely extended organic ligand.

3.2. Complexation of Tb(III) with 5-sulfosalicylic acid

The interaction of Tb(III) with 5-sulfosalicylic acid was studied recently by TRLFS [17,18]. The effect of complexation increases the emission intensity of Tb(III), which is ascribed to the energy transfer from a photo-excited ligand to Tb(III). Exciting at 250 nm in 10^{-4} M 5-sulfosalicylic acid at pH 6.5 at which absorptivity of ligand is strongly increased and that of Tb(III) is decreased compared to exciting at 368.9 nm, the emission intensity is higher by a factor of 1100 than in the absence of salicylate [18]. A detection limit of 8.8×10^{-12} mol/l Tb(III) under these conditions was found [18]. For the complexation study Tb(III), is excited at the peak maximum (368.9 nm) of the transition $^7F_6 \rightarrow {}^5L_{10}$, the emissions from $^5D_4$ to $^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ are detected in the wavelength region from 450 to 650 nm.

Emission spectra of the strongest transition $^5D_4 \rightarrow {}^7F_5$ are shown in Fig. 4 at selected pH between 4.8 and 9.0 in 0.1 M sulfosalicylic acid. The emission maximum of Tb^{3+}aq at 543.8 nm is red-shifted to 545.0 nm above pH 3. At higher pH the intensity of this peak is decreased and two other emission maxima at 541.9 and 547.5 nm build up. Peak deconvolution of emission spectra is performed in a similar way as described for Cm(III). Again, two complexes with 5-sulfosalicylic acid are derived. The emission spectra of the individual species Tb^{3+}aq, Tb(SSA) and Tb(SSA)$_2^{3-}$ are shown in Fig. 5. The calculated species concentrations are given in Table 2 and the intensity ratios according to Eqs. (4) and (5) are plotted in Fig. 3 together with the corresponding data for Cm(III). Again, the slopes of the regression line are close to 1, proving the stoichiometry of the postulated species. The average stability constants are:
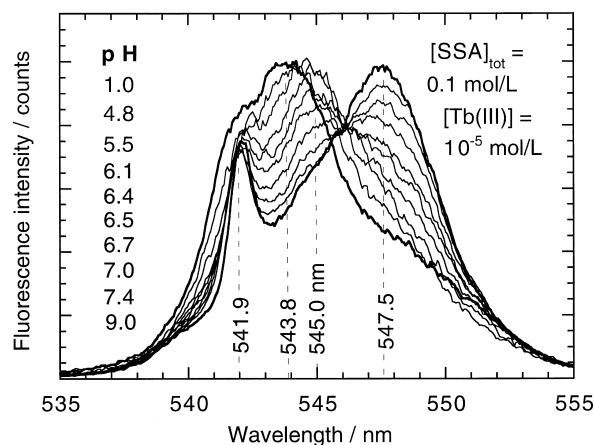

Fig. 4. Emission spectra of 10^{-5} mol/l Tb(III) in 5-salicylate solution (0.1 M Na$_2$HSSA) at various pH and in 0.1 M HClO$_4$. Spectra are normalized to same area.

$\log \beta_{101} = 7.32 \pm 0.04$,

$\log K_{102} = 5.53 \pm 0.02$,

$\log \beta_{102} = 12.85 \pm 0.05$.

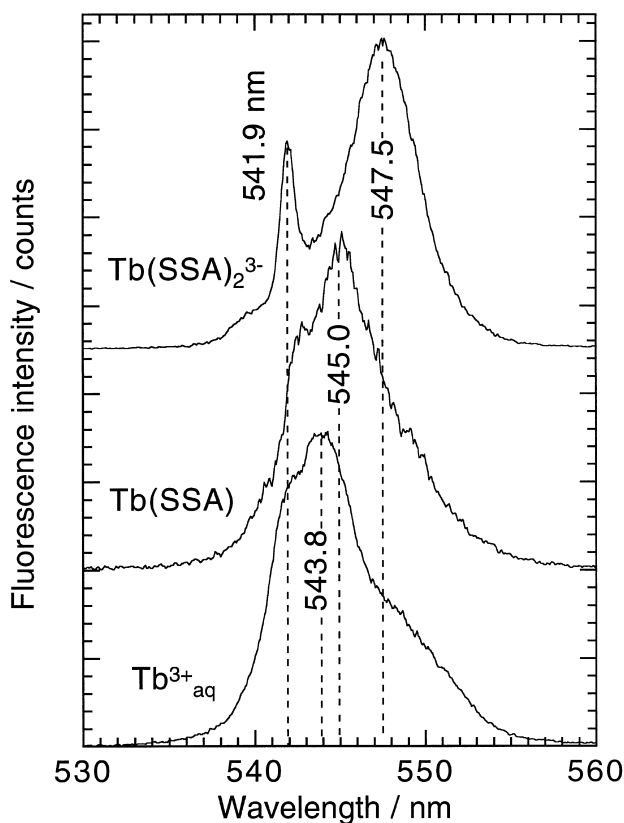The first stability constant is nearly 1 order of magnitude larger for Tb(III) than for Cm(III). The stepwise constant

Fig. 5. Emission spectra of individual species Tb^{3+}aq, Tb(SSA) and Tb(SSA)$_2^{3-}$.

Table 2
Analytical data, concentration ratios of Tb(III) species determined by spectroscopy and stability constants for the complexation of Tb with 5-sulfosalicylic acid

pH	$\log [SSA^{3-}]$ (mol/l)	$[Tb(SSA)]/$ $[Tb^{3+}]$	$[Tb(SSA)_2]/$ $[Tb(SSA)]$	$\log \beta_{101}$	$\log K_{102}$
4.78	−7.52	0.73	–	7.38	–
5.01	−7.29	1.09	–	7.33	–
5.48	−6.82	3.08	–	7.31	–
5.73	−6.57	4.79	0.09	7.25	5.51
6.08	−6.22	12.8	0.21	7.33	5.54
6.36	−5.94	–	0.38	–	5.52
6.48	−5.82	–	0.54	–	5.55
6.73	−5.57	–	0.96	–	5.55
6.98	−5.32	–	1.55	–	5.51

of the second complex, however, is almost identical to that of Cm(III).

For Tb(III) at 0.1 M ionic strength Kanekar et al. found $\log \beta_{101} = 8.42$ and $\log K_{102} = 6.19$ [8], and in 1 M NaClO$_4$ Cassol et al. derived $\log \beta_{101} = 6.95 \pm 0.03$ and $\log K_{102} = 5.91 \pm 0.05$ [9]. Using Bjerrum-Calvin pH-titration, Dubey et al. give a value of $\log \beta_{101} = 7.80$ in 0.1 M KNO$_3$ [10]. The only values known for trivalent actinides are $\beta_{101} = 8.57 \pm 0.15$, $\beta_{102} = 17.51 \pm 0.09$ for Pu(III) and $\beta_{101} = 8.06 \pm 0.02$, $\beta_{102} = 15.34 \pm 0.02$ for Am(III) in 1 M NaClO$_4$ by Nair and Chander [11]. The $\log \beta_{101}$ value we found for Tb(III) falls in the range of the values given for lanthanides by Kanekar et al. and by Cassol et al. which differ by about 1 order of magnitude. The difference may be due to different ionic strength used by the authors. The second stability constant of Tb(III) is about 0.5 log units lower than literature data [8,9]. Extrapolating the data for Pu(III) and Am(III) [11] as a function of the reciprocal ionic radius we would expect for Cm(III) a value of $\log \beta_{101} = 8.0$, which is much larger than $\log \beta_{101} = 6.44 \pm 0.03$

derived by TRLFS. Also, the values derived for $\log K_{102}$ by these authors ($\log K_{102}(Pu) = 8.94$ and $\log K_{102}(Am) = 7.28$) are much larger than we found for Cm ($\log K_{102} = 5.53 \pm 0.05$) and also for comparable data on lanthanide ions. Both $\log \beta_{101}$ and $\log \beta_{102}$ for Cm(III) fits nicely to the values of Sm(III) complexes ($\log \beta_{101} = 6.77 \pm 0.04$ and $\log K_{102} = 5.79 \pm 0.06$) given by Casoll et al. [9], which have about the same ionic radii.

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