

Eu(CO₃)₃³⁻ and the limiting carbonate complexes of other M³⁺ f-elements in aqueous solutions: a solubility and TRLFS study

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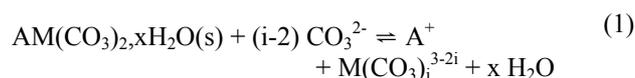
In the framework of environmental studies concerning radioactive waste management, the speciation of M³⁺ f-elements in concentrated carbonate solutions was investigated. Solubility measurements of NaEu(CO₃)₂·6H₂O(s) were performed at 23±1°C with [Na⁺] fixed by using NaClO₄. In 3 mol L⁻¹ Na⁺ aqueous solutions the limiting complex Eu(CO₃)₃³⁻ was identified in the range 0.01 < [CO₃²⁻] < 2 mol L⁻¹: experimental solubilities were modelled with Equilibrium NaEu(CO₃)₂·6H₂O(s) + CO₃²⁻ ⇌ Na⁺ + Eu(CO₃)₃³⁻ + 6 H₂O, and log of its equilibrium constant was found to be lg K_{s,3} = -4.2 ± 0.2. To interpret the measurements at different [Na⁺], the activity coefficients of the species were calculated with SIT Formula. Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) was used to verify the presence of a unique complex of Eu(III) in the aqueous solutions. From fluorescence lifetime measurements in 1 mol L⁻¹ Na₂CO₃ solutions of H₂O/D₂O mixtures, it was determined that about 2 water molecules remained in the first coordination sphere of Eu(CO₃)₃³⁻. From a critical review of literature data and sensitivity analysis, it was concluded that solubility results should be more reliable than solvent extraction and spectroscopic ones for determining the stoichiometry of limiting carbonate complexes. Tri-carbonate complexes of most M³⁺ f-elements appeared to be the limiting stable species in Na⁺ aqueous solutions, except for Ce(III) for which a tetra-carbonate complex had indeed been observed. Interestingly, K⁺-based supporting electrolytes can favour tetra-carbonate complexes at high ionic strength. Available values of thermodynamic constants related to various ionic media are compared on the basis of SIT Formula.

Introduction

Considerable efforts have been made in the past twenty years for obtaining reliable thermodynamic databases concerning the chemistry of long-lived radionuclides to assess their release from possible radioactive waste repositories into environmental waters: see typically the thorough reviews for the Thermochemical Data Base (TDB) of the OECD NEA on U,¹ Am,² Tc,³ Np and Pu,⁴ and their recent "Update".⁵ Nevertheless, the stoichiometry of the limiting carbonate complex is still puzzling for actinides at the +3 oxidation state, An(III). Am(CO₃)₃³⁻ was proposed by Robouch as the limiting species from investigation of the solubility of Am(III) in concentrated carbonate solutions up to 1 mol L⁻¹ CO₃²⁻ and at 3 mol L⁻¹ Na⁺.⁶ This conclusion was later confirmed in the solubility studies of Giffaut,⁷ and Runde *et al.*⁸ Accordingly, NEA-TDB had found no evidence for Am(CO₃)₄⁵⁻ aqueous complex,² while the NEA-TDB "Update" recently selected formation data for Cm(CO₃)₄⁵⁻.⁵ Indeed M(CO₃)₃³⁻⁶⁻⁹ and M(CO₃)₄⁵⁻¹⁰⁻¹⁴ complexes have been reported to be the limiting complexes for M = An(III) and Ln(III), their lanthanide analogues, based on different experimental conditions and techniques. Stabilities of Ln(CO₃)₄⁵⁻ complexes have been proposed in [C(NH₂)₃]₂CO₃ / [C(NH₂)₃]₃HCO₃ buffer solutions at pH 10.5 and ionic strength of 2.5 mol L⁻¹ to interpret solvent extraction data.¹⁵ Logarithmic plots of distribution ratios against carbonate concentration give confidence for the formation of tetra-carbonate complexes for all lanthanides, except Ce and Pm that were not studied. Rao *et al.* reported stability data for Eu(CO₃)₃³⁻ and Eu(CO₃)₄⁵⁻ in NaHCO₃ aqueous solutions at 1.0 mol L⁻¹ NaClO₄ by solvent extraction, interpreting their results by curve fitting techniques.¹² However in this study, [CO₃²⁻] never exceeded 0.02 mol L⁻¹, which seems too low to significantly observe Eu(CO₃)₄⁵⁻. Since no convincing sensitivity analysis was presented, it is not clear whether the formation constants values for M(CO₃)₄⁵⁻, and even for M(CO₃)₃³⁻, are reliable. Cm(CO₃)₄⁵⁻ was proposed for interpreting TRLFS results; the authors calculated that about

50% of Cm(CO₃)₄⁵⁻ was formed at 0.01 mol L⁻¹ CO₃²⁻ and 1 mol L⁻¹ NaCl,¹³ which disagrees with earlier results for Am(III) using a solubility method in 5 mol L⁻¹ NaCl, *i.e.* at a higher ionic strength, which should favour the formation of Am(CO₃)₄⁵⁻ that was actually not observed.⁸ This discrepancy was attributed in the NEA-TDB update review as an effect of the difference in the ionic radii of Cm³⁺ and Am³⁺, despite this difference was recognised to be very small.⁵ Similar TRLFS measurements were carried out in our laboratory for Cm and Eu, two fluorescing M³⁺ ions in the f-element series.¹⁶ Spectral changes are even more important for Eu than for Cm on carbonate additions, but sensitivity analysis could not draw a clear conclusion for choosing the best interpretation of our experimental observations: TRLFS data were as well interpreted with Eu(CO₃)_i³⁻²ⁱ species either for 0 ≤ i ≤ 3 or 0 ≤ i ≤ 4. Furthermore considering a possible erroneous species in speciation models or conversely omitting one species affected the numerical values of the stability constants fitted for the other complexes, *i.e.* the lower carbonate complexes (i ≤ 2 or 3 respectively).

Aside from Dumonceau's results on the stability of Ln(CO₃)₄⁵⁻,¹⁵ and in an attempt to reinterpret available published experimental data, only two studies appeared to clearly have evidenced M(CO₃)₄⁵⁻ species. In both cases, the authors studied Equilibria



for A⁺ = K⁺, M = Eu(III),¹⁷ and for A⁺ = Na⁺, M = Ce(III),¹⁰ respectively, using high carbonate concentrations for obtaining the limiting complexes, and constant high ionic strength to allow slope analysis; sensitivity analysis is indeed feasible when the complex is dominating in a broad enough domain of [CO₃²⁻] and activity coefficient effects are negligible. When M(CO₃)_i³⁻²ⁱ is practically the only soluble complex, Equilibrium 1 predicts that plotting log(solubility) vs. log[CO₃²⁻] would result in a straight

line with slope $(i-2)$, a way for determining i , related to $M(\text{CO}_3)_i^{3-2i}$. High carbonate concentrations necessarily imply OH^- concentrations ranging typically from 10^{-4} to 10^{-2} mol L^{-1} which can favour the formation of ternary mixed hydroxo-carbonate complexes. In the case of $\text{Am}(\text{III})$, they were shown to be minor species that can be neglected in the speciation.^{4,5} Studying carbonate complexes, Robouch carried out batch experiments in NaHCO_3 and Na_2CO_3 aqueous solutions, notably providing solubility data at about 10^{-2} mol L^{-1} CO_3^{2-} with a difference in $[\text{OH}^-]$ of more than 1 log unit; in both solutions $\text{Am}(\text{CO}_3)_2^-$ and $\text{Am}(\text{CO}_3)_3^{3-}$ were the major complexes with similar concentrations.⁶ Hence, no evidence of the stability of any mixed complexes was obtained. In this work, we have not performed systematic measurements varying $[\text{H}^+]$ to observe such complexes, but rather chosen relevant carbonate conditions to characterise the limiting complex of $\text{Eu}(\text{III})$.

We have performed solubility measurements of $\text{NaEu}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$ in concentrated Na_2CO_3 aqueous solutions of constant $[\text{Na}^+]$ obtained by NaClO_4 additions. The solid phases $\text{M}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{MOHCO}_3(\text{s})$ and $\text{M}(\text{OH})_3(\text{s})$ are also stable at 25°C ; their relative stability depends upon pH and CO_2 partial pressure as shown for $\text{M} = \text{Am}(\text{III})$.¹⁸ However $\text{NaM}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$ are the thermodynamically stable solid phases controlling solubility in concentrated sodium carbonate solutions,^{7,9,10,17,19} giving little chance for phase transformation during the experiments. The $\text{Eu}(\text{III})$ aqueous speciation was also monitored by using TRLFS. Finally, literature results will be discussed in an attempt to rationalise the data on the carbonate limiting complexes for M^{3+} ions of the $\text{Ln}(\text{III})$ and $\text{An}(\text{III})$ series.

Experimental details

All the preparations and procedures were performed at $(23 \pm 1)^\circ\text{C}$.

Materials

Millipore deionised water (Alpha-Q, 18.2 M Ω cm) was used throughout the preparations. The carbonate solutions were prepared from anhydrous Na_2CO_3 solid (Prolabo, Normapur[®], >99.8%), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Merck), and NaCl (Labosi, >99.9%). The Europium solid was prepared from $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Johnson Matthey, 99.99%). A stock solution of 1 mol L^{-1} HNO_3 was prepared from HNO_3 65% (Merck, Suprapur[®]) and titrated with 0.1 mol L^{-1} NaOH (Prolabo, Titrisol[®]), and used for sample preparation for inductively-coupled plasma – atomic emission spectroscopy (ICP-AES) analysis (Perkin Elmer, Optima 2000 DV). D_2O (Aldrich, 99.9% D) was used for TRLFS measurements.

Potentiometric measurements

$[\text{H}^+]$ was measured by using modified combined glass electrodes (Radiometer Analytical, XC161). Their reference solutions were replaced with a $\text{NaClO}_4 / 0.01$ mol L^{-1} NaCl solution with 0.1, 1 or 3 mol L^{-1} Na^+ in order to have approximately the same $[\text{Na}^+]$ as the solution in which $[\text{H}^+]$ was measured, and to minimise the junction potential that occurs between the reference and the working solutions. Each of them was calibrated before the series of measurements with three H^+ -buffer solutions containing appropriate amounts of NaClO_4 to keep $[\text{Na}^+]$ constant at either 0.1, 1 or 3 mol L^{-1} as that of the corresponding reference solution. So $-\lg[\text{H}^+]$ was used rather than pH. The calibration solutions were: (i) 0.01 mol L^{-1} HCl solution ($-\lg[\text{H}^+] = 2.00$ whatever $[\text{Na}^+]$); (ii) 0.1 mol L^{-1} NaHCO_3 solution equilibrated with 100% $\text{CO}_2(\text{g})$ ($-\lg[\text{H}^+] = 7.00, 6.74$ and 6.63 for 0.1, 1 or 3 mol L^{-1} Na^+ , respectively); and (iii) equimolar $\text{NaHCO}_3 / \text{Na}_2\text{CO}_3$ solutions ($-\lg[\text{H}^+] = 9.90, 9.78$ and 9.61 for 0.1, 1 or 3 mol L^{-1} Na^+ , respectively). The slopes of the electrodes were always more than 97% of the theoretical slope. Their correct responses were checked with the alkaline buffer solutions after each series of measurements to ensure that it did not deviate. One should note that measurements were performed outside of

the range of calibration due to the high alkalinity of Na_2CO_3 working solutions, which might have created additional errors on the $-\lg[\text{H}^+]$ numerical values. Nevertheless, they had little influence on the numerical values of the equilibrium constants measured in the present work. They were rather used to check that no important pH change of the working solutions occurred with time, which was observed in all cases.

TRLFS analysis

TRLFS recordings were carried out using our “FLUO 2001” experimental set-up that has been described elsewhere.²⁰ The main features of the excitation source are briefly given here as it was different from that used in previous studies. The excitation laser beam was generated by a 266 nm quadrupled Brilliant Nd-YAG laser, coupled to an optical parametric oscillator system (Quantel, France). The wavelength was tuned to 395 nm, providing about 2 mJ of energy in a 5 ns pulse with a repetition rate of 10 Hz.

The treatment procedure of the TRLFS spectra is given here. The acquisition parameters were chosen to optimise the measurements, as diluted and concentrated europium solutions were analysed. Particularly, the delay, D , and the gatewidth, L , parameters for the synchronisation of the activation of the detector with the laser pulses, were fixed at 10 μs and 800 μs respectively. This enables to measure the major part of the fluorescence of $\text{Eu}(\text{III})$ after laser excitation unless saturation of the detector occurred for too concentrated solutions. In this latter case, the time resolution parameters were changed, which was accounted by normalisation of the fluorescence intensity for each wavelength λ , as follows.

$$I_{\lambda, \text{norm}} = \frac{I_{\lambda}}{[\text{Eu}]_{\text{total}} E_{\text{laser}} t_{\text{int}}} \times \frac{\exp(-\frac{810}{\tau}) - \exp(-\frac{10}{\tau})}{\exp(-\frac{D+L}{\tau}) - \exp(-\frac{D}{\tau})} \quad (2)$$

I_{λ} is the measured fluorescence intensity at wavelength λ , E_{laser} is the laser energy, t_{int} is the integration time, τ is a mean fluorescence lifetime. The emission at 618 nm was monitored for lifetime determinations. The experimental value of τ results from the fit of the fluorescence decay using a mono-exponential function as it was observed that a bi-exponential function did not enhance the quality of the fit in all cases. τ was measured when the europium concentration was sufficiently high for detection. The fluorescence spectra were treated by using the decomposition software GRAMS/32[®].

Solid preparation

The sodium double carbonate $\text{NaEu}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$ was prepared by dissolving $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a 1 mol L^{-1} Na_2CO_3 solution. Although the solution was highly oversaturated, almost complete dissolution of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was achieved by using an ultrasonic bath until the solution was limpid. After 4 days, a fraction of the white precipitate was filtered and washed with deionised water, and analysed by X-ray diffraction (XRD). The XRD powder patterns are consistent with the ones reported for $\text{NaM}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}(\text{s})^{21}$ and for $\text{NaM}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})^{19,22}$ with $\text{M} = \text{Nd}$ and Eu . Our solid was also characterised by FTIR (Bruker Vector 22 FTIR) as a KBr pellet. The IR spectrum is very similar to IR spectra reported for analogous solid compounds.^{19,22} Particularly, a broad band centred at about 3360 cm^{-1} was observed, which is specific of the presence of water molecules. Consequently, it was assumed that $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ was formed since our preparation procedure is similar to the one of Fannin *et al.*²² The number of water molecules, x , in the solid stoichiometry is involved in activity corrections related to Equilibrium 1, leading to small corrections on solubility data; however, its influence is not negligible when deducing ε , the empirical SIT coefficients, from the fit of solubility data (see *Activity coefficients*).

After a 4-week equilibration period, the well-crystallised $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ solid was again filtered, washed with deionised water, and used as the initial solid for solubility experiments. XRD analyses were performed on a few samples when measuring their solubilities to ensure that no solid phase change occurred. No particular precaution was however taken for the storage of the solid before it was analysed by XRD; additional peaks were observed on the diffraction patterns when the solid was filtered a few days prior to XRD analysis, indicating the presence of $\text{Eu}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}(\text{s})$ and possibly $\text{Na}_2\text{CO}_3(\text{s})$ phases. The effect of drying conditions has been investigated by Fannin *et al.*²² whereas $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ is stable in aqueous conditions, exposure to dry air alters it, and the alteration product $\text{Eu}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}(\text{s})$ forms. This phenomenon occurred in a few of our samples, but not when analysis was performed immediately after the filtration of the solid. Thus it was concluded that a crystalline phase of $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ was stable in all the aqueous solutions.

Solubility experiments

Several $\text{Na}_2\text{CO}_3/\text{NaClO}_4$ solutions were prepared with different $[\text{CO}_3^{2-}]$ and $[\text{Na}^+]$. An additional batch containing NaCl instead of NaClO_4 was prepared to assess the influence of the ionic medium on the solubility. Few tens of mg of the $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ solid were added to 25-mL carbonate solutions, so that they were initially undersaturated. All the batches were continuously shaken for the whole period of the experiment. Sampling was made after 10 and 16 weeks: for each solution, $-\lg[\text{H}^+]$ was measured by the use of the appropriate modified electrode and an aliquot of the solution was taken out. Filtration was performed using a 0.22- μm porosity filter as it was verified that this pore size ensured efficient filtration. To our knowledge for concentrated carbonate solutions where highly-charged limiting complexes are dominating, colloids are not observed; and this was confirmed in this study. The filter was first saturated with about 2 mL of solution, which were discarded, and the next filtered few mL were used for analysis of $[\text{Eu}]$. A known volume of the filtrate was mixed with an appropriate volume of a 1 mol L^{-1} HNO_3 solution to neutralise CO_3^{2-} and keep a strong acidity, more than 0.5 mol L^{-1} H^+ . The concentrations of europium in these solutions were then measured by ICP-AES. The response of the detector was calibrated with europium solutions in 0.5 mol L^{-1} HNO_3 prepared from a commercial stock 10,000-ppm Eu standard solution (Spex, CertiPrep[®], 5% HNO_3). Based on the standard deviation, the error on $[\text{Eu}]$ in the samples was estimated to be less than 3%.

Methods

Interpretation of lifetime measurements

Hydration of the limiting carbonate complex has been investigated on the basis of the method developed by Horrocks *et al.*²³ Vibronic coupling of the excited $\text{Eu}(\text{III})$ ion with OH oscillators of coordinated water molecules leads to a radiationless de-excitation process. Consequently, the fluorescence lifetime of $\text{Eu}(\text{III})$ correlates to $n_{\text{H}_2\text{O}}$, the number of remaining water molecules in the first coordination sphere of Eu^{3+} . The correlation

$$n_{\text{H}_2\text{O}} = \frac{1.07}{\tau} - 0.62 \quad (3)$$

has been determined from lifetime measurements for $\text{Eu}(\text{III})$ doped Lanthanum compounds with known numbers of coordinated water molecules.²⁴ Eq. 3 has been shown to give consistent results with uncertainty of ± 0.5 water molecules. An analogous relationship for $\text{Cm}(\text{III})$ was applied to fluorescence lifetimes measured for $\text{Cm}(\text{III})$ soluble species resulting in reasonable values of $n_{\text{H}_2\text{O}}$.²⁴ Thus Eq. 3, determined for solid

compounds, is expected to be transferable to aqueous complexes. Alternatively, similar correlations can be directly obtained for aqueous complexes from lifetime measurements in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures since the non-radiative de-excitation process is far less effective for OD oscillators.²³ In this case, $n_{\text{H}_2\text{O}}$ can be expressed as

$$n_{\text{H}_2\text{O}} = {}^w n_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}} \quad (4)$$

where ${}^w n_{\text{H}_2\text{O}}$ is the hydration number of the $\text{Eu}(\text{III})$ species in pure water, and $x_{\text{H}_2\text{O}}$ the molar fraction of H_2O in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures. While $x_{\text{H}_2\text{O}}$ is experimentally determined, ${}^w n_{\text{H}_2\text{O}}$ is obtained by correlation with Eq. 3, giving the working equation

$${}^w n_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}} = \frac{1.07}{\tau} - 0.62 \quad (5)$$

which should be verified for a given value of ${}^w n_{\text{H}_2\text{O}}$. Then measuring lifetimes in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures enables an estimation of the best value of ${}^w n_{\text{H}_2\text{O}}$ by linear regression analysis.

Thermodynamic description

For $A^+ = \text{Na}^+$, $M = \text{Eu}(\text{III})$ and $x = 6$, Equilibrium 1 is the meaningful dissolution reaction of the solid compound $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in our experimental conditions.

$$K_{s,i} = \frac{[\text{Na}^+][\text{Eu}(\text{CO}_3)_i^{3-2i}]}{[\text{CO}_3^{2-}]^{i-2}} \quad (6)$$

is its equilibrium constant, which is a combination of the solubility product of $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$

$$K_s = [\text{Na}^+][\text{Eu}^{3+}][\text{CO}_3^{2-}]^2 \quad (7)$$

for Equilibrium



and the stepwise formation constant of $\text{Eu}(\text{CO}_3)_i^{3-2i}$

$$K_i = \frac{[\text{Eu}(\text{CO}_3)_i^{3-2i}]}{[\text{Eu}(\text{CO}_3)_{i-1}^{5-2i}][\text{CO}_3^{2-}]} \quad (9)$$

for Equilibrium



Activity coefficients and water activity are included in the equilibrium constants. Many other possible species, particularly hydroxide, hydroxo-carbonate and bicarbonate complexes might form. Their formations have been considered in our data treatment. However, after performing sensitivity analyses, it was concluded that their influences were within uncertainties on the interpretation model of the experimental results. As a consequence, the corresponding equations for the formation of these complexes are omitted for clarity.

When $\text{Eu}(\text{CO}_3)_i^{3-2i}$ predominates in the solution, $[\text{Eu}]$, the solubility of $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ is approximately $[\text{Eu}(\text{CO}_3)_i^{3-2i}]$, and Eq. 9 writes

$$\lg[\text{Eu}] + \lg[\text{Na}^+] \approx \lg[\text{Eu}(\text{CO}_3)_i^{3-2i}] + \lg[\text{Na}^+] \\ = \lg K_{s,i} + (i-2) \lg[\text{CO}_3^{2-}] \quad (11)$$

showing that solubility measurements can be used to determine i and $\lg K_{s,i}$. Namely, the plot of $(\lg[\text{Eu}] + \lg[\text{Na}^+])$ vs. $\lg[\text{CO}_3^{2-}]$ should be linear with slope $(i-2)$ and intercept $\lg K_{s,i}$.

Activity coefficients

The activity coefficients are used to account for the deviation from ideal solutions. Here, the equilibrium constants, K , are expressed with concentrations, which are experimentally determined, rather than activities. Consequently the activity coefficients are implicitly included in the formation constants,

and are calculated by using SIT Formula (Eq. 12-13), usually valid for ion concentrations up to about 4 mol L⁻¹.⁴

$$\lg K^{\text{DH}} = \lg K^{\circ} - \sum_{i,j} \varepsilon_{i,j} m_j - \nu_{\text{H}_2\text{O}} \lg a_{\text{H}_2\text{O}} \quad (12)$$

$$\lg K^{\text{DH}} = \lg K + \Delta \nu \lg p - \Delta z^2 D \quad (13)$$

where $\Delta \nu = \sum_i \nu_i$, $\Delta z^2 = \sum_i \nu_i z_i^2$, $D = A I_m^{1/2} / (1 + b r_i I_m^{1/2})$. K^{DH} includes the Debye-Hückel contribution to K in molal unit (mol kg⁻¹), ν_i is the stoichiometric coefficient of the reacting species i (positive for products and negative for reactants), p is the molar-to-molal conversion factor (for mixtures of electrolytes, p was taken as the concentration-weighted mean of tabulated values⁴), z_i is the charge of the species i , D is the Debye-Hückel term dependent on theoretical values of A , b and r_i , the ionic radius of i , I_m is the ionic strength in molal unit, K° is the equilibrium constant at zero ionic strength, $\varepsilon_{i,j}$ is the ion interaction coefficient for the species i and j , and is assumed to equal zero for neutral species and for ions of same charge-sign, m_j is the molality of the species j . Values of some parameters are given in the NEA-TDB review books; for example, at 25°C and 1 bar, $A = 0.509$ (kg mol⁻¹)^{0.5}, and $b r_i = 1.5$ (kg mol⁻¹)^{0.5} whatever the ions. Ref. 4 is the major update including explanations for the selection of $\varepsilon_{i,j}$ values.

The SIT terms $\varepsilon_{i,j} m_j$ can be introduced by virial expansions, or from van der Waals equation for gas. In the latter demonstration, a more appropriate volume exclusion term is also obtained. In both cases, $\varepsilon_{i,j} m_j$ is better written $\varepsilon_{i,j} m_j T^{\circ}/T$, where T° is the absolute temperature at which $\varepsilon_{i,j}$ was measured. However since $\varepsilon_{i,j}$ is an empirical parameter, it also fits possible systematic errors of the SIT formula: the theoretical 1/T dependency needs experimental confirmation. For this reason, we had rather proposed empirical developments for fitting $\varepsilon_{i,j}$ values variations with T .^{7,25} We recently applied the theoretical formula $\varepsilon_{i,j} m_j T^{\circ}/T$ which appeared to account reasonably well for several experimental data, but not for $\text{NpO}_2(\text{CO}_3)_3^{4-} / \text{NpO}_2(\text{CO}_3)_3^{5-}$,²⁶ this exception might be attributed to ion-pairing of Na^+ with the highly negatively-charged species $\text{NpO}_2(\text{CO}_3)_3^{5-}$, as already suggested for the U(V) analogue.^{1,27} In the present study, the working temperature was not 25°C, but rather (23±1)°C. It is possible to use the relationship $\varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}, 298.15 \text{ K}} = (T/298.15) \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}, T}$ to estimate the value of $\varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}}$ at 25°C. Since T is quite close to 298.15 K, the temperature correction, $\Delta \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}} / \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}, 298.15 \text{ K}}$, is within uncertainty: $298.15 / (295.15 \pm 1) - 1 = 0.007 \pm 0.003$, and this correction was not performed. For $\varepsilon_{\text{A}^+, \text{M}(\text{CO}_3)_4^{5-}}$, similar correction is more speculative since ion-pairing cannot be excluded.

Extrapolating solubility product to zero ionic strength

SIT Formula (Eq. 12) was used for extrapolating the values of the formation constants to other ionic conditions. It is particularly useful for comparing literature data, and for extracting standard values at zero ionic strength (typically K°) from experimental ones (typically K). This practical definition of the standard state we used is consistent with the one used in the NEA-TDB reviews that also applied SIT Formula. A few assumptions are commonly associated to SIT Formula: when a supporting electrolyte AX (usually NaClO_4 or NaCl) is introduced for maintaining constant ionic strength at m , the molality of AX, summation on j cancels in Eq. 12; thus for each ion i , only interactions with the main counter-ion A^+ or X^- are taken into account via $\varepsilon_{i, \text{A}^+}$ or $\varepsilon_{i, \text{X}^-}$. Moreover m has a little effect on ϕ_{AX} , the mean value of $\lg(a_{\text{H}_2\text{O}})/m$, which was therefore considered as constant: using the mean value $\phi_{\text{NaClO}_4} = -0.015_3$ kg mol⁻¹ we calculated water activities for various NaClO_4 concentrations that were in agreement with the values calculated with the Pitzer's formula and associated tabulated parameters.²⁸ This approximation is theoretically not consistent with SIT Formula, since the activity of water is related to the mean

activity coefficient, which, in turn, can be calculated by using SIT Formula and $\varepsilon_{\text{A}^+, \text{X}^-}$.^{27,29,30} However, we checked this approximation for many systems.³⁰ For Reaction 10 with $i \geq 3$, Eq. 12 writes

$$\lg K_i^{\text{DH}} = \lg K_i^{\circ} - \Delta \varepsilon_i m_{\text{Na}^+} \quad (14)$$

$$\Delta \varepsilon_i = \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_i^{3-2i}} - \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_i^{5-2i}} - \varepsilon_{\text{Na}^+, \text{CO}_3^{2-}} \quad (15)$$

Eq. 14 is valid, when one observes linear variations of $\lg K_i^{\text{DH}}$ vs. m_{Na^+} . In that case, intercept is $\lg K_i^{\circ}$ and slope ($-\Delta \varepsilon_i$). For Equilibrium 1, the above simplifications in SIT Formula do not stand anymore. For concentrated carbonate aqueous solutions with NaClO_4 , $m_{\text{CO}_3^{2-}}$ is not negligible against $m_{\text{ClO}_4^-}$, and, with $i \geq 2$, Eq. 12 now writes

$$\lg K_{s,i}^{\text{DH}} + \Delta(\varepsilon m) = \lg K_{s,i}^{\circ} - \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_i^{3-2i}} m_{\text{Na}^+} \quad (16)$$

$$\Delta(\varepsilon m) = \varepsilon_{\text{Na}^+, \text{CO}_3^{2-}} [m_{\text{CO}_3^{2-}} - (i-2) m_{\text{Na}^+}] + \varepsilon_{\text{Na}^+, \text{ClO}_4^-} m_{\text{ClO}_4^-} + 6 \lg a_{\text{H}_2\text{O}} \quad (17)$$

According to Eq. 16, one expects ($\lg K_{s,i}^{\text{DH}} + \Delta(\varepsilon m)$) vs. m_{Na^+} to vary linearly with intercept $\lg K_{s,i}^{\circ}$ and slope ($-\varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_i^{3-2i}}$). Finally, combining Eqs. 11 and 16 gives the working equations used later on for ionic strength corrections involved for Equilibrium 1 with $\text{A}^+ = \text{Na}^+$, $\text{M} = \text{Eu(III)}$, $x = 6$, and $i = 3$:

$$\lg K_{s,3}^{\text{DH}} + \Delta(\varepsilon m) = \lg K_{s,3}^{\circ} - \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}} m_{\text{Na}^+} \quad (18)$$

$$\Delta(\varepsilon m) = \varepsilon_{\text{Na}^+, \text{CO}_3^{2-}} [m_{\text{CO}_3^{2-}} - m_{\text{Na}^+}] + \varepsilon_{\text{Na}^+, \text{ClO}_4^-} m_{\text{ClO}_4^-} + 6 \lg a_{\text{H}_2\text{O}} \quad (19)$$

The working equations for the stepwise complexation constants are obtained from Eq. 14

$$\lg K_3^{\text{DH}} = \lg K_3^{\circ} - \Delta \varepsilon_3 m_{\text{Na}^+} \quad (20)$$

$$\lg K_4^{\text{DH}} = \lg K_4^{\circ} - \Delta \varepsilon_4 m_{\text{Na}^+} \quad (21)$$

for $i = 3$ and 4 respectively, where

$$\Delta \varepsilon_3 = \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}} - \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_2^{2-}} - \varepsilon_{\text{Na}^+, \text{CO}_3^{2-}} \quad (22)$$

$$\Delta \varepsilon_4 = \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_4^{5-}} - \varepsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}} - \varepsilon_{\text{Na}^+, \text{CO}_3^{2-}} \quad (23)$$

Eqs. 20-23 will be used for comparison and discussion of literature data.

Comparing solubilities measured in NaClO_4 and NaCl aqueous solutions

We also used SIT Formula for the small activity corrections on solubility measurements at constant $[\text{Na}^+]$ and $[\text{CO}_3^{2-}]$ between NaClO_4 and NaCl aqueous solutions. If i in Eq. 11 is assumed to be independent of the nature of the salt, it can be expected

$$\lg[\text{Eu}]_{\text{NaClO}_4} - \lg[\text{Eu}]_{\text{NaCl}} = \delta \quad (24)$$

where $\delta = \lg K_{s,i}(\text{NaClO}_4) - \lg K_{s,i}(\text{NaCl})$ with $K_{s,i}(\text{NaClO}_4)$ and $K_{s,i}(\text{NaCl})$ are the values of $K_{s,i}$ in NaClO_4 and NaCl aqueous solutions respectively. In NaCl media, p_{NaClO_4} , $\varepsilon_{\text{Na}^+, \text{ClO}_4^-}$ and ϕ_{NaClO_4} are changed for p_{NaCl} , $\varepsilon_{\text{Na}^+, \text{Cl}^-}$ and ϕ_{NaCl} respectively. Considering here that the assumptions described in the previous section are valid, *i.e.* $[\text{Na}_2\text{CO}_3]$ can be neglected against $[\text{NaCl}]$ or $[\text{NaClO}_4]$, and using Eq. 16, Eq. 24 writes

$$\delta = \Delta Z^2 (D_{\text{NaClO}_4} - D_{\text{NaCl}}) - (4-i) \lg (p_{\text{NaCl}}/p_{\text{NaClO}_4}) - [\text{Na}^+] ((\Delta \epsilon_{i(\text{NaClO}_4)} + x \phi_{\text{NaClO}_4}) p_{\text{NaClO}_4} - (\Delta \epsilon_{i(\text{NaCl})} + x \phi_{\text{NaCl}}) p_{\text{NaCl}}) \quad (25)$$

where D_{NaClO_4} and D_{NaCl} are the Debye-Hückel terms in NaClO_4 and NaCl aqueous solutions respectively, and

$$\Delta \epsilon_{i(\text{NaClO}_4)} = \epsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-2i}} + \epsilon_{\text{Na}^+, \text{CO}_3^{2-}} - \epsilon_{\text{Na}^+, \text{ClO}_4^-} \quad (26)$$

$$\Delta \epsilon_{i(\text{NaCl})} = \epsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-2i}} + \epsilon_{\text{Na}^+, \text{CO}_3^{2-}} - \epsilon_{\text{Na}^+, \text{Cl}^-} \quad (27)$$

Assuming values for i and x , δ can be calculated for given conditions by using Eq. 25. Finally, from Eqs. 11 and 24, it comes

$$\lg[\text{Eu}] + \lg[\text{Na}^+] + \delta = \lg K_{s,i(\text{NaClO}_4)} + (i-2) \lg[\text{CO}_3^{2-}] \quad (28)$$

which is the working equation for comparing solubility data measured in NaCl solutions on the same figure as for NaClO_4 solutions: we plotted $(\lg[\text{Eu}] + \lg[\text{Na}^+] + \delta)$ vs. $\lg[\text{CO}_3^{2-}]$ measured in NaClO_4 and NaCl aqueous solutions respectively ($\delta = 0$ in NaClO_4 solutions).

Results and discussion

TRLFS analysis

Fluorescence spectra were recorded for all the filtrated solutions, which were previously equilibrated with $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ (Table 1). The main emission was observed at 618 nm and is due to the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of $\text{Eu}(\text{III})$, an emission particularly sensitive to complexation (Fig. 1). Less sensitive transitions were observed from the ${}^5\text{D}_0$ excited state to the ${}^7\text{F}_0$, ${}^7\text{F}_1$, ${}^7\text{F}_3$, and ${}^7\text{F}_4$ states centred at about 580, 595, 653, and 698 nm, respectively. The relative intensities I_λ/I_{618} compare well, *i.e.* the shapes of the spectra were very similar for 3 mol L^{-1} Na^+ solutions, and the values of $I_{618, \text{norm}}$ did not vary more than the uncertainties with $\lg[\text{CO}_3^{2-}]$. This is good indication that there was a single major species of $\text{Eu}(\text{III})$ whatever the carbonate concentration, so that these spectra are actually a single spectrum, the one of the limiting carbonate complex of $\text{Eu}(\text{III})$. Other solutions with different $[\text{Na}^+]$ were analysed: spectra different from that of the limiting carbonate complex were indeed detected; shoulders appeared on the smaller wavelength side of the peaks centred at 595 and 618 nm, which suggested the presence of at least one additional species. This is also indicated by the slight increase of the full width at mid height (FWMH) and the decrease of $I_{618, \text{norm}}$ for the hypersensitive transition at 618 nm (see Fig. 2 and Table 1). These changes from the spectrum of the limiting complex occurred when $[\text{CO}_3^{2-}]$ and $[\text{Na}^+]$ were decreased, which is consistent with partial dissociation of the limiting carbonate complex. The rate of dissociation was assessed from spectral decompositions of the two spectra using the now known spectrum of the limiting carbonate complex. We determined that approximately 50 % of the species was dissociated at 1 mol L^{-1} Na^+ and $\lg[\text{CO}_3^{2-}] = -2.05$, and more than 60 % at 0.06 mol L^{-1} Na^+ and $\lg[\text{CO}_3^{2-}] = -1.56$.

Fluorescence lifetimes of $\text{Eu}(\text{III})$ in 1 mol L^{-1} Na_2CO_3 solutions were measured in pure H_2O and pure D_2O , and in their mixtures to vary $x_{\text{H}_2\text{O}}$. The best agreement with Eq. 5 is observed for ${}^w_{\text{H}_2\text{O}} = 1.8 \pm 0.5$ (Fig. 5). τ was also measured in filtrated solutions, previously equilibrated with $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, for $[\text{CO}_3^{2-}] > 1 \text{ mol L}^{-1}$ (Table 1): calculated ${}^w_{\text{H}_2\text{O}}$ values were ranging from 1.9 to 2.05. Assuming that CO_3^{2-} is a bidentate ligand and with ${}^w_{\text{H}_2\text{O}} \approx 2$, the coordination numbers of $\text{Eu}(\text{CO}_3)_3^{3-}$ and $\text{Eu}(\text{CO}_3)_4^{5-}$ would be about 8 and 10, respectively, in aqueous solution. This is to compare with 8.3, the number of coordinated water molecules for the free Eu^{3+} ion

in pure water.³¹ In our conditions the number of water molecules in the first coordination sphere of $\text{Eu}(\text{III})$ can be expected to be smaller than for Eu^{3+} as a result of electrostatic repulsions between the 3 CO_3^{2-} , and the decrease of the water activity (associated with increased ionic strength). Although this result suggests the presence of $\text{Eu}(\text{CO}_3)_3^{3-}$ under our experimental conditions, the relevant stoichiometry of the complex cannot be definitely concluded due to uncertainty of ${}^w_{\text{H}_2\text{O}}$.

Solubility measurements

Comparing the europium concentrations measured after 10 and 16-week equilibration periods evidenced that a steady state was reached. No significant change was observed whatever the solution. Therefore all these data were used for the quantitative thermodynamic interpretation and associated sensitivity analysis. Note that equilibrium was reached from undersaturation, except in the batch in which $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ was precipitated in 1 mol L^{-1} Na_2CO_3 . For this latter solution, analyses were performed after 16 and 20 weeks, and the measured solubility is similar to that measured by dissolution in a 1 mol L^{-1} Na_2CO_3 / 1 mol L^{-1} NaClO_4 solution, hence at higher Na^+ concentration and ionic strength. The slight difference almost disappears when taking into account the Na^+ concentrations according to Eq. 11. So the good agreement indicates that equilibrium conditions were achieved.

The experimental data at 3 mol L^{-1} Na^+ were interpreted assuming the formation of carbonate complexes according to Eq. 11. A straight line with a slope of 1 describes reasonably well the data (Fig. 3), which shows that $\text{Eu}(\text{CO}_3)_3^{3-}$ predominates for $0.01 \leq [\text{CO}_3^{2-}] \leq 1 \text{ mol L}^{-1}$ at 3 mol L^{-1} Na^+ . Our attempts to interpret the solubility measurements with the formation of hydroxide or hydroxo-carbonate complexes were unsuccessful, so insignificant influence of their stabilities was concluded. The effect of Cl^- on solubility was checked by using NaCl salt as the supporting electrolyte in one of the batches instead of ClO_4^- anion. The expected difference in the value of $\lg K_{s,3}$ in the NaCl and NaClO_4 media was calculated using Eq. 25 and tabulated data:⁴ for 3 mol L^{-1} Na^+ and 0.1 mol L^{-1} CO_3^{2-} , we obtained $\delta = 0.06_4$ for $i = 3$ and $x = 6$; this small correction was taken into account for interpretation. The data dots for the NaCl medium are consistent with others for NaClO_4 conditions, validating the ionic strength correction (notably anion-anion interaction parameters are not needed in SIT Formula), and suggesting that no chloride complexes were observed, which is in agreement with previous studies on $\text{Am}(\text{III})$.^{7,8} By linear regression analysis the values 0.88 ± 0.11 and $-4.3_6 \pm 0.1_4$ were obtained for the slope and the intercept, respectively (uncertainty equals 1.96σ , where σ is the standard deviation). Considering that only few data are used in the statistical analysis, the value of the slope was forced to equal 1 for consistency with the speciation model, which still agrees with all the data within their uncertainties; then we obtained $\lg K_{s,3} = -4.2 \pm 0.2$ at 3 mol L^{-1} Na^+ . We attempted to also take the hypothetical $\text{Eu}(\text{CO}_3)_4^{5-}$ complex into account (slope 2) for the highest $[\text{CO}_3^{2-}]$. Since this complex has not been observed by TRLFS, we determined a maximum value of $\lg K_4$, $\lg K_4^{\text{max}} = -0.38$, based on its possible formation at higher $[\text{CO}_3^{2-}]$ than 2 mol L^{-1} . These data are reported in Table 2 for comparison with literature data and their reliability is discussed below.

Extrapolating to zero ionic strength

The effect of ionic strength on the solubility of $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ was also investigated using SIT Formula for $K_{s,3}$ (Eq. 18-19). The validity of the interpretation of the experimental data at various Na^+ concentrations was assessed by plotting $(\lg K_{s,3}^{\text{DH}} + \Delta(\epsilon m))$ vs. m_{Na^+} , which, as expected from Eq. 18, appeared to be linear within reasonable uncertainty (Fig. 4). When dissociation of $\text{Eu}(\text{CO}_3)_3^{3-}$ was suspected from analysis of TRLF spectra, the data dots were excluded from the linear regression analysis. The linear regression provided

$\lg K_{s,3}^{\circ} = -5.60 \pm 0.2$ and $\epsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}} = 0.04 \pm 0.06$ ($\pm 1.96\sigma$) providing a fairly good correlation of the data. The value of $\epsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}}$ is quite different from the values for $\text{Am}(\text{CO}_3)_3^{3-}$, -0.15 ,⁶ -0.15 ± 0.05 ⁴ and -0.23 ± 0.07 ⁵. However the determination of $\epsilon_{\text{Na}^+, \text{Eu}(\text{CO}_3)_3^{3-}}$ was not only affected by the scattering of experimental data, but it also accounted for systematic errors when calculating values of $\Delta(\epsilon_m)$ and $\lg a_{\text{H}_2\text{O}}$. Hence, we increase the uncertainty on the value at zero ionic strength: $\lg K_{s,3}^{\circ} = -5.6 \pm 0.4$.

Discussion of literature data

For comparison purpose, we have compiled the available values of the stepwise formation constants, K_3 and K_4 , for Ln(III) and An(III) in Table 2. We used Eqs. 20-21 to represent these data on SIT plots (Fig. 6). A fair analogy between the M^{3+} f-element ions is observed within the large uncertainty. Linear correlations between the $\lg K_3$ data for Am(III) had also been suggested by the NEA-TDB according to Eq. 20.^{2,5} The straight line represented on Fig. 6 is the correlation proposed in the NEA-TDB "update" for Am(III).⁵ The correlation expected from Eq. 21 is not obvious because the values of $\lg K_4^{\text{DH}}$ are scattered. Previously published K_4 data are reliable only for Ce(III) solubility data,¹⁰ and for the Eu(III) solubility data in K^+ media¹⁷ (see Introduction). Maximum $\lg K_4^{\text{DH}}$ values for Eu(III) determined in the present work, and for Am(III),⁶ both also from solubility measurements are represented with downward error bars. The elevated charge of the tetra-carbonate complex can induce ion-pairing which would explain the difference between Na^+ and K^+ aqueous media. A closer look at each data is necessary to understand the reason of such scattering.

In a few studies, tri-carbonate complexes were characterised in limiting conditions. Rao *et al.* have measured the solubility of $\text{NaNd}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in Na_2CO_3 and NaHCO_3 solutions.⁹ The change of the ionic strength was taken into account by using Pitzer's Formula, and the authors concluded to the formation of $\text{Nd}(\text{CO}_3)_3^{3-}$ in up to 2 mol L^{-1} Na_2CO_3 aqueous solutions. They reported values of the standard chemical potentials of each species involved in the system at zero ionic strength, from which we recalculate $\lg K_{s,3}^{\circ} = -6.22$ (no uncertainty was given with the original data). The analogous complex $\text{Am}(\text{CO}_3)_3^{3-}$ has been evidenced at high ionic strengths by solubility measurements. Robouch carried out batch experiments in 3 mol L^{-1} NaClO_4 solutions, suggesting the stability of the limiting complex $\text{Am}(\text{CO}_3)_3^{3-}$ up to 1 mol L^{-1} CO_3^{2-} .⁶ The presence of a single species in limiting carbonate conditions was also pointed out by Robouch based on spectroscopic measurements; however he did not reported all the spectra. Although the initial solid, $\text{Am}_2(\text{CO}_3)_3(\text{s})$ is not the thermodynamically stable solid in concentrated carbonate solutions with high $[\text{Na}^+]$, both slope analysis and XRD analysis have shown that no phase transformation occurred in most of the batches, probably due to slow kinetics of formation of $\text{NaAm}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$. However, precipitation of $\text{NaAm}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$ is suspected for $[\text{CO}_3^{2-}] > 1 \text{ mol L}^{-1}$. Others studies were performed in NaCl solutions, but with carbonate concentrations less than 0.1 mol L^{-1} , which is too low to significantly observe a possible $\text{Am}(\text{CO}_3)_4^{5-}$.^{7,8} Only measurements in 4 mol L^{-1} NaCl solutions were carried out with $[\text{CO}_3^{2-}]$ higher than 0.1 mol L^{-1} ,⁷ however in addition to difficulties for the determination of the solubility-controlling solid, it is likely that oxidation of Am(III) into Am(V) occurred due to radiolysis, lowering the accuracy of the slope analysis. Finally, from the solubility studies of Robouch and Giffaut it is clear that there is no evidence of any tetra-carbonate Am(III) complex even at high $[\text{CO}_3^{2-}]$ and $[\text{Na}^+]$.

These results might be balanced with determinations of the stabilities of tetra-carbonate complexes. Faucherre *et al.* have admitted the existence of $\text{Ln}(\text{CO}_3)_4^{5-}$ for several lanthanide ions from solubility experiments and cryoscopic studies.¹⁷ Solubility measurements of $\text{KLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$, for which the solubility is much higher than that of the corresponding sodium solid

compounds, have been performed in 3.8 and 4.2 mol L^{-1} K^+ media. The authors deduced the formation of tetra-carbonate complexes from slope analysis similar to the interpretation we used in the present study. For Eu(III) and Gd(III), the measurements deviate from the model when $\lg[\text{CO}_3^{2-}] < -1.4$; the authors attributed this deviation to inaccuracy of their Ln(III) titration method for concentrations less than about $5 \times 10^{-4} \text{ mol L}^{-1}$. However, a non random dispersion of the data dots is observed, and the deviation may very well be attributed to the dissociation of the tetra-carbonate complexes into $\text{Eu}(\text{CO}_3)_3^{3-}$ (Fig. 3) and $\text{Gd}(\text{CO}_3)_3^{3-}$. Thus we re-interpreted these data and determined a value of K_4 , the stepwise formation constants of $\text{Eu}(\text{CO}_3)_4^{5-}$ and $\text{Gd}(\text{CO}_3)_4^{5-}$ (Table 2). Besides a cryoscopic method has been applied to the lanthanides heavier than Gd for which solubility was not high enough for accurate measurements; it consists in monitoring the lowering of temperature due to addition of a $\text{Eu}(\text{NO}_3)_3$ solution into a KHCO_3 - K_2CO_3 buffer solution in the KNO_3 -ice eutectic system. For all the studied Ln(III), tetra-carbonate complexes were evidenced. These results are not necessarily inconsistent with our determination of the stoichiometry $\text{Eu}(\text{CO}_3)_3^{3-}$ for the limiting complex: the highly negative tetra-carbonate complexes could very well be stabilised by ion-pairing with (less hydrated) K^+ , more efficiently than Na^+ ions. This type of difference between K^+ and Na^+ ions might also be at the origin of the difference in the solubilities of $\text{KEu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{s})$ and $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ (Fig. 3). Thus the existence of highly-charged complexes $\text{Ln}(\text{CO}_3)_4^{5-}$ could be favoured in concentrated K^+ ionic media. Similarly, tetra-carbonate complexes could also be stabilised by the $\text{C}(\text{NH}_2)_3^+$ guanidinium cation as observed by Dumonceau.¹⁵ The formation of $\text{Ce}(\text{CO}_3)_3^{3-}$ and $\text{Ce}(\text{CO}_3)_4^{5-}$ has been observed by Ferri *et al.* from solubility measurements of $\text{NaCe}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}(\text{s})$ at 3 mol L^{-1} Na^+ .¹⁰ Oxidation of Ce(III) into Ce(IV) was expected to be avoided by passing H_2 gas through the solutions in the presence of a Pd catalyst. We have verified that the reducing conditions were efficient to keep Cerium in its +3 oxidation state: we calculated that it was possible to fit the experimental data by replacing $\text{Ce}(\text{CO}_3)_4^{5-}$ by the Ce(IV) complex, $\text{Ce}(\text{CO}_3)_5^{6-}$ and assuming precipitation of $\text{CeO}_2(\text{s})$; however the resulting formation constant of $\text{Ce}(\text{CO}_3)_5^{6-}$ would then be several orders of magnitude higher than the ones of analogous $\text{M}(\text{CO}_3)_5^{6-}$ for $\text{M}^{4+} = \text{U}^{4+}$, Np^{4+} and Pu^{4+} ,^{14,5} which is not realistic. The formation of $\text{Ce}(\text{CO}_3)_4^{5-}$ even in Na^+ -based supporting electrolyte may be due to the larger ionic radius of Ce(III) than that of other Ln(III) (1.143 , 1.109 , 1.106 and 1.066 Å for 8-coordinated Ce(III), Nd(III), Am(III) and Eu(III), respectively).³² This trend suggests that the even larger La^{3+} can form a tetra-carbonate complex in limiting Na_2CO_3 conditions, but to our knowledge, it has not been studied.

Another approach has consisted in the investigation of structures of Sm(III),³³ Nd(III),^{34,35} and Ho(III)³⁶ carbonate solids by XRD analyses of single-crystals, using crystallising agents of Ln(III) complexes in concentrated K_2CO_3 , Na_2CO_3 or $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ solutions. From the positions of the oxygen atoms in crystals, 9-coordinate Nd(III) and Sm(III) ions and an 8-coordinate Ho(III) ion were observed, which is consistent with the expected trend along the lanthanide series, namely ionic radii slightly decrease with atomic numbers. Whereas mononuclear Ln(III) tetra-carbonate complexes have been characterised for Nd(III)³⁵ and Ho(III),³⁶ the molecular units determined for the Nd(III)³⁴ and Sm(III)³³ ions are bridged by carbonate ligands, forming chain structures. So Ln(III) carbonate complex structures seem to be affected by the crystal preparation procedure, and more particularly by the nature of the crystallising cation *i.e.* the carbonate salt. Comparing crystal structures with limiting carbonate complexes in aqueous solutions has been attempted for Nd(III) and Ho(III) by using UV-vis-near IR absorbance and diffuse reflectance spectroscopies,³⁵ and vibrational spectroscopy,³⁶ respectively. Differences between the spectra for the solid and the corresponding solution suggest the presence of

a lower carbonate species for both Nd(III) and Ho(III), possibly in addition to a tetra-carbonate complex. Thus these characterisations of limiting carbonate complexes are not considered as strictly conclusive for aqueous solutions.

A quantitative analysis of available stability constants was performed. Different sodium double carbonate solids were used in the reported studies since they are stable in aqueous solutions with high sodium and carbonate concentrations. In order to compare the values of $\lg K_s$ and $\lg K_{s,3}$ to assess whether analogy between the M^{3+} f-elements ions is verified, it was necessary to perform extrapolation to zero ionic of these data. Literature data and calculations are reported in the Table 3. The most meaningful comparison is made by using $\lg K_{s,3}^\circ$ values, since $\lg K_{s,3}$ is the constant that is experimentally determined for a given ionic medium: the calculated values agree very well for Nd, Eu and Am, which can be interpreted as a validation of the SIT parameters that were taken from Refs. 4 and 5 for Am(III), and used for all extrapolations (see footnotes ^a of Table 3). The value of $\lg K_{s,3}^\circ$ for Ce is significantly lower than the others, and probably correlated to the existence of a tetra-carbonate limiting complex for this element. Note that extrapolation to zero ionic strength with SIT Formula may deviate for 5 mol L⁻¹ NaCl since this formula is not much accurate for such a high ionic strength. Another comparison was made with $\lg K_s^\circ$ since more values are available. We deduced the solubility product of our NaEu(CO₃)₂·6H₂O(s) solid at 3 mol L⁻¹ Na⁺ by subtracting to $\lg K_{s,3}$, the sum of $\lg K_i$ (i = 1-3), determined by TRLFS after appropriate ionic strength corrections.¹⁶ Interestingly, the solubility products of NaAm(CO₃)₂·5H₂O(s) and NaEu(CO₃)₂·5H₂O(s) have been directly measured by Runde *et al.* at low [CO₃²⁻], even if these solids should not be stable under such conditions.⁸ Comparing Ce, Nd and Eu, Fannin observed that the solubility increased with the decrease of ionic radii of the lanthanides.³⁷ However, the solubility products were found to be $\lg K_s^\circ = -22.62 \pm 2.2$, -21.25 ± 0.95 and -20.48 ± 0.69 for each lanthanide, respectively. The value for Ce was determined from solutions with 1 or 2 mol L⁻¹ Na⁺ and using an extended Debye-Hückel equation which is not designed for such ionic strength correction, which should explain the large associated uncertainty. As reported by the author, $\lg K_s^\circ$ was calculated for every measurements using an aqueous database that included M(OH)_i³⁻¹ (i=1-3), MCO₃⁺ and M(CO₃)₂²⁻, but not M(CO₃)₃³⁻; hence, when using an NEA database for Am(III) that included $\lg K_3^\circ$, Fannin adjusted $\lg K_s^\circ$ to different values (-21.95 and -21.46 for Nd and Eu, respectively). We attempted to perform slope analysis on the raw solubility data to determine the stoichiometries of the main complexes; however, we observed experimental differences of more than 1 log unit on Eu solubility for solutions of same pH and carbonate concentration, which could be originated from difference in the crystallinity of the solids or from fair efficiency of the filtration due to the too large pore size of the filter (10-16 μm). Consequently, these data were not included in Table 3. A fair agreement is typically found between all the other values calculated at zero ionic strength within uncertainties (Table 3). These data may be reduced to the four values that have been obtained from $\lg K_{s,3}$, which is a more reliable determination; so a good agreement is observed for $\lg K_s^\circ$ between Ce, Nd, Eu and Am, in accordance with $\lg K_3^\circ = -21.0 \pm 0.5$, the value selected for Am(III) by NEA-TDB "Update".⁵

Summary

Finally, from solubility measurements of NaEu(CO₃)₂·6H₂O in concentrated carbonate solutions with high ionic strength (3 mol L⁻¹ NaClO₄), we observed the limiting complex Eu(CO₃)₃³⁻, in agreement with previous works on Am(III) and Nd(III). Solubility experiments in various ionic media were used to validate the speciation of Eu(III) by applying SIT Formula to these particular conditions. Novel values of the equilibrium

constants, K_s , $K_{s,3}$ and K_3 , as well as a maximum value for K_4 , have been proposed. The stability of Eu(CO₃)₃³⁻ has been confirmed by TRLFS, and we have estimated the coordination number of Eu(CO₃)₃³⁻ from fluorescence lifetimes which should be about 8 in aqueous solutions of high [Na⁺]. Analysis of literature data has emphasised a few interesting points: conversely, it was shown that Ce(CO₃)₄⁵⁻ preferentially forms in similar conditions, suggesting an effect of the larger ionic radius of Ce(III); tetra-carbonate complexes of heavier Ln(III) can also form in K⁺ solutions at high ionic strength, while it is not the case in Na⁺ aqueous solutions.

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Tables and table captions

Table 1 TRLFS results on filtered solutions after a 16-week equilibration period for solubility measurements. Acquisition parameters are the integration time t_{int} , the delay D, and the gatewidth L. $I_{618,\text{norm}}$ and τ are the normalised fluorescence intensity at 618 nm and the fluorescence lifetime, respectively.

$[\text{Na}_2\text{CO}_3]^{\text{a}}$ /mol L ⁻¹	$[\text{NaClO}_4]^{\text{a}}$ /mol L ⁻¹	t_{int} /s	D /μs	L /μs	$I_{618,\text{norm}}$ /a.u.	FWMH ^b /nm	τ^{c} /μs
2.00	0.00	0.5	300	50	91±17	9.1	430
1.00	0.00	0.5	50	50	90±15	9.3	410
1.00	1.00	0.5	50	100	95±15	9.3	400
0.30	2.40	0.8	10	800	79±10	9.6	-
0.10	2.80	1.5	10	800	90±11	9.1	-
0.03	2.94	2	10	800	100±13	9.3	-
0.01	2.98	8	10	800	87±11	9.5	-
0.30	0.40	0.5	50	300	82±13	9.9	350
0.10	0.80	0.5	10	800	75±9	9.7	-
0.01	0.98	10	10	800	60±8	10.5	-
0.30	0.00	0.5	50	50	91±12	9.9	340
0.03	0.00	3	10	800	50±6	12.1	-

Footnote text of Table 1:

^a Initial concentration.

^b Full width mid height for the peak at 618 nm estimated from a rough convolution of the peak by using a single mixed gaussian-lorentzian function.

^c Lifetime measurements were used for normalisation of some spectra; the variations with $[\text{CO}_3^{2-}]$ should be related to either small changes in the speciation or ionic strength effect.

Table 2 Comparison of literature data for K_i ($i=3$ or 4), the stepwise formation constants of the tri- and tetra-carbonate complexes for M^{3+} f-ions.

M	Method ^a	Medium	$m_{Na^+}/mol\ kg^{-1}$	$lg\ K_3$	$lg\ K_4$	Ref.
Ce	sol	3 mol L ⁻¹ NaClO ₄	3.50	1.5±0.2	1.1±0.2	10
Nd	sol	I → 0	0	2.88		9
Eu/Gd	sol	4.2 mol L ⁻¹ KCl	4.81 ^b		2.0±0.3	17, this work
Eu	dis	1 mol L ⁻¹ NaClO ₄	1.05	2.2	1.96	11
Eu	dis	1 mol L ⁻¹ NaClO ₄	1.05	2.37	1.9	12
Eu	TRLFS	0.1 mol L ⁻¹ NaClO ₄	0.10	2.5±0.3		16
Eu	sol	2 mol L ⁻¹ Na ₂ CO ₃	4.81		< -0.38	this work
Am	sol	3 mol L ⁻¹ NaClO ₄	3.50	2.52±0.15	< -1.44	6
Am	sol	I → 0	0	2.9±0.5		38
Am	sol	0.1 mol L ⁻¹ NaCl	0.10	1.80±0.26		7
Am	sol	4 mol L ⁻¹ NaCl	4.37	2.24±0.25		7
Am	sol	5 mol L ⁻¹ NaCl	5.61	3.2±0.5		8
Am	Review	I → 0	0	2.8±0.4		2
Am	Review	I → 0	0	2.1±0.8		5
Cm	TRLFS	1 mol L ⁻¹ NaCl	1.02	2.91±0.15	1.00±0.15	13
Cm	TRLFS	NaCl, I → 0	0	2.2±0.7	-2.16±0.7	14
Cm	Review	I → 0	0	2.1±0.8	-1.6±0.1	5

Footnote text of Table 2:

^a sol = solubility, dis = distribution.

^b value for m_{K^+} .

Table 3 Comparison of literature data for $\lg K_s$ and $\lg K_{s,3}$ for M^{3+} f-ions, extrapolated to zero ionic strength.

M	Solid	Medium	m /kg mol ⁻¹	$\lg K_{s,3}$	$\lg K_s$	$\lg K_{s,3}^{a}$	$\lg K_s^{ob}$	Ref.
Ce	NaCe(CO ₃) ₂ ·2H ₂ O	3 mol L ⁻¹ NaClO ₄	3.50	-4.9±0.2	-17.5±0.1	-6.9±0.3	-20.7±0.2	10
Nd	NaNd(CO ₃) ₂ ·6H ₂ O	I → 0	0	-6.22	-21.39	-6.22	-21.39	9
Eu	NaEu(CO ₃) ₂ ·5H ₂ O	5 mol L ⁻¹ NaCl	5.60	-	-18.1±0.2	-	-22.8±0.3	8
Eu	NaEu(CO ₃) ₂ ·6H ₂ O	3 mol L ⁻¹ NaClO ₄	3.50	-4.2±0.2	-17.5±0.4 ^c	-6.2±0.3	-20.9±0.5	this work
Am	NaAm(CO ₃) ₂ ·5H ₂ O	5 mol L ⁻¹ NaCl	5.60	-3.6±0.5	-16.5±0.5	-6.0±0.5	-21.2±0.5	8

Footnote text of Table 3:

^a $\lg K_{s,3}^o = \lg K_{s,3}^{DH} + (\Delta\epsilon_{AX} + x\phi_{AX}) m$, applied to NaM(CO₃)₂·xH₂O(s)
 $\rightleftharpoons Na^+ + M(CO_3)_3^{3-} + 2 CO_3^{2-} + x H_2O$ with $\Delta\epsilon_{NaCl} = -0.04$ kg mol⁻¹,
 $\Delta\epsilon_{NaClO_4} = -0.06$ kg mol⁻¹, $\phi_{NaClO_4} = -0.015_3$, and $\phi_{NaCl} = -0.019_4$.

^b $\lg K_s^o = \lg K_s^{DH} + (\Delta\epsilon_{AX} + x\phi_{AX}) m$, applied to NaM(CO₃)₂·xH₂O(s) =
 $Na^+ + M^{3+} + 2 CO_3^{2-} + x H_2O$ with $\Delta\epsilon_{NaCl} = 0.1$ kg mol⁻¹, $\Delta\epsilon_{NaClO_4} = 0.34$
 kg mol⁻¹, $\phi_{NaClO_4} = -0.015_3$, and $\phi_{NaCl} = -0.019_4$.

^c Estimated from TRLFS measurements of K_1 , K_2 and K_3 .¹⁶

Figures

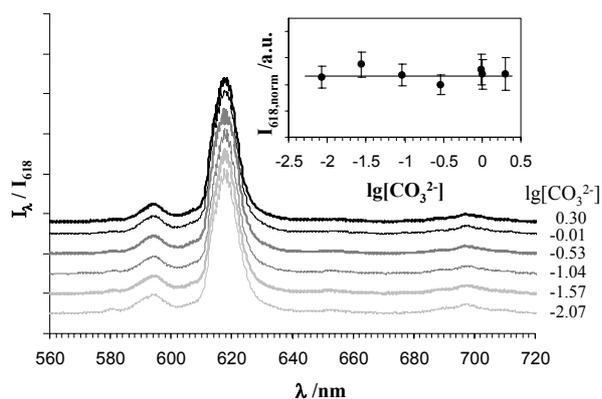


Fig. 1 Controlling Eu aqueous speciation in the solubility experiments. Evidence of a limiting carbonate complex of Eu(III) in $\text{Na}_2\text{CO}_3/\text{NaClO}_4$ solutions with $3 \text{ mol L}^{-1} \text{ Na}^+$. Relative fluorescence intensity I_λ/I_{618} as a function of the emission wavelength and $\lg[\text{CO}_3^{2-}]$. The incrustated graph shows the constant value of $I_{618, \text{norm}}$ with $\lg[\text{CO}_3^{2-}]$ (see **Table 1**).

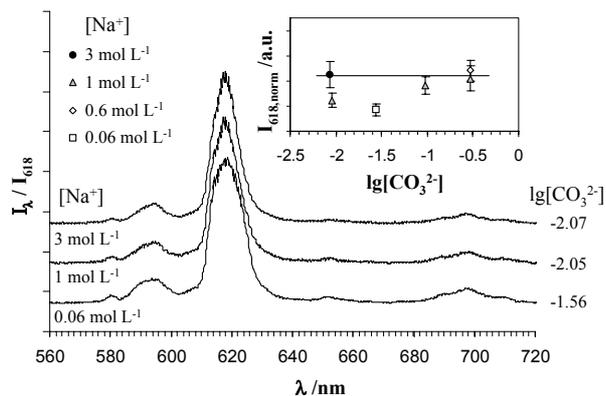


Fig. 2 Detection of the dissociation of the limiting carbonate complex of Eu(III) in $\text{Na}_2\text{CO}_3/\text{NaClO}_4$ solutions (see caption of **Fig. 1**).

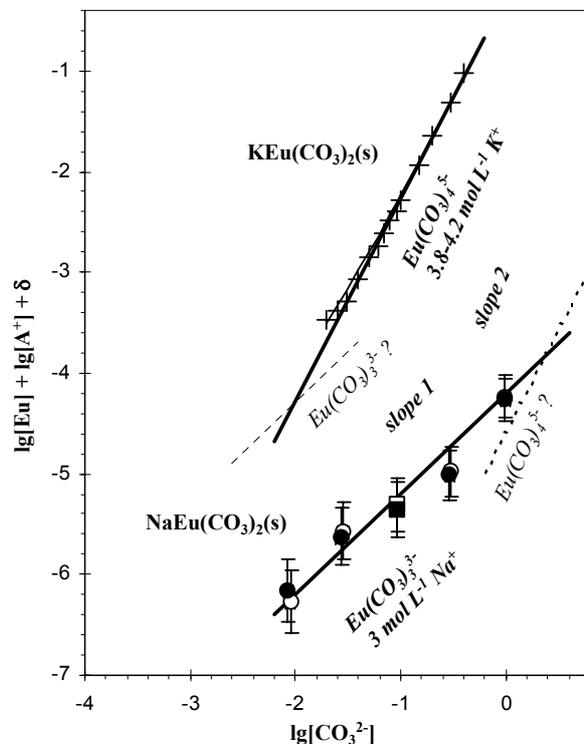


Fig. 3 Variations of $\text{AEu}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$ solubility ($\text{A}^+ = \text{Na}^+, \text{K}^+$) vs. $[\text{CO}_3^{2-}]$ at constant $[\text{A}^+]$ for determining the stoichiometry of the limiting carbonate complexes. Solubility of $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in $3 \text{ mol L}^{-1} \text{ Na}^+$ (NaClO_4) aqueous solutions after equilibration periods of 10 (\circ) and 16 weeks (\bullet) is compared to solubility of $\text{KEu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{s})$ in 3.8 to $4.2 \text{ mol L}^{-1} \text{ K}^+$ aqueous solutions ($+$).¹⁷ The appropriate activity corrections were performed for NaCl (\blacksquare) by adding δ (see text and Eq. 25).

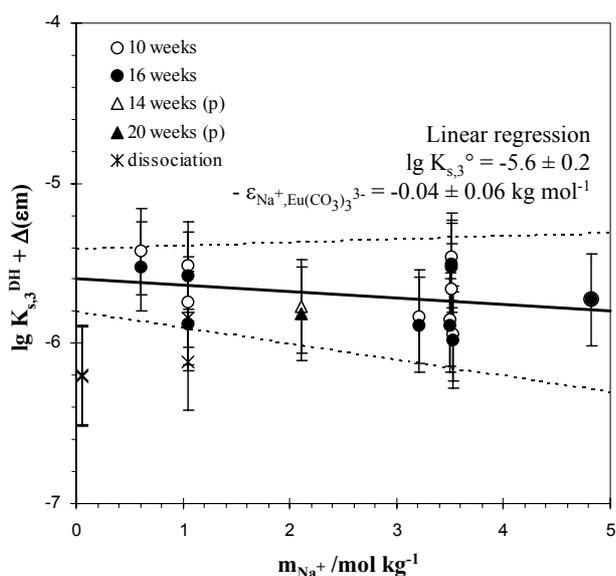


Fig. 4 Extrapolation to zero ionic strength of $\lg K_{s,3}$. Linear regression analysis of $(\lg K_{s,3}^{DH} + \Delta(\epsilon m))$ vs. m_{Na^+} (Eq. 18-19). The notation (p) means that the equilibrium is reached from oversaturation with the precipitation of $NaEu(CO_3)_2 \cdot 6H_2O(s)$. Crosses denotes partial dissociation of $Eu(CO_3)_3^{3-}$.

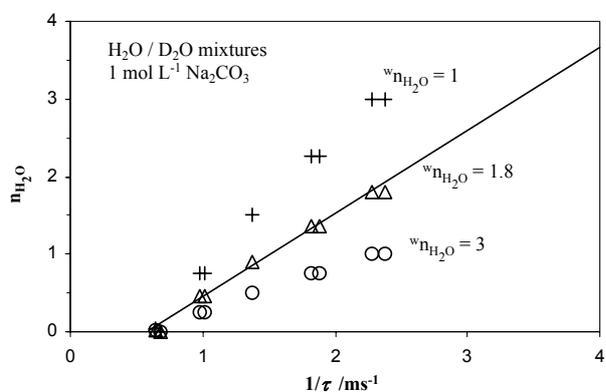


Fig. 5 Determination of $w_{n_{H_2O}}$ for $Eu(CO_3)_3^{3-}$ according to Eq. 4-5. The straight line represents the relationship determined by Kimura *et al.*: $n_{H_2O} = 1.07/\tau - 0.62$.²⁴

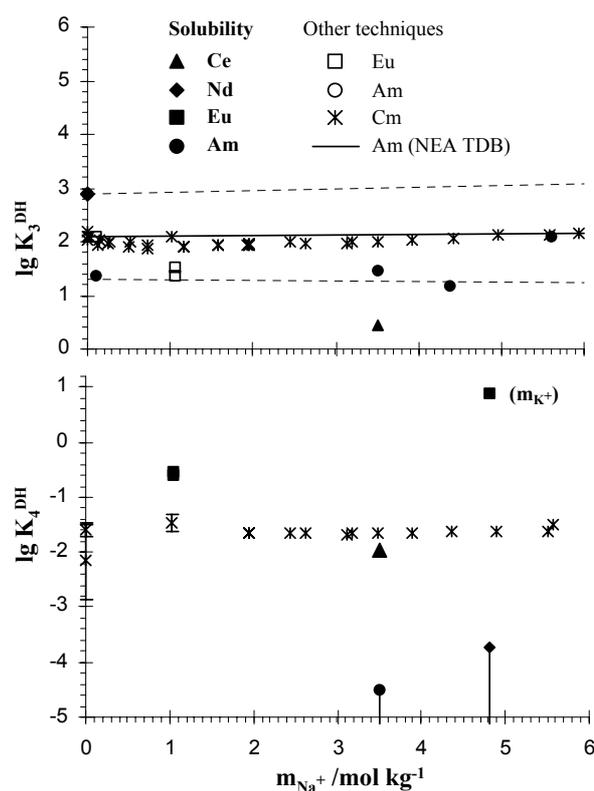


Fig. 6 SIT plots for comparison of the literature values of the stepwise formation constants K_3 and K_4 for M^{3+} f-ions in Na^+ aqueous solutions excepted when for the data in K^+ media indicated on the figure. The straight line is the NEA-TDB correlation for Am(III).⁵ K_4 data are considered reliable only for Ce solubility data, and for the Eu solubility data in K^+ media (see text).