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Stabilities of the Aqueous Complexes $\text{Cm}(\text{CO}_3)_3^{3-}$ and $\text{Am}(\text{CO}_3)_3^{3-}$ in the Temperature Range 10-70°C

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ABSTRACT

The carbonate complexation of curium(III) in aqueous solutions with high ionic strength was investigated below solubility limits in the temperature range 10-70°C by TRLFS. The equilibrium constant, K_3 , for Reaction $\text{Cm}(\text{CO}_3)_2^- + \text{CO}_3^{2-} \rightleftharpoons \text{Cm}(\text{CO}_3)_3^{3-}$ was determined: $\log K_3 = 2.01 \pm 0.05$ at 25°C, $I = 3 \text{ M}$ (NaClO_4), and compared to scattered previously published values. $\log K_3$ for Cm(III) was found to increase linearly with $1/T$ reflecting negligible temperature influence on the corresponding molar enthalpy change $\Delta_r H_3 = 12.2 \pm 4.4 \text{ kJ mol}^{-1}$, and molar entropy change $\Delta_r S_3 = 79 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$. These values were extrapolated to $I = 0$ with the SIT formula: $\Delta_r H_3^\circ = 9.4 \pm 4.8 \text{ kJ mol}^{-1}$, $\Delta_r S_3^\circ = 48 \pm 23 \text{ J mol}^{-1} \text{ K}^{-1}$, $\log K_3^\circ = 0.88 \pm 0.05$ at 25°C. Virtually the same values were obtained from solubility data for the analogous Am(III), which were re-interpreted considering the transformation of the solubility-controlling solid. The studied reaction was found to be driven by the entropy. This was interpreted as a result of hydration changes. As expected, excess energy changes of the reaction showed a greater influence of ionic strength on $\Delta_r S_3$ than on $\Delta_r H_3$.

KEYWORDS: curium, americium, carbonate, equilibrium constant, temperature, thermodynamics, TRLFS.

1. Introduction

Safety assessments of possible underground repositories for high-level radioactive wastes require the prediction of the radiotoxicity induced by the release of radionuclides into natural aquifers.¹ The migration of radionuclides would be limited by their solubilities and interactions on inorganic materials, *i.e.* sorption, in the environment. Conversely aqueous complexation can increase their migration. Tremendous efforts have been made to acquire the data needed for modelling the aqueous speciation of the relevant radionuclides as typically actinides (An) and lanthanides (Ln). For equilibrated deep groundwaters, this modelling is based on the corresponding thermodynamic data: Gibbs energies of reaction, $\Delta_r G$, or equivalently equilibrium constants for given temperature and pressure. Due to their important roles in underground waters for f-block element ions, redox reactions, hydrolysis and complexation reactions with carbonate have focused major attention.² Several f-block elements are stable at the +3 oxidation state as typically the radioelements Am and Cm, as well as radionuclides of lanthanides, some of which being important fission products. Furthermore, it cannot be excluded that aqueous Pu(IV) could be reduced to Pu(III) in chemical conditions of deep groundwaters. We typically calculated the aqueous speciation at 25°C in interstitial waters of clayey materials for the Callovo-Oxfordian formation, which is being studied as a possible disposal site for high-level radioactive wastes in France. According to the standard $\text{Pu}^{4+}/\text{Pu}^{3+}$ redox potential and formation constants selected by the Nuclear Energy Agency (NEA),³ Pu(III) would predominate in the reducing conditions of the groundwater⁴ ($E = -181 \text{ mV/SHE}$) at pH 7.3 and $I = 0.09 \text{ M}$ in the forms Pu^{3+} (32%), PuOH^{2+} (28%), $\text{Pu}(\text{OH})_2^+$ (21%) and PuCO_3^+ (19%).

Thermochemical databases have been constructed from experimental data on An(III), and may also rely on analogies between Pu, Am and Cm,^{3,5,6} as well as with Ln(III) for the missing

thermodynamic data.^{7,8} However, a lack of measurements for the temperature influence on aqueous speciation has been pointed out. In the early stage of the disposal the radioactive decays can increase the temperature in the vicinity of the waste packages. Even though the storage should be designed to limit this temperature increase to about 90°C, it is still useful to investigate the effects of temperature on the behaviors of An(III) and Ln(III) in carbonated aqueous solutions. Since the solubility of M³⁺ f-block element ions in such chemical systems at room temperature is usually lower than 10⁻⁴ M down to less than 10⁻⁸ M, formation constants of aqueous complexes were often derived from solubility measurements.^{5, 9-15} At room temperature it might be difficult to achieve equilibrium conditions within reasonable time, and a metastable solid phase of poor crystallinity might control the solubility. The determination of thermodynamic data for aqueous species equilibrated with metastable solid phases should still be relevant, even though scattering of data, as observed for the stability of the limiting carbonate complex Am(CO₃)₃³⁻,^{5,15} may result from the difficulty in interpreting solubility measurements. At temperatures higher than room temperature, the thermodynamic interpretations of experimental results were found to be complicated by crystallinity changes and other transformations of the solid phase, as observed for Np(V)^{3,16,17} and Am(III) carbonate compounds.^{5,12,18} Since there are very few published data about the temperature influence on M³⁺ carbonate complexes, it seems reasonable to re-examine the available solubility data, typically the single solubility study of Am(III) at elevated temperatures,¹² trying several possible interpretations. Other studies about the temperature influence on the formation of M³⁺ carbonate complexes have been performed under chemical conditions that allowed to work below solubility limits. Cantrell *et al.* studied the carbonate complexation of Eu(III) by solvent extraction method at pH < 7 and controlled CO₂(g).¹⁹ From the slight increase of the stability constants in a quite restricted temperature range (15 to 35°C), the formations of EuCO₃⁺, Eu(CO₃)₂⁻ and EuHCO₃²⁺ were found to be endothermic,

and $\Delta_r H$ values were determined at 0.68 mol kg^{-1} ionic strength. Wruck *et al.* studied the formation of AmCO_3^+ between 25 and 75°C using pulsed laser photoacoustic spectroscopy.²⁰ The authors proposed an estimation of the enthalpy of reaction at 0.1 mol kg^{-1} , on the basis of determinations at two temperatures, 25 and 50°C . These results were fairly consistent with the $\Delta_r H$ value for analogous EuCO_3^+ , but not selected in the recent thermochemical database (TDB) of the OECD NEA (Organization for Economic Co-operation and Development, Nuclear Energy Agency), due to insufficient experimental details in the paper; the authors of the NEA-TDB argued that the series of spectra at elevated temperatures did not exhibit isobestic points as was expected.¹⁵

Calorimetry is widely used for measuring enthalpy changes of reactions. Unfortunately, it is not sensitive enough for most of the carbonate complexes of Ln(III) and An(III) since they are formed in chemical conditions where their solubilities are too low. Alternatively, $\Delta_r H$ can be deduced from the dependency of the corresponding equilibrium constant, K , with temperature on the basis of the van't Hoff isochore, *i.e.* from the slope of $\log K$ vs. $1/T$ plot.²¹ It has been applied to carbonate systems.^{19,20} As any slope analysis, it is less accurate than direct measurements; on the other hand when the experimental determinations of K are associated with speciation measurements, this gives more confidence on the stoichiometry of the reaction(s) used to interpret the experiments, a key problem for the carbonate complexes of Ln(III) and An(III).²² Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) has recently been used to study the formation of carbonate complexes of the Eu^{3+} and Cm^{3+} ions at room temperature below their solubility limits.²³⁻²⁶ There has been increasing interest in the capabilities of TRLFS for probing complexes of fluorescing f-block element ions, namely Eu^{3+} , Cm^{3+} and UO_2^{2+} , outside the temperature range $20\text{-}25^\circ\text{C}$. Studies at high temperatures by TRLFS rather focused on

the dependency of fluorescence lifetimes with the temperature. Fluorescence properties of hydroxides,²⁷⁻³⁰ sulfate and fluoride complexes²⁸ of UO_2^{2+} were determined as well as for complexes of Eu^{3+} .³¹ On the basis of speciation predictions, the lifetime, τ , of each species was deduced, and the expected Arrhenius law was verified for the dependency of τ with the temperature, enabling an estimation of activation energies. In recent studies, stability constants has been determined by TRLFS at variable temperature,^{32,33} but to our knowledge no experiment has been carried out using this technique for carbonate complexation studies.

Many complexes of stoichiometries $\text{Am}(\text{CO}_3)_i(\text{OH})_j^{3-2i-j}$ had been proposed for M^{3+} f-block elements to interpret experimental observations in $\text{OH}^-/\text{CO}_3^{2-}/\text{HCO}_3^-$ aqueous solutions at room temperature. Robouch had first evidenced that the solubility of $\text{Am}_2(\text{CO}_3)_3(\text{s})$ at 25°C only depends on $[\text{CO}_3^{2-}]$ for variable pH, which indicated that only carbonate complexes of Am(III) are formed.¹⁰ Beside discrepancies between published formation constants for carbonate complexes,^{5,15} there is still a debate on the limiting carbonate complex: $\text{M}(\text{CO}_3)_3^{3-}$ and $\text{M}(\text{CO}_3)_4^{5-}$ stoichiometries have been proposed for An^{3+} and Ln^{3+} ions. We recently pointed out that the limiting complex is $\text{Eu}(\text{CO}_3)_3^{3-}$ in $\text{Na}^+/\text{CO}_3^{2-}$ aqueous solutions, while the $\text{M}(\text{CO}_3)_4^{5-}$ stoichiometry had been demonstrated for $\text{M}^{3+} = \text{Ce}^{3+}$, a large lanthanide ion, in the same $\text{Na}^+/\text{CO}_3^{2-}$ conditions, and for $\text{M}^{3+} = \text{Eu}^{3+}$ in chemical conditions where Na^+ was replaced with K^+ .²² These stoichiometries were essentially evidenced by classical slope analysis of solubility measurements, since the shapes of the solubility curves are clearly different for $\text{M}(\text{CO}_3)_3^{3-}$ and $\text{M}(\text{CO}_3)_4^{5-}$ predominant stoichiometries. By the same data treatment, the stoichiometry of the Am(III) limiting complex was also shown to be $\text{Am}(\text{CO}_3)_3^{3-}$ during solubility measurements in $\text{Na}^+/\text{CO}_3^{2-}$ aqueous solutions at room temperature,^{10,12,13} and this was qualitatively confirmed by spectrophotometry.¹⁰ For this reason, in $\text{Na}^+/\text{CO}_3^{2-}$ aqueous solutions, we expect the $\text{M}(\text{CO}_3)_3^{3-}$

stoichiometry for the limiting complexes of Ln^{3+} and An^{3+} ions at least smaller (or equivalently heavier) than Eu^{3+} and Am^{3+} . Consequently, the expected stoichiometry of the limiting carbonate complex for Cm^{3+} is $\text{Cm}(\text{CO}_3)_3^{3-}$ in such ionic conditions, although this stoichiometry disagrees with the interpretations of TRLFS data for NaCl solutions at 25°C that used a limiting complex of stoichiometry $\text{Cm}(\text{CO}_3)_4^{5-}$.^{23,24}

Aiming to decrease the scattering of the published values for the formation constant of $\text{Cm}(\text{CO}_3)_3^{3-}$ at 25°C, and to determine the corresponding $\Delta_r H$, we report in this paper the first determination of equilibrium constants for carbonate complexes of Cm(III) in the temperature range 10-70°C by using TRLFS. This study was focused on the formation of $\text{Cm}(\text{CO}_3)_3^{3-}$ in aqueous solutions mainly at high ionic strength, 3 M Na^+ , with CO_3^{2-} concentrations higher than 10^{-3} M. The choice of these conditions was motivated by (i) the possibility of studying solutions in which only two species, $\text{Cm}(\text{CO}_3)_2^-$ and $\text{Cm}(\text{CO}_3)_3^{3-}$, are formed, and thereby to avoid mixtures of too many species that might have altered the selectivity of the technique; (ii) the easier control of the carbonate speciation, particularly possible changes of P_{CO_2} when varying the temperature, which could modify the CO_3^{2-} concentration; (iii) the high fluorescence yield of $\text{Cm}(\text{CO}_3)_3^{3-}$ that was detected even at concentrations lower than 3×10^{-8} M. In order to compare with the dissociation of analogous $\text{Am}(\text{CO}_3)_3^{3-}$, and to choose between the scattered published values for its stability, we also re-interpreted solubility measurements of Am(III) in 4 M NaCl solutions between 20 and 70°C from data that only appeared in Giffaut's thesis.¹² The influence of temperature on equilibrium constants is finally discussed to evidence whether the stepwise formation reaction of the limiting carbonate complex is enthalpy or entropy driven, and compared with thermodynamic data for other systems.

2. Experimental section

2.1. Materials

Millipore de-ionized water (Alpha-Q, 18.2 M Ω cm) was used throughout the preparations. All the curium solutions were prepared by dilution of a ^{248}Cm solution in 0.1 M HNO_3 with a concentration of 4.54×10^{-6} M measured by inductively coupled plasma mass spectrometry. $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (>99.0%), and anhydrous Na_2CO_3 (>99.8%) were purchased from Merck (R.P. Normapur[®]), and NaHCO_3 (100.0%) from Sigma, and used without further purification. Specified gas mixtures were obtained from Messer (CO_2/Ar 100.0/0.0 and 10.0/90.0).

2.2. Preparation procedure

Small volumes of the ^{248}Cm stock solution were added to NaHCO_3 and Na_2CO_3 solutions, so that the Cm concentration ranged between 2.27×10^{-8} and 2.42×10^{-8} M, and was sufficiently low to prevent from precipitation. NaClO_4 salt was used to fix the Na^+ concentration at 3 M. In one of the bicarbonate solutions, pH was lowered by bubbling a 10 % CO_2 gas mixture that was first passed through a NaClO_4 solution with the same ionic strength (3 M) to saturate the gas with water. The CO_2 partial pressure was calculated the same way as in Spahiu's work: $^{34} P_{\text{CO}_2} = (P_{\text{T}} - P_{\text{H}_2\text{O}}) x_{\text{CO}_2}$, where P_{T} is the total pressure inside the glove-box where experiments were performed, $P_{\text{H}_2\text{O}}$ is the water vapour pressure at 23°C,³⁵ and $x_{\text{CO}_2} = 0.1$.

2.3. $[\text{H}^+]$ measurements and carbonate speciation

$[\text{H}^+]$ was measured inside the fluorescence cells using combined glass micro-electrodes (Radiometer Analytical, XC161). The KCl solutions in the reference compartments were replaced with a 2.99 or 0.09 M NaClO_4 + 0.01 M NaCl solution to avoid KClO_4 precipitation at the electrode liquid junction. Each electrode was calibrated at $(23 \pm 1)^\circ\text{C}$ with a 0.01 M HCl solution,

a 0.1 M NaHCO₃ solution equilibrated with 100% CO₂ gas, and an equimolar Na₂CO₃/NaHCO₃ solution, all containing appropriate amounts of NaClO₄ to keep [Na⁺] constant at 3 (-log[H⁺] = 2.00, 7.00 and 9.61, respectively) and 0.1 M (-log[H⁺] = 2.00, 6.63 and 9.90, respectively). The H⁺ concentrations in these standard solutions were calculated with the formula of the Specific ion Interaction Theory (SIT) using equilibrium constants and SIT parameters for the protonations of CO₃²⁻ from Ref. 3 (the SIT parameters are given at 25°C, but the temperature difference led to negligible corrections), and is given as Supporting Information (Table S1). The slope of the electrode was typically higher than 98% of the theoretical slope for each calibration. Measurements were performed using the modified electrode that had the same [Na⁺] as the solution in which -log[H⁺] was measured.

Potentiometric measurements were only performed at (23 ± 1)°C to avoid calibrations at different temperatures that could introduce systematic errors in -log[H⁺], and to limit the perturbation of the solutions, particularly CO₂(g) leakage when opening the cell. Since the working solutions were actually buffers, the numbers of moles of HCO₃⁻ and CO₃²⁻ did not vary with temperature, and this was used to calculate the corresponding concentrations at each temperature. So [HCO₃⁻] and [CO₃²⁻] were only corrected for volume variations using the thermal dilatation coefficients for NaCl solutions³⁶ (see Table S2 of the Supporting Information), which were assumed to be representative of the NaClO₄ solutions. These corrections were anyhow lower than 0.02 in log₁₀ unit on the concentration values.

2.4. Temperature cycles

The temperature of the solution in the fluorescence cell was controlled by circulating water through the cell support from a constant-temperature bath. For each temperature, the solution was equilibrated for at least 20 min, which was sufficient to reach stable temperature in every

conditions. For given temperatures of the circulating water, the actual temperatures of the solutions in the cell were estimated by measuring them in a curium-free solution. The uncertainty was estimated to be $\pm 0.5^\circ\text{C}$. After $-\log[\text{H}^+]$ was measured at 23°C , the solution underwent a temperature cycle: Typically it was first equilibrated at 25°C , then cooled down to 10°C , and heated to 37 , 50 and 70°C ; the cycle was ended after the solution was equilibrated again at 25°C to control that the fluorescence spectrum had not changed.

2.5. Time-resolved laser-induced fluorescence spectroscopy

The fluorescence was induced by a Nd-YAG Laser delivering a 6-mJ pulsed laser beam at 355 nm. The laser beam was driven to the quartz cell placed in a glove-box through two lenses that focused and shaped the beam with an optimized geometry. The emitted light was collected using a combination of mirrors and lenses in a spectrometer with a 600 mm^{-1} grating (Roper Scientific). Fluorescence was detected using a CCD camera cooled down to -18°C providing fluorescence spectra with a resolution of 0.2 nm. The fluorescence signal was increased by the use of two spherical mirrors in the cell support that reflected the laser and the fluorescence lights.

The fluorescence spectra were recorded with constant gate delay (10 μs) and gate width (600 μs) in order to collect the largest part of the fluorescence that was emitted by Cm(III). Fluorescence lifetimes were derived from the decay of the intensity measured by varying the gate delay for a constant gate width (50 μs). The decay curves were fitted with monoexponential functions so that average values of lifetimes were obtained. Uncertainties of 10 % were assigned to the fluorescence intensity on the basis of expected errors on the curium concentrations in relation to dilution and possible sorption of Cm(III) on the wall of the quartz cell, as already observed in similar experiments.²³ As the curium concentration was very low, even the removal of small amounts of Cm(III) from the bulk solution could be significant. Consequently, the cells

containing the solution were gently shaken just before they were placed in the cell support for better homogenization, except when the solution was equilibrated with CO₂(g).

2.6. Solubility measurements of Am(III)

Here are outlined experimental details described in Giffaut's thesis.¹² Am₂(CO₃)₃(s) was prepared under 1 atm CO₂(g) for 10 days at pH 7.2, and partially dissolved into Na⁺/HCO₃⁻/CO₃²⁻ solutions with 4 M NaCl. Radiolytic oxidation of Am(III) into Am(V) was first observed due to the high Cl⁻ concentration,³⁷ and Fe(s) powder was added to obtain reducing conditions. The solubility of Am(III) in a few Na⁺/HCO₃⁻/CO₃²⁻ solutions with 0.1 M NaCl, where no oxidation into Am(V) was expected, was not altered by the presence of Fe(s): Although iron hydroxide compounds may have formed, no indication of a co-precipitation with Am(III) was found. Thus, it was assumed that the Am(III) solubility was controlled by a solid phase of Am(III) in the 4 M NaCl solutions, with no significant effect of Fe compounds. The under-saturated batch solutions were heated at 70°C, which was the initial temperature of the cycle. The solubility was followed with time: The shape of the experimental solubility curves vs. [CO₃²⁻] evidenced a solid phase transformation, and slope analysis was consistent with the formation of NaAm(CO₃)₂(s) for [CO₃²⁻] > 0.01 M. Equilibration lasted 8 weeks to allow complete phase transformation at 70°C, and to achieve equilibrium conditions. The temperature was then varied from 70 down to 20°C by 10°C steps, and then back from 20 up to 70°C to ensure that equilibrium had been obtained in all the conditions. All the batches were continuously stirred. The temperature was controlled within ±1°C. Aliquots of solutions were taken out and filtered using 0.22-µm porosity filters, since it was verified that this pore size ensured efficient filtration. The ²⁴¹Am concentrations in the filtrates were measured by α-counting (LKB 1219) with a reproducibility better than 8 %. [H⁺] was measured using glass combined electrodes (Tacussel, XC111) with a 4 M NaCl

solutions in the compartment of the Ag/AgCl reference electrode. Calibration was performed at each temperature with three standard solutions at $I = 4$ M: 0.05 M $\text{Na}_2\text{CO}_3 + 0.05$ M $\text{NaHCO}_3 + 3.81$ M NaCl ; 0.025 M $\text{KH}_2\text{PO}_4 + 0.025$ M $\text{Na}_2\text{HPO}_4 + 3.905$ M NaCl ; 0.001 M $\text{HCl} + 4$ M NaCl . The pK_a of the buffers were estimated for the different temperatures and 4 M NaCl ionic medium.

3. Treatment of data

3.1. Fitting of the fluorescence measurements

The treatment of the spectroscopic data was based on decomposition of the measured fluorescence spectra into reference spectra corresponding to individual curium species. In this study, we focused on the dissociation of the limiting carbonate complex of Cm(III), $\text{Cm}(\text{CO}_3)_3^{3-}$. The most relevant equation is given here since the sensitivity analysis of our data towards speciation models showed that $\text{Cm}(\text{CO}_3)_3^{3-}$ likely dissociated into only $\text{Cm}(\text{CO}_3)_2^-$; it will be shown below that the dissociation of the limiting complex actually corresponds to the loss of one carbonate ion, without any OH^- or H^+ involved in the dissociation reaction. For a given wavelength λ , the corresponding equation for fitting experimental fluorescence measurements, $F_{\text{mes},\lambda}$, is

$$\frac{F_{\text{mes},\lambda}}{[\text{Cm}]_{\text{T}}} = \frac{F_{2,\lambda} + F_{3,\lambda} K_3 [\text{CO}_3^{2-}]}{1 + K_3 [\text{CO}_3^{2-}]} \quad (1)$$

The molar fluorescence intensities $F_{2,\lambda}$, and $F_{3,\lambda}$, correspond to the intensities at the wavelength λ , for solutions of pure $\text{Cm}(\text{CO}_3)_2^-$ and $\text{Cm}(\text{CO}_3)_3^{3-}$, respectively. For each temperature, the stepwise formation constant, K_3 , was fitted to the $F_{\text{mes},\lambda}$ data in the range of wavelengths, where fluorescence was detected, *i.e.* 580 to 630 nm. A range of acceptable $\log K_3$ values was

determined by examination of the standard deviation of the fit in order to assess the uncertainties of $\log K_3$: The uncertainties were taken as to cover this interval.

3.2. Thermodynamic data

The dissociation of the limiting carbonate complex of Cm(III) was described by the equilibrium



with the equilibrium constant

$$K_3 = \frac{[\text{Cm}(\text{CO}_3)_3^{3-}]}{[\text{Cm}(\text{CO}_3)_2^-][\text{CO}_3^{2-}]} \quad (3)$$

When the ionic strength was fixed (typically at 3 M), γ 's, the activity coefficients remained constant, and no correction was required; namely the three terms were constant in

$$\log K_3^\circ(\text{T}) = \log K_{3,\text{m}}(\text{T}) + \Delta_r \log \gamma_3(\text{T}) \quad (4)$$

where $^\circ$ denotes the reference state (zero ionic strength), the subscript m denotes the molality scale (mol kg^{-1}), and $K_{3,\text{m}}$ is related to K_3 through molal-to-molar conversion factors.¹⁵ For different ionic conditions, we used a simple SIT formula to calculate

$$\Delta_r \log \gamma_3(\text{T}) = -4\text{D}(\text{T}) + \Delta\epsilon_3(\text{T}) I_{\text{m}} \quad (5)$$

where $\text{D}(\text{T}) = \text{A}(\text{T}) I_{\text{m}}^{1/2} / (1 + a_j \text{B}(\text{T}) I_{\text{m}}^{1/2})$ is a Debye-Hückel term, I_{m} is the ionic strength (mol kg^{-1}), $\Delta\epsilon_3$ is the difference of empirical ion pair coefficients (kg mol^{-1}).³ $\text{D}(\text{T}^\circ)$, the value at the temperature 298.15 K, was calculated with the usual parameters $\text{A}(\text{T}^\circ) = 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $a_j \text{B}(\text{T}^\circ) = 1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ at 1 bar.³ For ionic strength corrections at temperatures different from 25°C, the parameters were calculated as follows: Second-order polynomial equations were fitted to tabulated values of $\text{A}(\text{T})$ and $\text{B}(\text{T})$.³ No temperature-dependency was assumed for a_j , which

was calculated as $a_j = 1.5/B(T^\circ) = 1.5/0.3284 = 4.568 \text{ \AA}$. The calculated values are reported in Table S3 of the Supporting Information. $\Delta\varepsilon_3(T^\circ) = -0.02 \pm 0.04 \text{ kg mol}^{-1}$ was calculated from the individual ε values for Am(III) at 25°C.⁵ The temperature influence on $\Delta\varepsilon_3$ is not known; however in theory, $\Delta\varepsilon(T) = \Delta\varepsilon(T^\circ) T^\circ/T$, since $\Delta\varepsilon(T) I_m$ is a second virial expansion term. This correction was less than $0.003 \text{ kg mol}^{-1}$ for $\Delta\varepsilon_3$ in the temperature range of 10-70°C, and was therefore neglected: For calculating $\Delta_r \log \gamma_3(T)$ we used the constant value $\Delta\varepsilon_3(T) = -0.02 \pm 0.04 \text{ kg mol}^{-1}$, *i.e.* only $D(T)$ varied with T in Eq.(5) for ionic strength corrections.

The enthalpy and heat capacity changes for Reaction (2) were deduced from the integration of the van't Hoff isochore.²¹ In Model A, the enthalpy variation $\Delta_r H_3$ was assumed to be temperature-independent:

$$\log K_3(T) = \log K_3(T^\circ) - \frac{\Delta_r H_3(T^\circ)}{r} \left(\frac{1}{T} - \frac{1}{T^\circ} \right) \quad (6)$$

where $r = R \ln 10 = 19.14487 \pm 0.00016 \text{ J K}^{-1} \text{ mol}^{-1}$, R is the molar gas constant. In Model B, the heat capacity change $\Delta_r C_{p3}$ was assumed to be constant:

$$\log K_3(T) = \log K_3(T^\circ) - \frac{\Delta_r H_3(T^\circ)}{r} \left(\frac{1}{T} - \frac{1}{T^\circ} \right) + \frac{\Delta_r C_{p3}}{r} \left(\frac{T^\circ}{T} - 1 + \ln \frac{T}{T^\circ} \right) \quad (7)$$

Note that in this case $\Delta_r H_3$ varies linearly with temperature, and $\left(\frac{T^\circ}{T} - 1 + \ln \frac{T}{T^\circ} \right) \approx \frac{1}{2} \left(\frac{T^\circ}{T} \right)^2$ so the last term is a second order term. Both models were tested on the experimental data.

The ionic strength influences on the thermodynamic functions $\Delta_r H_3$ and $\Delta_r S_3$ are the excess enthalpy change

$$\Delta_r H^{\text{ex}} = -rT^2 \left(\frac{\partial \Delta_r \log \gamma}{\partial T} \right)_P \quad (8)$$

and the excess entropy change

$$\Delta_r S^{\text{ex}} = -r(\Delta_r \log \gamma + T \left(\frac{\partial \Delta_r \log \gamma}{\partial T} \right)_P) \quad (9)$$

respectively,³⁷ which are also temperature (and pressure, P) dependent. Thus neglecting the temperature influence on $\Delta_r \log \gamma$ is equivalent to neglect $\Delta_r H^{\text{ex}}$, the ionic strength corrections on $\Delta_r H$, an usual approximation assuming only entropic ionic strength corrections on equilibrium constants.³ According to Eq.(5) and assuming that the temperature dependency of $\Delta \epsilon_3$ is negligible,

$$\left(\frac{\partial \Delta_r \log \gamma_3}{\partial T} \right)_P \approx -4 \left(\frac{\partial D(T)}{\partial T} \right)_P \quad (10)$$

which are calculated from Table S3 of the Supporting Information.

Table 1. Chemical conditions of the TRLFS measurements at 25°C.

Solution label	I_m / mol kg ⁻¹	$-\log[\text{H}^+]$	$\log[\text{CO}_3^{2-}]$	$\log[\text{HCO}_3^-]$	$\log P_{\text{CO}_2}$	$\tau^{(b)}$ / μs (N _{H2O})
b0	0.10	8.93	-2.07	-1.08	-2.38	98 (5.8)
B1	3.48	7.96	-2.71	-1.06	-1.02 ^(a)	
B2	3.52	8.57	-2.70	-1.66	-2.23	107 (5.2)
B3	3.48	9.05	-1.75	-1.19	-2.24	
B4	3.42	9.62	-1.30	-1.31	-2.94	189 (2.6)
C1	3.48	10.40	-1.84	-2.63	-5.03	
C2	3.48	10.60	-1.53	-2.52	-5.12	
C3	3.49	10.80	-1.02	-2.21	-5.01	
C4	3.48	10.95	-0.81	-2.15	-5.10	
C5	3.49	11.17	-0.51	-2.07	-5.24	
C6	3.49	11.54	-0.01	-1.94	-5.47	197 (2.5)
C7	4.93	11.95	0.30	-1.98	-5.68	

(a) Bubbling of 10 % CO₂(g). (b) ±10 μs.

4. Results and discussion

4.1. Spectroscopic features of Cm(III)

The fluorescence of Cm(III) in aqueous solution corresponds to the transition from the lowest excited state A to the ground state Z. Strong spin-orbit coupling mixes several spectroscopic terms among which the most significant contributions are due to $^8S_{7/2}$ for Z, and $^6P_{7/2}$ and $^6D_{7/2}$ for A.³⁸⁻⁴⁰ Depending on the symmetry of the Cm^{3+} surrounding, and the strength of chemical bonds, both states can split into several ligand-field components. However, in aqueous solutions, the ligand-field splitting is not resolved at room temperature. When Cm^{3+} is coordinated, fluorescence is shifted towards the red wavelengths as a result of increased splitting that lowers the energy gap between Stark levels of the excited and ground states; the fluorescence peak of a Cm(III) complex in solution is usually large with shoulders. Small temperature variations, *i.e.* between 10 and 70°C, may have some effects on spectroscopy in addition to changes in the aqueous speciation. First, increasing the temperature will lower the intensities of the radiative transitions in favour of non-radiative decays. Temperature changes may also affect slightly the populations of the vibronic and electronic levels. This effect was evaluated using energy gaps related to Cm^{3+} in $LaCl_3$ and ThO_2 host crystals,⁴⁰ giving weak and strong crystal-fields, respectively. The population changes in both cases were assessed by calculating the occupation rates of the levels at 10 and 70°C. Values were obtained by comparing kT (k is the Boltzmann constant) with the energy gap between a given Stark level and the lowest one, and using a Boltzmann distribution. Such a temperature range was concluded to have no significant effect on the population of the levels of the ground state since the $^8S_{7/2}$ splitting is very weak. Besides the occupation rate of the lowest level of the A state would vary from 0.74 to 0.70 for $Cm^{3+}:LaCl_3$ and from 0.82 to 0.78 for $Cm^{3+}:ThO_2$ in this temperature interval; the population change is even

less when considering other compounds with different crystal-field characteristics.⁴⁰ Thus, each component of the fluorescence peak should be slightly broadened when the temperature is increased, and should slightly modify the overall fluorescent peak. Consequently, minor changes on the spectroscopic fingerprints of each complexes are expected over the range 10-70°C, so that the identification of each species by TRLFS is made easier, allowing the speciation analysis.

4.2. Carbonate complexes at 25°C

The chemical conditions used for the TRLFS measurements at 25°C are reported in Table 1. Fluorescence was unchanged when $[\text{CO}_3^{2-}]$ was higher than 0.1 M, *i.e.* for solutions C3-C7 (Figure 1(a)). The maximum of the peak was found at 607.4 nm. When $[\text{CO}_3^{2-}]$ was lower than 0.1 M, the fluorescence peak decreased, and its maximum was shifted to 606.1 nm for the solution B2, which was interpreted as dissociation of the limiting carbonate complex $\text{Cm}(\text{CO}_3)_3^{3-}$, into $\text{Cm}(\text{CO}_3)_2^-$. The loss of a single CO_3^{2-} in the dissociation reaction was supported by the examination of the shapes of the curves which were fitted to the intensities at 607.4 nm (Figure 1(b)). The present interpretation was also supported by the $\log K_3$ values as discussed below. The fluorescence spectrum of $\text{Cm}(\text{CO}_3)_3^{3-}$ was directly measured whereas the one for $\text{Cm}(\text{CO}_3)_2^-$ as well as $\log K_3$ were deduced from spectral decomposition. The value $\log K_3 = 2.08 \pm 0.10$ was obtained from Reaction (2) at $I = 3$ M. The uncertainty of $\log K_3$ accounted for the experimental errors on the intensities. The validity of the speciation model, *i.e.* sensitivity analysis for the formation of $\text{Cm}(\text{CO}_3)_2^-$, was checked by comparing measured spectra for a given ratio $R = [\text{Cm}(\text{CO}_3)_3^{3-}]/[\text{Cm}(\text{CO}_3)_2^-]$ ($= [\text{CO}_3^{2-}] K_3$), but different chemical conditions: $-\log[\text{H}^+] = 7.96$ and 8.57 , and $I = 0.1$ and 3 M (Figure 2). We chose the value $R = 0.22 \pm 0.02$ corresponding to $\log R = -0.66 \pm 0.04$, and $(72 \pm 3)\%$ of $\text{Cm}(\text{CO}_3)_2^-$ and $(28 \pm 3)\%$ of $\text{Cm}(\text{CO}_3)_3^{3-}$. Solution B1 was prepared by bubbling a 10 % CO_2 gas mixture into a 0.1 M NaHCO_3 solution with $I = 3$ M in

order to keep $[\text{CO}_3^{2-}]$ as in B2, but a lower $-\log[\text{H}^+]$ value at 7.96. The pH change had no significant influence on the spectrum, which confirmed that under these conditions no exchange of H^+ or OH^- was involved in the reaction, in agreement with Reaction (2). The solution b0 was a 0.1 M NaHCO_3 solution without NaClO_4 . According to $\log K_3(0.1 \text{ M}) = 1.37 \pm 0.10$ calculated from the extrapolation of $\log K_3(3 \text{ M}) = 2.08 \pm 0.10$ to $I = 0.1 \text{ M}$ with Eqs.(4) and (5), the same speciation as in B2 was expected in b0 (virtually the same R value). This was confirmed by the similarity of the spectra shown in Figure 2.

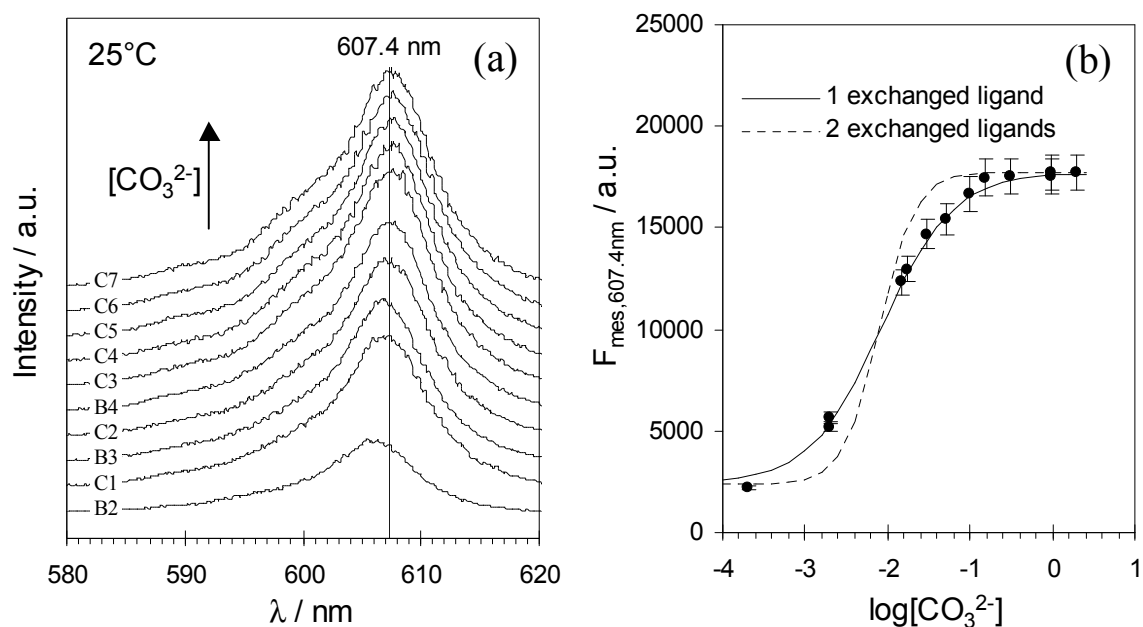


Figure 1. $[\text{CO}_3^{2-}]$ influence on the speciation of Cm(III) in bicarbonate and carbonate solutions at $I = 3 \text{ M}$ and 25°C . (a) Fluorescence spectra corresponding to the solutions whose labels are indicated on the graphic, referring to Table 1. (b) Fluorescence intensities at 607.4 nm, the wavelength of the maximum intensity for $\text{Cm}(\text{CO}_3)_3^{3-}$, over $\log[\text{CO}_3^{2-}]$: The curves were adjusted considering the exchange of 1 (—) and 2 (---) ligands, and evidenced the exchange of one CO_3^{2-} in the dissociation reaction.

In 1 M Na_2CO_3 solution (C6), the fluorescence decreased with time as a monoexponential function. The corresponding lifetime, τ , was found to be $197 \pm 10 \mu\text{s}$, that was then assigned to $\text{Cm}(\text{CO}_3)_3^{3-}$. This lifetime has the same order of magnitude than the ones measured in similar

conditions by various authors: The values $160 \mu\text{s}$,³⁹ $215 \mu\text{s}$ ⁴¹ and $230 \mu\text{s}$ ²³ were typically measured in 1 M Na_2CO_3 . In a previous work, Decambox *et al.* reported the values 200 and 240 μs measured in 1 M K_2CO_3 solutions for the excitation wavelengths 337 and 385 nm, respectively.⁴² These values are also inside the range 160-240 μs even if the formation of the tetra-carbonato complex $\text{Cm}(\text{CO}_3)_4^{5-}$ can be suspected in K^+ media as observed for lanthanides.²²

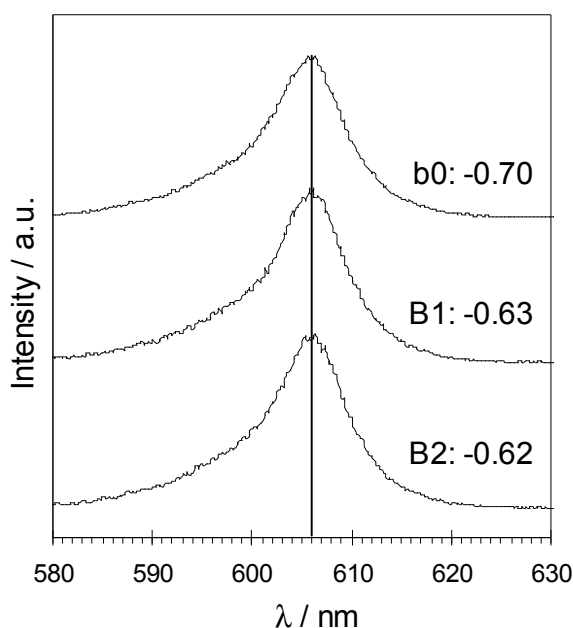


Figure 2. Sensitivity analysis for $\text{Cm}(\text{CO}_3)_2^-$ formation at 25°C . The value at $I = 3 \text{ M}$, $\log K_3 = 2.08$, was used to calculate the values of $\log([\text{CO}_3^{2-}] K_3)$ written on the figure, while $[\text{CO}_3^{2-}] K_3 = [\text{Cm}(\text{CO}_3)_3^{3-}]/[\text{Cm}(\text{CO}_3)_2^-]$. These values are similar for the solutions b0, B1 and B2 (Table 1). The spectra are identical although different values were measured for the pH of solutions B1 and B2: $-\log[\text{H}^+] = 7.96$ and 8.57 , respectively. This evidences no influence of $[\text{OH}^-]$. Similarly the spectrum for b0 at $I = 0.1 \text{ M}$ is identical to the other ones, which were obtained at higher ionic strength: $I = 3 \text{ M}$, in agreement with the corresponding ionic strength corrections calculated by using Eqs.(4) and (5).

The average number of remaining water molecules in the first hydration sphere of the $\text{Cm}(\text{III})$ triscarbonato species was calculated using the Kimura's relationship⁴³ to be 2.5 ± 0.5 from the lifetime ($197 \pm 10 \mu\text{s}$) measured in 1 M Na_2CO_3 solution: As CO_3^{2-} is expected to be a bidentate ligand toward the Cm^{3+} ion, the $[\text{Cm}(\text{CO}_3)_3(\text{H}_2\text{O})_{2.5}]^{3-}$ stoichiometry would result in the average

coordination number 8.5 ± 0.5 , which is a little lower than 9.2 ± 0.5 , the value that has been estimated for the aquo Cm^{3+} ion.⁴³ The lifetime measured at 25°C for the solution B2 would suggest 5.2 ± 0.5 for the average number of remaining water molecules (Table 1): We estimated that it corresponded to 5.8 ± 1.0 water molecules in the first hydration shell of $\text{Cm}(\text{CO}_3)_2^-$ according to the relative ratio of each species in these solutions, $R \approx 0.24$. This calculation suggested the average stoichiometry $[\text{Cm}(\text{CO}_3)_2(\text{H}_2\text{O})_{5.8}]^-$, and a coordination number of 9.8 ± 1.0 , which has a large uncertainty and is in agreement with the estimated value for the aquo ion. It should be noted that the coordination number of the $\text{Cm}(\text{CO}_3)_3^{3-}$ complex may be lowered by steric hindrance, even though this is not clearly evidenced by lifetimes measurements due to large uncertainties.

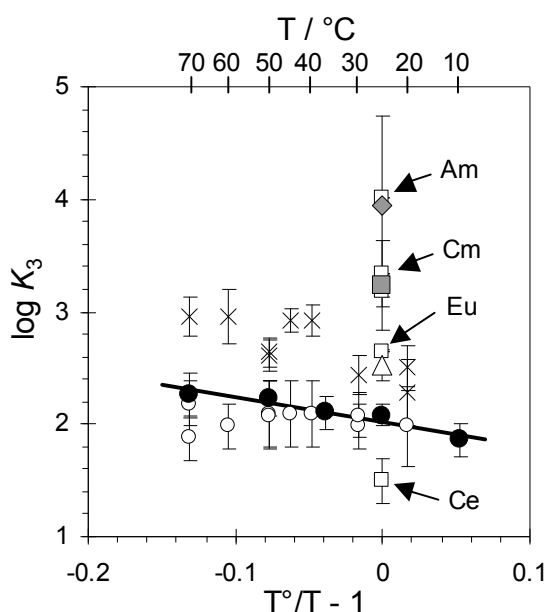


Figure 3. Comparison of $\log K_3$ values at various temperatures for An(III) and Ln(III). K_3 values were corrected to $I = 3$ M NaClO_4 with the SIT formula (Eqs.(4) and (5)). (●) TRLFS data for Cm(III) from this work (Table 2); Am(III) solubility data obtained (Δ) in 3 M NaClO_4 ,¹⁰ (\times) in 4 M NaCl media¹² and (\circ) our re-interpretation; selected constants (\blacklozenge) for Am(III)⁵ and (\blacksquare) for Am/Cm(III);¹⁵ (\square) literature data for Am(III),¹¹ Cm(III),²³⁻²⁴ Ce(III),⁹ and Eu⁴⁴ as indicated on the graphic.

From spectra at 25°C, we obtained $\log K_3 = 2.08 \pm 0.10$, leading to $\log K_3^\circ = 0.94 \pm 0.24$ after correction to $I = 0$ using Eqs.(4) and (5). This result has been compared with all the available $\log K_3$ values measured at room temperature for tri-cations of various f-block elements: Ce(III),⁹ Eu(III),⁴⁴ Am(III),¹⁰⁻¹² and Cm(III).^{23,24} These data have been corrected to $I = 3$ M (NaClO₄) using Eqs.(4) and (5) and plotted on Figure 3 (for $T^\circ/T - 1 = 0$).

Ce(CO₃)₃³⁻ was observed to be less stable since $\log K_3 = 1.5 \pm 0.2$ ⁹ was lower than $\log K_3 = 2.08 \pm 0.10$ at $I = 3$ M (NaClO₄). We have already pointed out that Ce(III) has a different behaviour than smaller f-block element ions as it can actually form Ce(CO₃)₄⁵⁻; a difference in $\log K_3$ was therefore not unexpected. A solvent extraction study also provided stability constants for Eu(CO₃)₃³⁻ and Eu(CO₃)₄⁵⁻ at $I = 1$ M (NaClO₄).⁴⁴ The corresponding data, $\log K_3 = 2.65$ for $I = 3$ M (NaClO₄), is indicated on Figure 3. However, according to the carbonate concentrations in the experimental solutions, these two complexes would have been formed at very low concentrations; hence, the stoichiometries as well as the corresponding stability constants are questionable.

The NEA-TDB gave a very interesting and thorough qualitative discussion of each published work on Am(III), and found discrepancies between equilibrium constants extracted from these studies, even when re-interpretations were attempted.⁵ To resolve these discrepancies, the solubility data that used badly characterized solid phase¹² were excluded, and even data from reasonably well characterized but metastable one (Am₂(CO₃)₃(s)) in carbonate solutions.¹⁰ Hence, the selection of a $\log K_3^\circ$ value was based on a single value from measurements of the solubility of AmOHCO₃(s) at variable ionic strength,¹¹ giving $\log K_3^\circ = 2.9 \pm 0.5$.⁵ The exclusion of Robouch's data might be questionable since the solubility-controlling solid, Am₂(CO₃)₃(s), had been well characterized by its X-ray diffraction pattern. Furthermore, X-ray characterization after two distinct preparation procedures and at different times (pages 51, 57 and 58 in Ref. 10)

showed that, at room temperature, the $\text{Am}_2(\text{CO}_3)_3(\text{s})$ compound was always detected even in chemical conditions where it was metastable; the only detected solid phase transformation gave $\text{NaAm}(\text{CO}_3)_2(\text{s})$ after 8 weeks in a 1 M Na_2CO_3 solution, while the other possible stable phase $\text{AmOHCO}_3(\text{s})$ was never detected. The $\log K_3$ value was determined to be 2.52 ± 0.14 at $I = 3$ M (NaClO_4) and should be relevant.¹⁰ In the updated NEA-TDB review, thermodynamic data for both Am(III) and Cm(III) were considered, and $\log K_3^\circ = 2.1 \pm 0.8$ was determined in order to cover all the selected values.¹⁵ Cm(III) values were taken from TRLFS studies, $\log K_3^\circ = 2.09 \pm 0.15$ ²³ and $\log K_3^\circ = 2.00$,²⁴ but the TRLF spectra were interpreted assuming the $\text{Cm}(\text{CO}_3)_4^{5-}$ stoichiometry for the limiting complex, while the expected limiting complex should rather be $\text{Cm}(\text{CO}_3)_3^{3-}$.²² It might very well be the reason why the NEA-TDB selected value, $\log K_3^\circ = 2.1 \pm 0.8$,¹⁵ is different than $\log K_3^\circ = 0.94 \pm 0.24$ found in the present work. Finally, we found possible reasons for understanding the discrepancies of the data at 25°C for f-block tri-cations on the basis of chemical behaviour, *i.e.* for Ce(III), characterisation of the solubility-controlling solid, *i.e.* for Am(III), or possible misinterpretations. These statements may be supported by the consistency of the TRLFS results and solubility data obtained at variable temperature for Cm(III) and Am(III) respectively, as presented below.

4.3. Carbonate complexes of Cm(III) over 10-70°C

Temperature cycles were carried out on solutions for which $[\text{CO}_3^{2-}]$ was calculated and reported in Table 2. For each temperature, fluorescence was measured as a function of $[\text{CO}_3^{2-}]$. An example is given in Figure 4 for measurements at 50°C. As for experiments at 25°C, the limiting complex $\text{Cm}(\text{CO}_3)_3^{3-}$ was detected as the single species in solutions when $[\text{CO}_3^{2-}] > 0.1$ M, and dissociated for lower values. As a result, the spectrum recorded for the solution C6 (Table 2) corresponds to the one of $\text{Cm}(\text{CO}_3)_3^{3-}$. In addition to a decrease of the fluorescence

intensity with increased temperatures, the maximum of the peak was shifted towards the red wavelengths as shown on Figure 5. For a given temperature, the intensity of the spectrum of $\text{Cm}(\text{CO}_3)_2^-$ is about four times lower than that of $\text{Cm}(\text{CO}_3)_3^{3-}$ and the shift of the peak is about 2 nm towards the short wavelengths. In order to display the spectral changes at each temperature, the intensities measured at the wavelength corresponding to the maximum intensity for $\text{Cm}(\text{CO}_3)_3^{3-}$ are plotted over $\log[\text{CO}_3^{2-}]$ on Figure 6, in the same manner as the analysis at 25°C (Figure 1(b)). The curves were calculated using Eq.(1) with the values of $\log K_3$ obtained from the spectral decompositions and spectroscopic parameters for each temperature (Table 2). As it was concluded for the results at 25°C, a single CO_3^{2-} is exchanged in the dissociation reaction of $\text{Cm}(\text{CO}_3)_3^{3-}$ according to the shape of the curves. Thus, $\text{Cm}(\text{CO}_3)_2^-$ and $\text{Cm}(\text{CO}_3)_3^{3-}$ are still the predominant forms of Cm(III), and only $\log K_3$ is affected by the temperature.

Table 2. Chemical conditions of the TRLFS measurements and spectral characteristics of $\text{Cm}(\text{CO}_3)_2^-$ and $\text{Cm}(\text{CO}_3)_3^{3-}$ at various temperatures. $\lambda_{\text{max},3}$ is the wavelength of the maximum of the $\text{Cm}(\text{CO}_3)_3^{3-}$ peak, $F_{2,\lambda_{\text{max},3}}$ and $F_{3,\lambda_{\text{max},3}}$ are the molar intensities at $\lambda_{\text{max},3}$ for $\text{Cm}(\text{CO}_3)_2^-$ and $\text{Cm}(\text{CO}_3)_3^{3-}$ respectively, which were measured in 3 M Na^+ solutions. The $\log K_3$ values were determined by spectral decomposition.

	T / °C	10	25	37	50	70
Solution label	I_m / mol kg ⁻¹	$\log[\text{CO}_3^{2-}]$				
B2	3.52	-2.69	-2.70	-2.70	-2.70	-2.71
C1	3.48	-1.84	-1.84	-1.84	-1.84	-1.85
C2	3.48	-1.52	-1.53	-1.53	-1.53	-1.54
B4	3.42	-1.30	-1.30	-1.30	-1.30	-1.31
C3	3.49	-1.01	-1.02	-1.02	-1.02	-1.03
C5	3.49	-0.51	-0.51	-0.51	-0.51	-0.52
C6	3.49	0.00	-0.01	-0.01	-0.01	-0.02
C7	4.93	0.30	0.30	0.29	0.29	0.29
$\lambda_{\text{max},3}$ / nm		607.2	607.4	607.6	608.1	608.7
$F_{2,\lambda_{\text{max},3}}$ (a.u)		3730	2380	2010	1830	1050
$F_{3,\lambda_{\text{max},3}}$ (a.u)		20920	17720	15690	15630	12380
$\log K_3$ (3 M)		1.86 ± 0.15	2.08 ± 0.10	2.10 ± 0.15	2.23 ± 0.15	2.26 ± 0.20

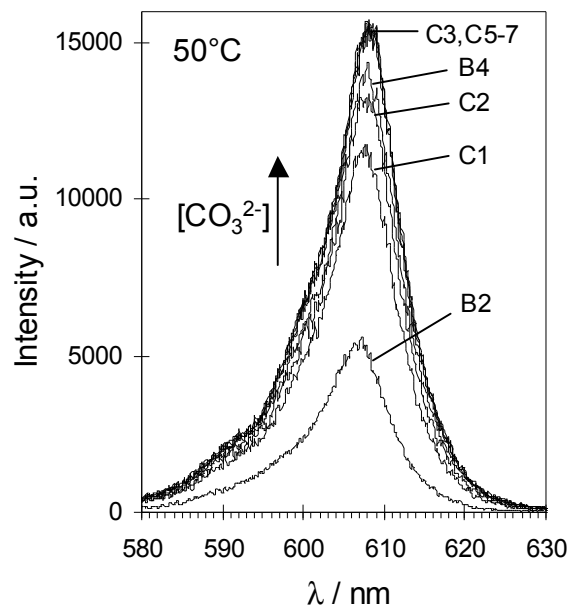


Figure 4. Influence of $[\text{CO}_3^{2-}]$ on the fluorescence spectra measured at 50°C . The solution labels are indicated on the graphic, referring to Table 2.

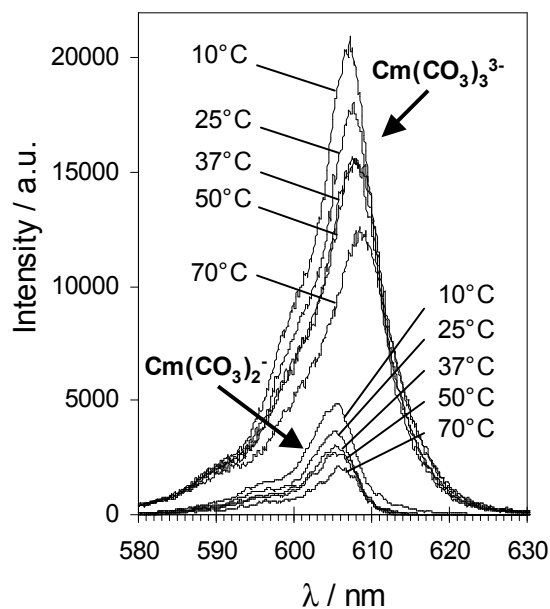


Figure 5. Temperature influence on the fluorescence spectra of $\text{Cm}(\text{CO}_3)_3^{3-}$ as measured in solution C6 (Table 1), and $\text{Cm}(\text{CO}_3)_2^-$ as deduced from spectral decomposition.

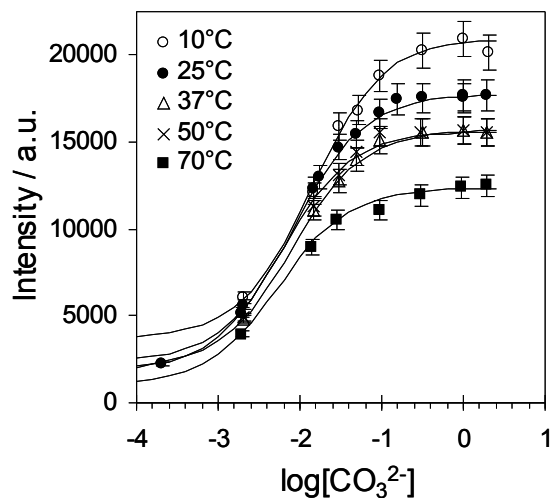


Figure 6. $[\text{CO}_3^{2-}]$ and temperature influences on the fluorescence intensities measured at the wavelength corresponding to the maximum intensity for $\text{Cm}(\text{CO}_3)_3^{3-}$, $\lambda_{\text{max},3}$. The chemical conditions and the parameters ($F_{2,\lambda_{\text{max},3}}$, $F_{3,\lambda_{\text{max},3}}$ and $\log K_3$) for drawing the curves are reported in Table 2.

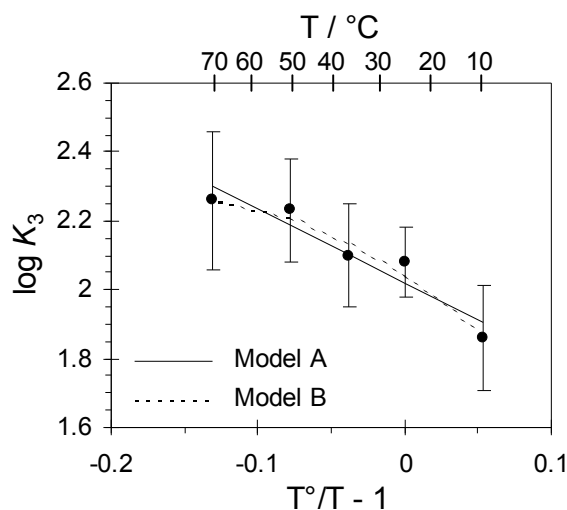


Figure 7. Temperature influence on $\log K_3$ at $I = 3$ M. Symbols and lines correspond to experimental values (Table 2) and fitting curves, respectively. The fitted parameters for Models A and B are reported in Table 3.

4.4. Effect of temperature on K_3 and $\Delta_r H_3$

The values of $\log K_3$ for the formation of $\text{Cm}(\text{CO}_3)_3^{3-}$ (Table 2) are plotted as a function of temperature in Figure 7. In the range 10-70°C, a slight increase of $\log K_3$ was observed. Uncertainties were found to be $\pm 0.1-0.2$, a usual value for the uncertainties associated to measured complexation constants. The dependency of $\log K_3$ with temperature was virtually within uncertainty. Consequently, two models were applied to the experimental data determined at $I = 3 \text{ M}$ as well as to the values extrapolated to $I = 0$. Model A (Eq. (6)) gave a linear correlation and fitted reasonably well the experimental data (Figure 7). The resulting values are $\Delta_r G_3(298 \text{ K}) = -11.5 \pm 0.2 \text{ kJ mol}^{-1}$, $\Delta_r H_3(298 \text{ K}) = 12.2 \pm 2.3 \text{ kJ mol}^{-1}$ and $\Delta_r S_3(298 \text{ K}) = 79 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$. The estimations from Model B (Eq. (7)) are also reported in Table 3. The standard deviation σ of the fit was examined when changing the values of $\Delta_r G_3(298 \text{ K})$, $\Delta_r H_3(298 \text{ K})$, $\Delta_r C_{p3}(298 \text{ K})$ and $\Delta_r S_3(298 \text{ K})$ around the values obtained with Model B. As σ did not increase symmetrically on both sides of the values adjusted with Model B, we determined another set of parameters (Model B'): We assessed the limiting values for which the fit was visually acceptable according to experimental uncertainties; we then calculated the mean values of each data. The thermodynamic data obtained with any of the methods B and B' did not significantly differ within their uncertainties. Neglecting heat capacity effects (Model A) or not (Model B) resulted in similar values for $\Delta_r G_3$, but somewhat different values for $\Delta_r H_3$ (even if the uncertainty ranges still overlapped) due to the influence of $\Delta_r C_{p3}$ (Table 3). It is not clear whether Model B is meaningful because it assumes constant $\Delta_r C_{p3}$, while it is not specially expected to be constant for solutes in aqueous solutions: The values fitted for $\Delta_r C_{p3}$ and associated uncertainties are probably only a maximum range of variations, rather than an estimation of its value at 25°C or even a mean value. Anyhow, one may expect $\Delta_r C_{p3}$ to be small since Reaction (2) is isoelectric: It has

indeed been proposed that the main contributions to the temperature dependency are the electrostatic interactions, and that they should balance out to a large extent.³⁶ Hence, the enthalpy of reaction would be constant with temperature. Thus, Model A is expected to be a relevant approximation for the dependency of $\log K_3$ with temperature. The corresponding thermodynamic constants are therefore considered reliable, but the uncertainties were increased to cover the values obtained with the other models (Table 3).

Table 3. Thermodynamic constants obtained at 25°C for $\text{Cm}(\text{CO}_3)_2^- + \text{CO}_3^{2-} \rightleftharpoons \text{Cm}(\text{CO}_3)_3^{3-}$ from K_3 values (Table 2, Figure 7) measured at constant ionic strength $I = 3 \text{ M NaClO}_4$ (Table 2). The proposed values (bolded) are taken from Model A with increased uncertainty to encompass the values obtained with the other models.

Model	I	$\Delta_r G_3$ / kJ mol^{-1}	$\Delta_r H_3$ / kJ mol^{-1}	$\Delta_r C_{p3}$ / $\text{J mol}^{-1} \text{K}^{-1}$	$-\text{T}^\circ \Delta_r S_3$ / kJ mol^{-1}	$\log K_3$	$\Delta_r S_3$ / $\text{J mol}^{-1} \text{K}^{-1}$
A	3	-11.5±0.2	12.2±2.3		-23.7±2.3	2.01±0.04	79±8
B	3	-11.7±0.1	16.4±2.8	-330±180	-28.1±2.8	2.05±0.02	94±9
B'	3	-11.8±0.5	16.6±1.0	-400±300	-28.4±1.1	2.07±0.09	95±4
		-11.5±0.3	12.2±4.4		-23.7±4.7	2.01±0.05	79±16
A	0	-5.0±0.2	9.4±2.4		-14.4±2.4	0.88±0.04	48±8
B	0	-5.2±0.2	13.9±2.9	-350±180	-19.1±2.9	0.91±0.04	64±10
B'	0	-5.1±0.4	14.2±1.7	-300±200	-19.3±1.7	0.89±0.07	65±6
		-5.0±0.3	9.4±4.8		-14.4±6.9	0.88±0.05	48±23

A = constant enthalpy approach

B = constant heat capacity approach

B' = same as B, but the best fit was visually decided (see text)

4.5. Solubility data for Am(III) between 20 and 70°C

In this section, solubility results for Am(III) at different temperatures reported in Ref. 12 are described, followed by a new interpretation of these measurements. Solubility measurements of Am(III) in 4 M NaCl media had been interpreted with the controlling phases $\text{NaAm}(\text{CO}_3)_2(\text{s})$ at 40, 45, 50 and 70°C, and $\text{AmOHCO}_3(\text{s})$ at 20, 30, 50, 60 and 70°C.¹² Interestingly, the results showed that, under these conditions, Am(III) was less soluble when increasing the temperature. From slope analysis of the solubility curves, equilibrium constants had been determined for the

dissolution reactions of each solid compound into the carbonate complexes AmCO_3^+ , $\text{Am}(\text{CO}_3)_2^-$ and $\text{Am}(\text{CO}_3)_3^{3-}$ at the different temperatures. Values of $\log K_3$ ($\text{Am}(\text{CO}_3)_2^- + \text{CO}_3^{2-} \rightleftharpoons \text{Am}(\text{CO}_3)_3^{3-}$) had been deduced (Table 4), and were corrected for the effect of the ionic medium: From $I = 4$ M NaCl, to $I = 3$ M NaClO₄ using Eqs.(4) and (5). These corrections were found to be negligible; typically the $\log K_3$ values were lowered by 0.02 log₁₀ unit whatever the temperature. These $\log K_3$ values for Am(III) are slightly higher than the ones for Cm(III) (Figure 3). Although a slight increase of $\log K_3$ with increased temperature had been proposed for Am(III),¹² in agreement with the TRLFS results for Cm(III), the scattering of the data did not allow to accurately determine $\Delta_r H_3$ and $\Delta_r S_3$. The uncertainties were obviously too large probably as a result of solid phase transformations. As the interpretation of these solubility data had only been based on slope analyses and had not been confirmed by any other solid characterisation, we tried other possible slope analyses corresponding to other solid compounds that would have controlled the solubility.

Table 4. Values for $\log K_3$ at various temperatures for $\text{Am}(\text{CO}_3)_2^- + \text{CO}_3^{2-} \rightleftharpoons \text{Am}(\text{CO}_3)_3^{3-}$ from solubility measurements in 4 M NaCl, from Ref. 12 and as re-interpreted in the present work.

T /°C	Ref. 12	this work
20	2.3±0.3	2.0±0.2
30	2.45±0.17	2.0±0.2
30		2.1±0.2
40	2.94±0.14	2.1±0.2
45	2.94±0.10	2.1±0.2
50	2.62±0.14	2.1±0.2
50	2.66±0.13	2.1±0.2
60	2.98±0.24	2.0±0.2
70	2.98±0.17	1.9±0.2
70		2.2±0.2

The relative stabilities of the solids $\text{AmOHCO}_3(\text{s})$ and $\text{Am}_2(\text{CO}_3)_3(\text{s})$ is determined by P_{CO_2} ,^{5,18} for better estimating this parameter, we corrected the original experimental data for the possible

leak of $\text{CO}_2(\text{g})$, particularly at high temperature: Rather than using mass balance, the carbonate speciation was re-calculated on the basis of the electro-neutrality of the solutions, which does not need to assume no exchange of $\text{CO}_2(\text{g})$ with air. The corrections on $[\text{CO}_3^{2-}]$ were only significant for bicarbonate solutions for which P_{CO_2} ranged between 0.001 and 0.02 atm. This corresponds to conditions in which $\text{Am}_2(\text{CO}_3)_3(\text{s})$, the initial solid, may transform into $\text{AmOHCO}_3(\text{s})$.¹⁸ However, consistently with the kinetic observation of Robouch,¹⁰ theoretical curves better fitted the data assuming $\text{Am}_2(\text{CO}_3)_3(\text{s})$ and $\text{NaAm}(\text{CO}_3)_2(\text{s})$ as relevant phases, with the solid phase transformation between these two compounds at about 0.01 M CO_3^{2-} for 4 M Na^+ (Figure S1 of the Supporting Information). The corrected measurements were found to be reasonably consistent with this interpretation, whereas the stability of $\text{AmOHCO}_3(\text{s})$, which had been previously considered for the original (not-corrected) experimental data¹² was now even less convincing. A new set of equilibrium constants was determined, particularly values for $\log K_3$ at each temperature (Table 4). These results are clearly different from the original interpretation as shown on Figure 3. Not only the $\log K_3$ values are less scattered, but they also appear to be in good agreement with the TRLFS results for Cm(III) in the range 20-50°C; at higher temperature, they are still in agreement, but the solubility results for Am(III) are slightly more scattered. This could be attributed to the crystallographic structures of the solid at 70°C that may have changed from the beginning to the end of the temperature cycle. Despite the influence of the solid phase on the data, these new results support the formation constants for $\text{Cm}(\text{CO}_3)_3^{3-}$ measured by TRLFS.

4.6. Discussion on the effect of temperature on $\log K_3$

The stepwise formation of $\text{Cm}(\text{CO}_3)_3^{3-}$ is an endothermic reaction and is driven by the entropy, since $T^\circ\Delta_rS_3(298\text{ K})$ is larger than $\Delta_rH_3(298\text{ K})$ whatever the model used to interpret the data

(Table 3). This observation is consistent with the common trend observed for the complexation of lanthanides and actinides.⁷ The enthalpy of reaction is usually described as the summation of the dehydration energy and the binding energy; de-solvation generally overcomes the formation of cation – ligand bonds contributing to positive $\Delta_r H$ and $\Delta_r S$, which is the case for Reaction (2). The entropy of reaction $\Delta_r S_3$ was indeed found to be positive and contributed in a larger extent to the Gibbs energy of reaction (Table 3). Changes in the hydration of the species probably accompanied the formation of the tri-carbonate complex of Cm^{3+} . The dehydration entropy contribution is certainly favourable for Reaction (2) and might very well be the most important effect.

In an attempt to compare the thermodynamic constants for carbonate complexation determined in this work with other data, the reactions for the formation of tri-acetate complexes of Nd^{3+} and UO_2^{2+} were examined as the binding properties of both carbonate and acetate ligands and the effective charge on the cations ($\sim +3.2$ for UO_2^{2+} ⁴⁵) are likely to be nearly similar. $\Delta_r H_3(298 \text{ K}) \approx 3.8 \text{ kJ mol}^{-1}$ and $-T^\circ \Delta_r S_3 \approx -7.3 \text{ kJ mol}^{-1}$ have been determined for the stepwise formation of $\text{Nd}(\text{Ac})_3(\text{aq})$ at $I = 2.2 \text{ mol kg}^{-1}$ (NaClO_4) and 25°C .⁴⁶ The signs of these thermodynamic parameters are consistent with what was found for the stepwise formation of $\text{Cm}(\text{CO}_3)_3^{3-}$. In contrast, a slightly negative enthalpy change ($\Delta_r H_3 \approx -2 \text{ kJ mol}^{-1}$) was published for the formation of $\text{UO}_2(\text{Ac})_3^-$ although $\Delta_r H_1(\text{UO}_2\text{Ac}^+)$ and $\Delta_r H_2(\text{UO}_2(\text{Ac})_2(\text{aq}))$ have been found to be positive.⁴⁷ Such changes have been interpreted with different coordination modes of acetate towards the uranyl ion: The third acetate ligand was proposed to be unidentate in contrast to the bidentate coordination of the first and second acetate anions; the coordination is indeed more constrained around UO_2^{2+} since the ligands are roughly in its equatorial plane. Conversely, all the carbonate anions should act as bidentate ligands towards M^{3+} , and therefore positive enthalpy changes may

be expected even for the third stepwise formation reaction. It should be noted that the heat capacity $\Delta_r C_{p3}$ that was assessed with Model B was negative whereas the ones measured for reactions of acetate with Nd^{3+} ,⁴⁶ Th^{4+} ⁴⁸ and UO_2^{2+} ,⁴⁷ have been found to be positive in all cases. This supports the assumption that $\Delta_r C_{p3}$ is small for Reaction (2) and even negligible over the range 10-70°C, in agreement with the values from Model A that are proposed here.

The effect of ionic strength on thermodynamic constants was assessed by similar data treatment of $\log K_3^\circ$ values at zero ionic strength calculated for each temperature using Eqs.(4) and (5). As expected, the complexation constants were lower than those at high ionic strength (as any highly negatively-charged species, the limiting complex is more stabilized at high ionic strength), hence $\Delta_r G_3^\circ$ is higher than $\Delta_r G_3(3 \text{ M})$ (Table 3). $\Delta_r H_3$ and $\Delta_r S_3$ were both found to be smaller at zero ionic strength. Applying Eqs.(8) and (9) to Reaction (2) enabled to calculate $\Delta_r H_3^{\text{ex}}$ and $\Delta_r S_3^{\text{ex}}$ at a given ionic strength, which gave direct insight for how much the thermodynamic functions depend on I . Since $\Delta \epsilon_3$ is small and expected to be not temperature-dependent, $\Delta_r \log \gamma_3$ (Eq.(5)) and its first derivative (Eq.(10)) can be calculated with a very little influence from the use of fitted parameters. For instance, at $I = 3 \text{ M}$, we obtained $(\partial D(T)/\partial T)_p = (4 \pm 1) \times 10^{-4} \text{ K}^{-1}$ and $\Delta_r \log \gamma_3 = -1.07 \pm 0.05$; hence, $\Delta_r H_3^{\text{ex}}(298 \text{ K}) = 2.7 \pm 0.8 \text{ kJ mol}^{-1}$ and $-T^\circ \Delta_r S_3^{\text{ex}}(298 \text{ K}) = -8.8 \pm 0.9 \text{ kJ mol}^{-1}$. $\Delta_r H_3^{\text{ex}}(298 \text{ K})$ is not zero, but as expected, the effect of I on the thermodynamic functions is greater for the entropy of reaction than for the enthalpy of reaction. This is again consistent with the stabilization of highly negatively-charged complexes such as $\text{Cm}(\text{CO}_3)_3^{3-}$ at high ionic strength.

5. Conclusion

We have demonstrated the reliability of time-resolved laser-induced fluorescence spectroscopy for measuring stability constants (or equivalently Gibbs energy of reactions) of carbonate complexes of Cm³⁺ at various temperatures, which are currently lacking in thermochemical databases. This appeared useful for the system here studied, since TLRFS allowed to work below the solubility limit, while solubility studies for such systems previously gave scattered thermodynamic data as a result of difficulties in achieving solubility equilibrium. The stepwise formation constant of Cm(CO₃)₃³⁻ was measured at 10, 25, 37, 50 and 70°C. The experimental data at $I = 3$ M could satisfactorily be interpreted neglecting the temperature influence on the enthalpy of the reaction, a classical approximation for such an isoelectric reaction: $\Delta_r H_3(298\text{ K}) = 12.2 \pm 4.4\text{ kJ mol}^{-1}$ and $\Delta_r S_3(298\text{ K}) = 79 \pm 16\text{ J mol}^{-1}\text{ K}^{-1}$. The dependency of $\log K_3$ was in good agreement with values for Am(III) that were obtained from re-interpreted solubility data. As expected, the formation of the limiting tri-carbonate complex was found to be entropy-driven, probably due to hydration changes of the species.

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Supporting Information Available: Characteristics of the solutions for calibrating the glass electrodes, volume dilatation data, Debye-Hückel term of the SIT formula calculated at various temperatures and ionic strengths, graphical interpretation of Am(III) solubility data at 30 and 70°C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Synopsis

$\log K_3 = 2.01 \pm 0.05$ was determined at $T^\circ = 25^\circ\text{C}$ by time-resolved laser-induced fluorescence spectroscopy at high ionic strength ($I = 3 \text{ M NaClO}_4$). The analysis of spectral data at various temperatures between 10 and 70°C , gave $\Delta_r H_3 = 12.2 \pm 4.4 \text{ kJ mol}^{-1}$. The formation of the limiting tri-carbonate complex was found to be entropy-driven: $T^\circ \Delta_r S_3 = 23.6 \pm 4.8 \text{ kJ mol}^{-1}$.

