PAPER

NJC
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$Eu(CO_3)_3^{3-}$ and the limiting carbonate complexes of other M^{3+} f-elements in aqueous solutions: a solubility and TRLFS study†

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Received (in Toulouse, France) 31st August 2004, Accepted 26th November 2004
First published as an Advance Article on the web 18th February 2005

Within the framework of environmental studies regarding radioactive waste management, the speciation of M^{3+} f-elements in concentrated carbonate solutions was investigated. Solubility measurements of $NaEu(CO_3)_2 \cdot 5H_2O(s)$ were performed at 23 ± 1 °C under fixed $[Na^+]$, by using $NaClO_4$. In 3 mol l^{-1} Na^+ aqueous solutions, the limiting complex $Eu(CO_3)_3^{3-}$ was identified in the range $0.01 < [CO_3^{2-}] < 2$ mol l^{-1}; experimental solubilities were modelled with the equilibrium: $NaEu(CO_3)_2 \cdot 5H_2O(s) + CO_3^{2-} \rightleftharpoons Na^+ + Eu(CO_3)_3^{3-} + 5H_2O$, and the logarithm of the corresponding equilibrium constant was found to be $\log K_{s,3} = -4.2 \pm 0.2$. To interpret the measurements at different $[Na^+]$, the activity coefficients of the species were calculated with the SIT formula. Time-resolved laser-induced fluorescence spectroscopy was used to verify the presence of a single complex of Eu(III) in aqueous solutions. From fluorescence lifetime measurements in 1 mol l^{-1} Na_2CO_3 solutions in H_2O–D_2O mixtures, it was determined that about two water molecules remained in the first coordination sphere of $Eu(CO_3)_3^{3-}$. 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 results in determining the stoichiometry of limiting carbonate complexes. Tricarbonate complexes of most M^{3+} f-elements appeared to be the limiting stable species in Na^+ aqueous solutions, except for Ce(III), for which a tetracarbonate complex was indeed observed. Interestingly, supporting electrolytes based on K^+ can favour tetracarbonate complexes at high ionic strength. Available values of thermodynamic constants related to various ionic media are compared on the basis of the SIT formula.

Introduction

Considerable efforts have been made in the past twenty years to construct a 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 database (TDB) of the OECD NEA (Organisation for Economic Co-operation and Development, Nuclear Energy Agency) 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 in the +3 oxidation state, An(III). $Am(CO_3)_3^{3-}$ 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} CO_3^{2-} and at 3 mol l^{-1} Na^+.[6] This conclusion was later confirmed by the solubility studies of Giffaut,[7] and Runde and Kim.[8] Accordingly, the NEA-TDB provides no evidence for the $Am(CO_3)_4^{5-}$ aqueous complex,[2] while the NEA-TDB Update gives formation data for $Cm(CO_3)_4^{5-}$.[5] Indeed, the $M(CO_3)_3^{3-}$ and $M(CO_3)_4^{5-}$ complexes have been reported[6–9, 10–14] to be the limiting complexes for M = An(III) and Ln(III), that is, their lanthanide analogues, based on different experimental conditions and techniques.

The stability of $Ln(CO_3)_4^{5-}$ complexes in $[C(NH_2)_3]_2CO_3$–$[C(NH_2)_3]HCO_3$ buffer solutions at pH 10.5 and ionic strength of 2.5 mol l^{-1} has been proposed to interpret solvent extraction data.[15] Logarithmic plots of distribution ratios against carbonate concentration give confidence in the formation of tetracarbonate complexes for all lanthanides except Ce and Pm, which were not studied. Rao and Chatt reported stability data for $Eu(CO_3)_3^{3-}$ and $Eu(CO_3)_4^{5-}$ in $NaHCO_3$ aqueous solutions at 1.0 mol l^{-1} $NaClO_4$ by solvent extraction, interpreting their results by curve fitting techniques.[12] However, in their study, $[CO_3^{2-}]$ never exceeded 0.02 mol l^{-1}, which seems too low to observe $Eu(CO_3)_4^{5-}$ in significant concentration. Since no convincing sensitivity analysis was presented, it is not clear whether the formation constants values for $M(CO_3)_4^{5-}$, or even for $M(CO_3)_3^{3-}$, are reliable.

$Cm(CO_3)_4^{5-}$ was proposed for interpreting time-resolved laser-induced fluorescence spectroscopy (TRLFS) results; the authors calculated that about 50% of $Cm(CO_3)_4^{5-}$ was formed at 0.01 mol l^{-1} CO_3^{2-} and 1 mol l^{-1} NaCl,[13] which is in disagreement with earlier results for Am(III) using a solubility method in 5 mol l^{-1} NaCl, that is, at a higher ionic strength,

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† Electronic supplementary information (ESI) available: Solubility data and calculations from dissolution experiments of $NaEu(CO_3)_2 \cdot xH_2O(s)$ in Na_2CO_3–$NaClO_4$ solutions; Bragg reflections of nonaltered and altered $NaEu(CO_3)_2 \cdot xH_2O(s)$ and literature data; XRD pattern of solubility-controlling phase and IR spectrum of $NaEu(CO_3)_2 \cdot xH_2O(s)$. See http://www.rsc.org/suppdata/nj/b4/b413002b/

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DOI: 10.1039/b413002b

which should favour the formation of $Am(CO_3)_4^{5-}$, which was not actually observed.[8] This discrepancy was attributed in the NEA-TDB update review as an effect of the difference in the ionic radii of Cm^{3+} and Am^{3+}, despite the fact that this difference was recognised to be very small.[5] Similar TRLFS measurements were carried out in our laboratory for Cm and Eu, two fluorescing M^{3+} ions in the f-element series.[16] Spectral changes are even more important for Eu than for Cm on carbonate addition, but sensitivity analysis could not draw a clear conclusion to choose the best interpretation of our experimental observations: TRLFS data were also interpreted with $Eu(CO_3)_i^{3-2i}$ species, for either $0 \leq i \leq 3$ or $0 \leq i \leq 4$. 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, that is, the lower carbonate complexes ($i \leq 2$ or 3, respectively).

Apart from Dumonceau's results on the stability of $Ln(CO_3)_4^{5-}$,[15] only two studies appeared to have clearly evidenced $M(CO_3)_4^{5-}$ species. In both cases, the authors studied the equilibria:

$$AM(CO_3)_2 \cdot xH_2O(s) + (i-2)CO_3^{2-} \rightleftharpoons A^+ + M(CO_3)_i^{3-2i} + xH_2O \qquad (1)$$

for $A^+ = K^+$, M = Eu(III)[17] and for $A^+ = Na^+$, M = Ce(III),[10] respectively, using high carbonate concentrations to obtain the limiting complexes and constant high ionic strength to allow slope analysis; sensitivity analysis is indeed feasible when the complex is dominating over a broad enough domain of $[CO_3^{2-}]$ and activity coefficient effects are negligible. When $M(CO_3)_i^{3-2i}$ is practically the only soluble complex, equilibrium (1) predicts that plotting log(solubility) *vs.* $\log[CO_3^{2-}]$ would result in a straight line with slope $(i-2)$, which is a way to determine i, related to $M(CO_3)_i^{3-2i}$. High carbonate concentrations necessarily imply significant OH^- concentrations, ranging typically from 10^{-4} to 10^{-2} mol l^{-1}, which can favour the formation of ternary mixed hydroxocarbonate complexes. In the case of Am(III), they were shown to be minor species that can be neglected in the speciation.[4,5] While 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 $[OH^-]$ of more than one log unit; in both solutions $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ 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 $[H^+]$ to observe such complexes, but rather have chosen the appropriate carbonate conditions to characterise the limiting complex of Eu(III).

We have performed solubility measurements of $NaEu(CO_3)_2 \cdot xH_2O(s)$ in concentrated Na_2CO_3 aqueous solutions with constant $[Na^+]$, obtained by $NaClO_4$ additions. The solid phases $M_2(CO_3)_3 \cdot xH_2O(s)$, $MOHCO_3(s)$ and $M(OH)_3(s)$ are also stable at 25 °C; their relative stability depends on pH and CO_2 partial pressure, as shown for M = Am(III).[18] However, $NaM(CO_3)_2 \cdot xH_2O(s)$ is the thermodynamically stable solid phase controlling solubility in concentrated sodium carbonate solutions,[7,9,10,17,19] giving little chance to phase transformation during the experiments. The Eu(III) aqueous speciation was also monitored by 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 Ln(III) and An(III) series.

Experimental

All preparations and procedures were performed at (23 ± 1) °C.

Materials

Millipore de-ionised water (Alpha-Q, 18.2 MΩ cm) was used for the preparations. The carbonate solutions were prepared from solid anhydrous Na_2CO_3 (Prolabo, Normapur®, >99.8%), $NaClO_4 \cdot H_2O$ (Merck), and NaCl (Labosi, >99.9%). The solid europium was prepared from $Eu(NO_3)_3 \cdot 6H_2O$ (Johnson Matthey, 99.99%). A stock solution of 1 mol l^{-1} HNO_3 was prepared from HNO_3 65% (Merck, Suprapur®), 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

$[H^+]$ was measured by using modified combined glass electrodes (Radiometer Analytical, XC161). Reference solutions were replaced by a $NaClO_4$–0.01 mol l^{-1} NaCl solution with 0.1, 1 or 3 mol l^{-1} Na^+ in order to have approximately the same $[Na^+]$ as the solution in which $[H^+]$ 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 $[Na^+]$ constant at either 0.1, 1 or 3 mol l^{-1}, the same as the corresponding reference solution. So $-\log[H^+]$ was used rather than pH. The calibration solutions were: (i) 0.01 mol l^{-1} HCl solution ($-\log[H^+] = 2.00$ for all $[Na^+]$); (ii) 0.1 mol l^{-1} $NaHCO_3$ solution equilibrated with 100% $CO_2(g)$ ($-\log[H^+]$ = 7.00, 6.74 and 6.63 for 0.1, 1 or 3 mol l^{-1} Na^+, respectively); and (iii) equimolar $NaHCO_3$–Na_2CO_3 solutions ($-\log[H^+]$ = 9.90, 9.78 and 9.61 for 0.1, 1 or 3 mol l^{-1} Na^+, respectively). The slopes of the calibration straight lines were always more than 97% of the theoretical slope. The response of the electrodes was 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 $-\log[H^+]$ numerical values. Nevertheless, they had little influence on the numerical values of the equilibrium constants measured in the present work. They were used instead to confirm that, in all cases, no important pH change of the working solutions occurred with time.

TRLFS analysis

Time-resolved laser-induced fluorescence spectroscopy recordings were carried out using our "FLUO 2001" experimental setup 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 the 266 nm quadrupled output of a 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 was as follows. 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*, that is, the parameters for the synchronisation of the activation of the detector with the laser pulses, were fixed at 10 μs and 800 μs, respectively. This enabled us to measure the major part of the fluorescence of Eu(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 for by normalisation of the fluorescence intensity for each wavelength λ as follows:

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

I_λ is the measured fluorescence intensity at wavelength λ, E_{laser} is the laser energy, t_{int} is the integration time, τ is the 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®.

Preparation of solids

The sodium double carbonate $NaEu(CO_3)_2 \cdot xH_2O(s)$ was prepared by dissolving $Eu(NO_3)_3 \cdot 6H_2O$ in a 1 mol l^{-1} Na_2CO_3 solution. Although the solution was highly oversaturated, almost complete dissolution of $Eu(NO_3)_3 \cdot 6H_2O$ was achieved by use of an ultrasonic bath until the solution was limpid. After 4 days, a fraction of the white precipitate was filtered and washed with de-ionised water, then analysed by X-ray diffraction (XRD). The XRD powder patterns (Fig. S1, see ESI) are consistent with those reported for $NaM(CO_3)_2 \cdot 5H_2O(s)$[21] and for $NaM(CO_3)_2 \cdot 6H_2O(s)$[19,22] with M = 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 $NaEu(CO_3)_2 \cdot 5H_2O(s)$ was formed since the position of the peaks in the XRD powder patterns were consistent with those reported for the pentahydrate solid [21] (Table S2 of ESI), despite differences in relative intensities. 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 (Specific ion Interaction Theory) coefficients, from the fit of solubility data (see the activity coefficients section below).

After a four-week equilibration period, the well-crystallised $NaEu(CO_3)_2 \cdot 5H_2O(s)$ solid was again filtered, washed with de-ionised water, and used as the initial solid for solubility experiments. XRD analyses were performed on a few samples when measuring their solubility 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 in the diffraction patterns when the solid was filtered a few days prior to XRD analysis, indicating the presence of $Eu_2(CO_3)_3 \cdot yH_2O(s)$ and possibly $Na_2CO_3(s)$ phases (see ESI). The effect of drying conditions has been investigated by Fannin *et al.*;[22] whereas $NaEu(CO_3)_2 \cdot 6H_2O(s)$ is stable under aqueous conditions, exposure to dry air alters it and the product $Eu_2(CO_3)_3 \cdot 8H_2O(s)$ forms. This phenomenon occurred in a few of our samples, but not when analysis was performed immediately after filtration of the solid. Thus, it was concluded that a crystalline phase of $NaEu(CO_3)_2 \cdot 5H_2O(s)$ is stable in all of the aqueous solutions.

Solubility experiments

Several Na_2CO_3–$NaClO_4$ solutions were prepared with different $[CO_3^{2-}]$ and $[Na^+]$. An additional batch containing NaCl instead of $NaClO_4$ was prepared to assess the influence of the ionic medium on the solubility. A few tens of milligrams of the $NaEu(CO_3)_2 \cdot 5H_2O(s)$ solid were added to 25 ml carbonate solutions, so that they were initially undersaturated. All batches were continuously shaken for the entire time of the experiments. Samples were taken after 10 and 16 weeks: For each solution, $-\log[H^+]$ 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, in concentrated carbonate solutions in which highly charged limiting complexes dominate, colloids are not observed; this was confirmed in this study. The filter was first saturated with about 2 ml of solution, which were discarded, and the following filtered few millilitres were used for analysis of [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 maintain a strong acidity, at more than 0.5 mol l^{-1} H^+. The concentration of europium in these solutions was 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 of 10 000 ppm Eu standard solution (Spex, CertiPrep®, 5% HNO_3). Based on the standard deviation, the error on [Eu] in the samples was estimated to be less than 3%.

Data analysis

Interpretation of lifetime measurements

Hydration of the limiting carbonate complex has been investigated on the basis of the method developed by Horrocks and Sudnick.[23] Vibronic coupling of the excited Eu(III) ion with OH oscillators of coordinated water molecules leads to a radiationless de-excitation process. Consequently, the fluorescence lifetime of Eu(III) correlates to n_{H_2O}, the number of remaining water molecules in the first coordination sphere of Eu^{3+}. The correlation

$$n_{H_2O} = \frac{1.07}{\tau} - 0.62 \qquad (3)$$

has been determined from lifetime measurements for Eu(III) doped lanthanum compounds with known numbers of coordinated water molecules.[24] Eqn. (3) has been shown to give consistent results with uncertainty of ±0.5 water molecules. An analogous relationship for Cm(III) was applied to fluorescence lifetimes measured for Cm(III) soluble species, resulting in reasonable values of n_{H_2O}.[24] Thus, eqn. (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 H_2O–D_2O mixtures since the nonradiative de-excitation process is far less effective for OD oscillators.[23] In this case, n_{H_2O} can be expressed as:

$$n_{H_2O} = {}^{w}n_{H_2O} \cdot x_{H_2O} \qquad (4)$$

where ${}^{w}n_{H_2O}$ is the hydration number of the Eu(III) species in pure water and x_{H_2O} the molar fraction of H_2O in H_2O–D_2O mixtures. While x_{H_2O} is experimentally determined, ${}^{w}n_{H_2O}$ is obtained by correlation with eqn. (3), giving the working equation:

$${}^{w}n_{H_2O} \cdot x_{H_2O} = \frac{1.07}{\tau} - 0.62 \qquad (5)$$

which should be verified for a given value of ${}^{w}n_{H_2O}$. Then measuring lifetimes in H_2O–D_2O mixtures enables an estimation of the best value of ${}^{w}n_{H_2O}$ by linear regression analysis.

Thermodynamic description

For $A^+ = Na^+$, M = Eu(III) and $x = 5$, equilibrium (1) is the meaningful dissolution reaction of the solid compound

$NaEu(CO_3)_2 \cdot 5H_2O(s)$ under our experimental conditions.

$$K_{s,i} = \frac{[Na^+][Eu(CO_3)_i^{3-2i}]}{[CO_3^{2-}]^{i-2}} \qquad (6)$$

is its equilibrium constant, which is a combination of the solubility product of $NaEu(CO_3)_2 \cdot 5H_2O(s)$:

$$K_s = [Na^+][Eu^{3+}][CO_3^{2-}]^2 \qquad (7)$$

for the equilibrium

$$NaEu(CO_3)_2 \cdot 5H_2O(s) \rightleftharpoons Na^+ + Eu^{3+} + 2CO_3^{2-} + 5H_2O \qquad (8)$$

and the stepwise formation constant of $Eu(CO_3)_i^{3-2i}$:

$$K_i = \frac{[Eu(CO_3)_i^{3-2i}]}{[Eu(CO_3)_{i-1}^{5-2i}][CO_3^{2-}]} \qquad (9)$$

for the equilibrium

$$Eu(CO_3)_{i-1}^{5-2i} + CO_3^{2-} \leftrightharpoons Eu(CO_3)_i^{3-2i} \qquad (10)$$

Activity coefficients and water activity are included in the equilibrium constants. Many other possible species, particularly hydroxide, hydroxocarbonate and bicarbonate complexes might form. Their formation has been considered in our data treatment. However, after performing sensitivity analyses, it was concluded that their influence was within the uncertainties in the interpretation model of the experimental results. As a consequence, the corresponding equations for the formation of these complexes are omitted for clarity. When $Eu(CO_3)_{2i}^{3-2i}$ predominates in the solution, [Eu], the solubility of $NaEu(CO_3)_2 \cdot 5H_2O(s)$, is approximately $[Eu(CO_3)_i^{3-2i}]$ and eqn. (6) gives:

$$\log[Eu] + \log[Na^+] \approx \log[Eu(CO_3)_i^{3-2i}] + \log[Na^+] = \log K_{s,i} + (i-2)\log[CO_3^{2-}] \qquad (11)$$

showing that solubility measurements can be used to determine i and $\log K_{s,i}$. Namely, a plot of $(\log[Eu] + \log[Na^+])$ *vs.* $\log[CO_3^{2-}]$ should be linear with slope $(i-2)$ and intercept $\log K_{s,i}$.

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 the SIT formula [eqns. (12) and (13)], usually valid for ion concentrations up to about 4 mol l^{-1}:[4]

$$\log K^{DH} = \log K^0 - \sum_{i,j} \varepsilon_{i,j} m_j - \nu_{H_2O} \log a_{H_2O} \qquad (12)$$

$$\log K^{DH} = \log K + \Delta\nu \log p - \Delta z^2 D \qquad (13)$$

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 units (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 values[4]), 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 units, K^0 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 having same 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 br_i = 1.5 (kg mol^{-1})$^{0.5}$, irrespective of the ion. 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 the van der Waals equation for gases. In the latter demonstration, a more appropriate volume exclusion term is also obtained. In both cases, $\varepsilon_{i,j} m_j$ is better written as $\varepsilon_{i,j} m_j T^0/T$, where T^0 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 in the SIT formula: the theoretical $1/T$ dependency needs experimental confirmation. For this reason, we instead proposed empirical developments for fitting the variation of $\varepsilon_{i,j}$ with T.[7,25] We recently applied the theoretical formula $\varepsilon_{i,j} m_j T^0/T$, which appears to account reasonably well for several experimental data, but not for $NpO_2(CO_3)_3^{4-}/NpO_2(CO_3)_3^{5-}$;[26] this exception might be attributed to ion-pairing of Na^+ with the highly negatively charged species $NpO_2(CO_3)_3^{5-}$, 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 $\varepsilon_{Na^+Eu(CO_3)_3^{3-},298.15\ K} = (T/298.15) \times \varepsilon_{Na^+Eu(CO_3)_3^{3-},T}$ to estimate the value of $\varepsilon_{Na^+Eu(CO_3)_3^{3-}}$ at 25 °C. Since T is quite close to 298.15 K, the temperature correction, $\Delta\varepsilon_{Na^+Eu(CO_3)_3^{3-}}/\varepsilon_{Na^+Eu(CO_3)_3^{3-},298.15\ K}$, is within the uncertainty: $[298.15/(296.15 \pm 1)] - 1 = 0.007 \pm 0.003$, so this correction was not made. For $\varepsilon_{A^+M(CO_3)_4^{5-}}$, a similar correction is more speculative since ion-pairing cannot be excluded.

Extrapolating solubility product to zero ionic strength

The SIT formula [eqn. (12)] was used to extrapolate 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^0) from experimental ones (typically K). This practical definition of the standard state that we used is consistent with the one used in the NEA-TDB reviews, which also applied SIT formula. A few assumptions are commonly associated with the SIT formula: when a supporting electrolyte AX (usually $NaClO_4$ or NaCl) is introduced to maintain constant ionic strength at m, the molality of AX, summation on j cancels in eqn. (12); thus, for each ion i, only interactions with the main counterion A^+ or X^- are taken into account *via* $\varepsilon_{A^+,i}$ or ε_{i,X^-}. Moreover, m has little effect on ϕ_{AX}, the mean value of $\log(a_{H_2O})/m$, which was therefore considered as constant: using the mean value $\phi_{NaClO_4} = -0.015_3$ kg mol^{-1} we calculated water activities for various $NaClO_4$ concentrations that were in agreement with the values calculated with Pitzer's formula and associated tabulated parameters.[28] This approximation is theoretically not consistent with the SIT formula, since the activity of water is related to the mean activity coefficient, which, in turn, can be calculated by using the SIT formula and ε_{A^+,X^-}.[27,29,30] However, we verified this approximation for many systems.[30] For eqn. (10) with $i \geq 3$, eqn. (12) is written as:

$$\log K_i^{DH} = \log K_i^0 - \Delta\varepsilon_i m_{Na^+} \qquad (14)$$

$$\Delta\varepsilon_i = \varepsilon_{Na^+Eu(CO_3)_i^{3-2i}} - \varepsilon_{Na^+Eu(CO_3)_{i-1}^{5-2i}} - \varepsilon_{Na^+CO_3^{2-}} \qquad (15)$$

Eqn. (14) is valid when one observes linear variations of $\log K_i^{DH}$ *vs.* m_{Na^+}. In that case, the intercept is $\log K_i^0$ and the slope $(-\Delta\varepsilon_i)$. For equilibrium (1), the above simplifications in the SIT formula no longer hold. For concentrated carbonate aqueous solutions with $NaClO_4$, $m_{CO_3^{2-}}$ is not negligible compared to $m_{ClO_4^-}$ and, with $i \geq 2$, eqn. (12) now becomes:

$$\log K_{s,i}^{DH} + \Delta(\varepsilon m) = \log K_{s,i}^0 - \varepsilon_{Na^+Eu(CO_3)_i^{3-2i}} m_{Na^+} \qquad (16)$$

$$\Delta(\varepsilon m) = \varepsilon_{Na^+CO_3^{2-}}[m_{CO_3^{2-}} - (i-2)m_{Na^+}] + \varepsilon_{Na^+ClO_4^-} m_{ClO_4^-} + 5\log a_{H_2O} \qquad (17)$$

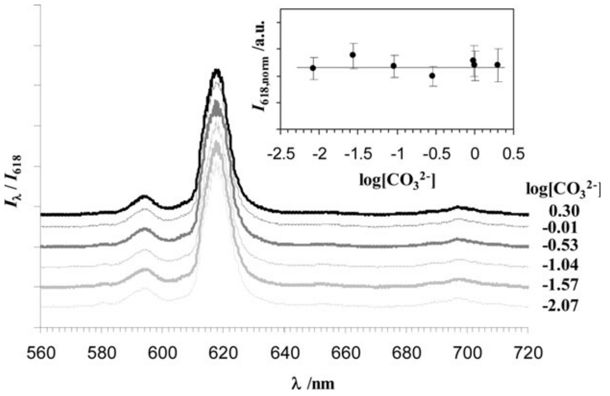

Fig. 1 Eu aqueous speciation in the solubility experiments probed by TRLFS. Evidence of a limiting carbonate complex of Eu(III) in Na_2CO_3–$NaClO_4$ solutions with 3 mol l^{-1} Na$^+$. Relative fluorescence intensity I_λ/I_{618} as a function of the emission wavelength and log[CO$_3^{2-}$]. The inserted graph shows the constant value of $I_{618,\mathrm{norm}}$ with log[CO$_3^{2-}$] (see Table 1).

According to eqn. (16), one expects $[\log K_{s,i}^{DH} + \Delta(\varepsilon m)]$ *vs.* m_{Na^+} to vary linearly with an intercept $\log K_{s,i}^0$ and a slope $-\varepsilon_{Na^+Eu(CO_3)_i^{3-2i}}$. Finally, combining eqns. (11) and (16) gives the working equations used later on for the ionic strength corrections involved for equilibrium (1) with A$^+$ = Na$^+$, M = Eu(III), x = 5, and i = 3:

$$\log K_{s,3}^{DH} + \Delta(\varepsilon m) = \log K_{s,3}^0 - \varepsilon_{Na^+Eu(CO_3)_3^{3-}} m_{Na^+} \quad (18)$$

$$\Delta(\varepsilon m) = \varepsilon_{Na^+CO_3^{2-}}[m_{CO_3^{2-}} - m_{Na^+}] + \varepsilon_{Na^+ClO_4^-} m_{ClO^-_3} + 5\log a_{H_2O} \quad (19)$$

The working equations for the stepwise complexation constants are obtained from eqn. (14):

$$\log K_3^{DH} = \log K_3^0 - \Delta\varepsilon_3\, m_{Na^+} \quad (20)$$

$$\log K_4^{DH} = \log K_4^0 - \Delta\varepsilon_4\, m_{Na^+} \quad (21)$$

for i = 3 and 4, respectively, where

$$\Delta\varepsilon_3 = \varepsilon_{Na^+Eu(CO_3)_3^{3-}} - \varepsilon_{Na^+Eu(CO_3)_2^-} - \varepsilon_{Na^+CO_3^{2-}} \quad (22)$$

$$\Delta\varepsilon_4 = \varepsilon_{Na^+Eu(CO_3)_4^{5-}} - \varepsilon_{Na^+Eu(CO_3)_3^{3-}} - \varepsilon_{Na^+CO_3^{2-}} \quad (23)$$

Eqns. (20)–(23) will be used for comparison and discussion with literature data.

Comparing solubilities measured in NaClO$_4$ and NaCl aqueous solutions

We also used the SIT formula for the small activity corrections on solubility measurements at constant [Na$^+$] and [CO$_3^{2-}$] between NaClO$_4$ and NaCl aqueous solutions. If i in eqn. (11) is assumed to be independent of the nature of the salt, it can be expected that

$$\log[Eu]_{NaClO_4} - \log[Eu]_{NaCl} = \delta \quad (24)$$

where $\delta = \log K_{s,i(NaClO_4)} - \log K_{s,i(NaCl)}$ and $K_{s,i(NaClO_4)}$ and $K_{s,i(NaCl)}$ are the values of $K_{s,i}$ in NaClO$_4$ and NaCl aqueous solutions, respectively. In NaCl media, p_{NaClO_4}, $\varepsilon_{Na^+ClO_4^-}$ and ϕ_{NaClO_4} are replaced by p_{NaCl}, $\varepsilon_{Na^+Cl^-}$ and ϕ_{NaCl}, respectively. Considering here that the assumptions described in the previous section are valid, that is, [Na$_2$CO$_3$] can be neglected compared to [NaCl] or [NaClO$_4$], and using eqn. (16), eqn. (24) becomes:

$$\delta = \Delta z^2(D_{NaClO_4} - D_{NaCl}) - (4-i)\log(p_{NaCl}/p_{NaClO_4}) - [Na^+]\{[\Delta\varepsilon_{i(NaClO_4)} + x\phi_{NaClO_4}]p_{NaClO_4} - [\Delta\varepsilon_{i(NaCl)} + x\phi_{NaCl}]p_{NaCl}\} \quad (25)$$

where D_{NaClO_4} and D_{NaCl} are the Debye–Hückel terms in NaClO$_4$ and NaCl aqueous solutions, respectively, and

$$\Delta\varepsilon_{i(NaClO_4)} = \varepsilon_{Na^+Eu(CO_3)_i^{3-2i}} + \varepsilon_{Na^+CO_3^{2-}} - \varepsilon_{Na^+ClO_4^-} \quad (26)$$

$$\Delta\varepsilon_{i(NaCl)} = \varepsilon_{Na^+Eu(CO_3)_i^{3-2i}} + \varepsilon_{Na^+CO_3^{2-}} - \varepsilon_{Na^+Cl^-} \quad (27)$$

Assuming values for i and x, δ can be calculated for given conditions by using eqn. (25). Finally, from eqns. (11) and (24), we get:

$$\log[Eu] + \log[Na^+] + \delta = \log K_{s,i(NaClO_4)} + (i-2)\log[CO_3^{2-}] \quad (28)$$

which is the working equation for comparing solubility data: we plotted (log[Eu] + log[Na$^+$] + δ) *vs.* log[CO$_3^{2-}$] measured in both NaClO$_4$ and NaCl aqueous solutions (δ = 0 in NaClO$_4$ solutions).

Results and discussion

TRLFS analysis

Fluorescence spectra were recorded for all the filtrated solutions, which were previously equilibrated with NaEu(CO$_3$)$_2\cdot$5H$_2$O(s) (Table 1). The main emission was observed at 618 nm and is due to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III), an emission particularly sensitive to complexation (Fig. 1).

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. $I_{618,\mathrm{norm}}$ and τ are the normalised fluorescence intensity at 618 nm and the fluorescence lifetime, respectively

[Na$_2$CO$_3$]^a/mol l^{-1}	[NaClO$_4$]^a/mol l^{-1}	t_{int}/s	D/μs	L/μs	$I_{618,\mathrm{norm}}$/a.u.	FWHM^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	—

[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 [CO$_3^{2-}$] should be related to either small changes in the speciation or ionic strength effect.

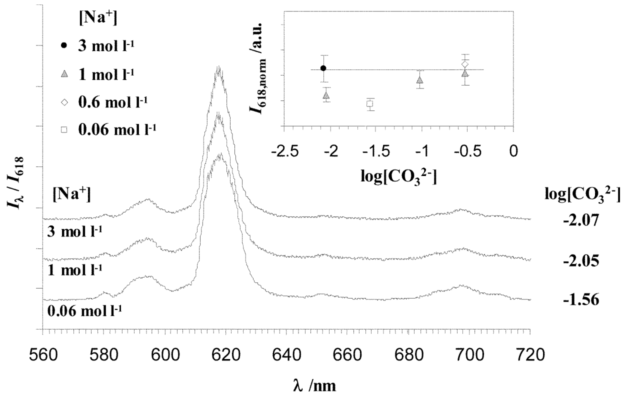

Fig. 2 Detection of the dissociation of the limiting carbonate complex of Eu(III) in Na_2CO_3–$NaClO_4$ solutions. Relative fluorescence intensity I_λ/I_{618} as a function of the emission wavelength, $\log[CO_3^{2-}]$ and $\log[Na^+]$. The inset graph shows the variation of $I_{618,\mathrm{norm}}$ with $\log[CO_3^{2-}]$.

Less sensitive transitions were observed from the $^5D_0$ excited state to the $^7F_0$, $^7F_1$, $^7F_3$, and $^7F_4$ states centred at about 580, 595, 653, and 698 nm, respectively. The relative intensities I_λ/I_{618} compare well, that is, the shapes of the spectra were very similar for 3 mol l^{-1} Na^+ solutions, and the values of $I_{618,\mathrm{norm}}$ did not vary more than the uncertainties with $\log[CO_3^{2-}]$. This is a good indication that there is a single major species of Eu(III), whatever the carbonate concentration, so that these spectra are actually a single spectrum, the one of the limiting carbonate complex of Eu(III). Other solutions with different $[Na^+]$ were analysed: spectra different from that of the limiting carbonate complex were indeed detected; shoulders appeared on the shorter 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 $I_{618,\mathrm{norm}}$ for the hypersensitive transition at 618 nm (see Fig. 2 and Table 1). These changes from the spectrum of the limiting complex occurred when $[CO_3^{2-}]$ and $[Na^+]$ 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 $\log[CO_3^{2-}] = -2.05$, and more than 60% at 0.06 mol l^{-1} Na^+ and $\log[CO_3^{2-}] = -1.56$.

Fluorescence lifetimes of Eu(III) in 1 mol l^{-1} Na_2CO_3 solutions were measured in pure H_2O, pure D_2O, and in their mixtures to vary x_{H_2O}. The best agreement with eqn. (5) is observed for $^{w}n_{H_2O} = 1.8 \pm 0.5$ (Fig. 3). τ was also measured in

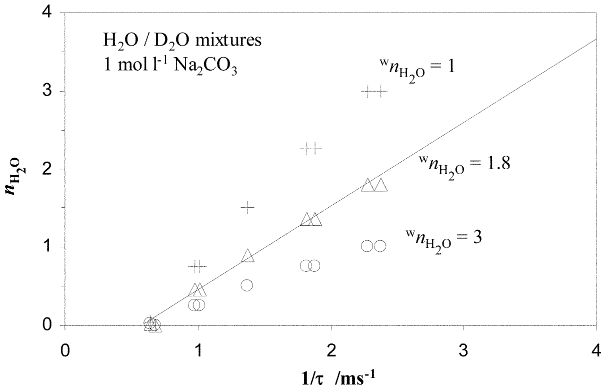

Fig. 3 Determination of $^{w}n_{H_2O}$ for $Eu(CO_3)_3^{3-}$ according to eqns (4) and (5). The straight line represents the relationship determined by Kimura *et al.*: $n_{H_2O} = (1.07/\tau) - 0.62$.[24]

filtrated solutions, previously equilibrated with $NaEu(CO_3)_2 \cdot 5H_2O(s)$, for $[CO_3^{2-}] > 1$ mol l^{-1} (Table 1): calculated $^{w}n_{H_2O}$ values ranged from 1.9 to 2.05. Assuming that CO_3^{2-} is a bidentate ligand and with $^{w}n_{H_2O} \approx 2$, the coordination numbers of $Eu(CO_3)_3^{3-}$ and $Eu(CO_3)_4^{5-}$ 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 Eu(III) can be expected to be smaller than for Eu^{3+} as a result of electrostatic repulsions between the three CO_3^{2-} and the decrease of the water activity (associated with increased ionic strength). Although this result suggests the presence of $Eu(CO_3)_3^{3-}$ under our experimental conditions, the relevant stoichiometry of the complex cannot be definitely determined, due to the uncertainty in $^{w}n_{H_2O}$.

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 $NaEu(CO_3)_2 \cdot 5H_2O(s)$ 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 eqn. (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 eqn. (11). A straight line with a slope of 1 describes reasonably well the data (Fig. 4), which shows that $Eu(CO_3)_3^{3-}$ predominates for $0.01 \leq [CO_3^{2-}] \leq 1$ mol l^{-1} at 3 mol l^{-1} Na^+. Our attempts to interpret the solubility measurements with the formation of hydroxide or hydroxocarbonate complexes were unsuccessful, so an insignificant influence of their stability 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 $\log K_{s,3}$ in the NaCl and $NaClO_4$ media was calculated using eqn. (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 $x = 5$; this small correction was taken into account for the interpretation. The data points for the NaCl medium are consistent with others in $NaClO_4$ conditions, validating the ionic strength correction (notably anion-anion interaction parameters are not needed in the SIT formula), and suggesting that no chloride complexes were observed, which is in agreement with previous studies on Am(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 $1.96 \cdot \sigma$, where σ is the standard deviation). Considering that only a 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 $\log K_{s,3} = -4.2 \pm 0.2$ at 3 mol l^{-1} Na^+. We attempted to also take the hypothetical $Eu(CO_3)_4^{5-}$ complex into account (slope 2) for the highest $[CO_3^{2-}]$. Since this complex has not been observed by TRLFS, we determined a maximum value of $\log K_4$, $\log K_4^{\max} = -0.38$, based on its possible formation at $[CO_3^{2-}]$ higher than 2 mol l^{-1}. These data are reported in Table 2 for comparison with literature data and their reliability is discussed below.

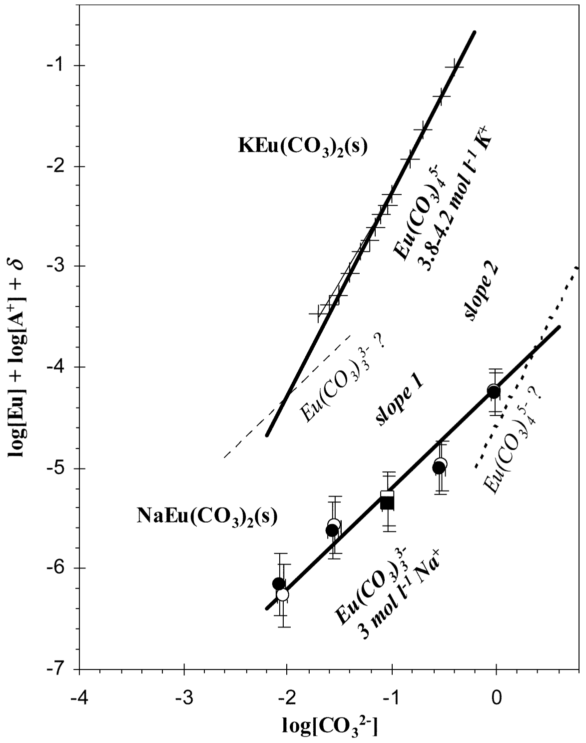

Fig. 4 Variations of $AEu(CO_3)_2 \cdot xH_2O(s)$ solubility ($A^+ = Na^+$, K^+) *vs.* $[CO_3^{2-}]$ at constant $[A^+]$ for the determination of the stoichiometry of the limiting carbonate complexes. Solubility of $NaEu(CO_3)_2 \cdot 5H_2O(s)$ in 3 mol l^{-1} Na^+ ($NaClO_4$) aqueous solutions after equilibration periods of (○) 10 and (●) 16 weeks is compared to the solubility of $KEu(CO_3)_2 \cdot 3H_2O(s)$ in 3.8–4.2 mol l^{-1} K^+ aqueous solutions (+).[17] The appropriate activity corrections were performed for NaCl (■) by adding δ [see text and eqn. (25)].

Extrapolating to zero ionic strength

The effect of ionic strength on the solubility of $NaEu(CO_3)_2 \cdot 5H_2O(s)$ was also investigated using the SIT formula for $K_{s,3}$ [eqns. (18) and (19)]. The validity of the interpretation of the experimental data at various Na^+ concentrations was assessed by plotting $[\log K_{s,3}^{DH} + \Delta(\varepsilon m)]$ *vs.* m_{Na^+}, which, as expected from eqn. (18), appeared to be linear within reasonable uncertainty (Fig. 5). When dissociation of $Eu(CO_3)_3^{3-}$ was suspected from the analysis of TRLF spectra, the data points were excluded from the linear regression analysis. The proposed values $\log K_{s,3}^0 = -5.6_0 \pm 0.2$ and $\varepsilon_{Na^+Eu(CO_3)_3^{3-}} = 0.03 \pm 0.06$ kg mol^{-1} ($\pm 1.96 \cdot \sigma$) were calculated by linear regression, excluding the data in the 2 mol l^{-1} Na_2CO_3 aqueous solution, since it was out of the valid ionic strength range for the SIT formula (usually about 4 mol kg^{-1}). However, it appeared that the linear regression still provided a fairly good correlation even for the data at the highest ionic strengths. The value of $\varepsilon_{Na^+Eu(CO_3)_3^{3-}}$ is quite different from the values for $Am(CO_3)_3^{3-}$, −0.15,[6] −0.15 ± 0.05 [4] and −0.23 ± 0.07.[5] However, the determination of $\varepsilon_{Na^+Eu(CO_3)_3^{3-}}$ was not only affected by the scattering of experimental data, but it also accounted for systematic errors when calculating values of $\Delta(\varepsilon m)$ and $\log a_{H_2O}$. Hence, we increase the uncertainty on the value at zero ionic strength: $\log K_{s,3}^0 = -5.6 \pm 0.4$.

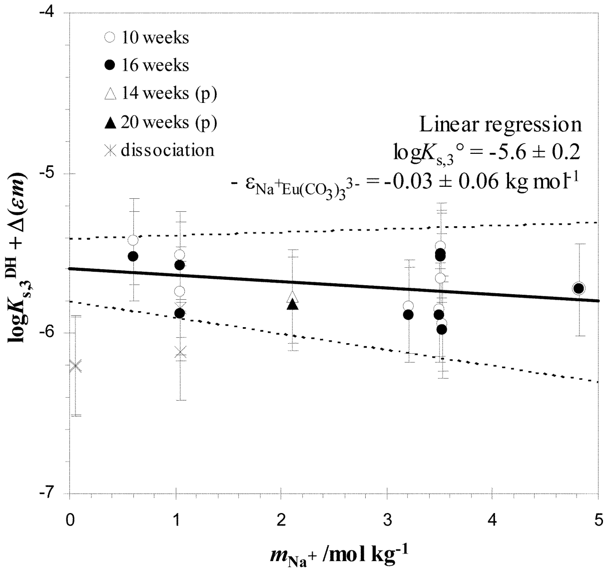

Fig. 5 Extrapolation to zero ionic strength of $\log K_{s,3}$. Linear regression analysis of $[\log K_{s,3}^{DH} + \Delta(\varepsilon m)]$ *vs.* m_{Na^+} [eqn. (18) and (19)]. The notation (p) means that the equilibrium is reached from oversaturation with the precipitation of $NaEu(CO_3)_2 \cdot 5H_2O(s)$. Crosses denote partial dissociation of $Eu(CO_3)_3^{3-}$.

Discussion of literature data

For comparison purposes, we have compiled the available values of the stepwise formation constants, K_3 and K_4, for

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

M	Method[a]	Medium	m_{Na^+}/mol kg^{-1}	$\log K_3$	$\log K_4$	Ref.
Ce	sol	3 mol l^{-1} $NaClO_4$	3.50	1.5 ± 0.2	1.1 ± 0.2	10
Nd	sol	$I \to 0$	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_2CO_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	$I \to 0$	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	$I \to 0$	0	2.8 ± 0.4	—	2
Am	Review	$I \to 0$	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, $I \to 0$	0	2.2 ± 0.7	−2.16 ± 0.7	14
Cm	Review	$I \to 0$	0	2.1 ± 0.8	−1.6 ± 0.1	5

[a] sol = solubility, dis = distribution. [b] Value for m_{K^+}.

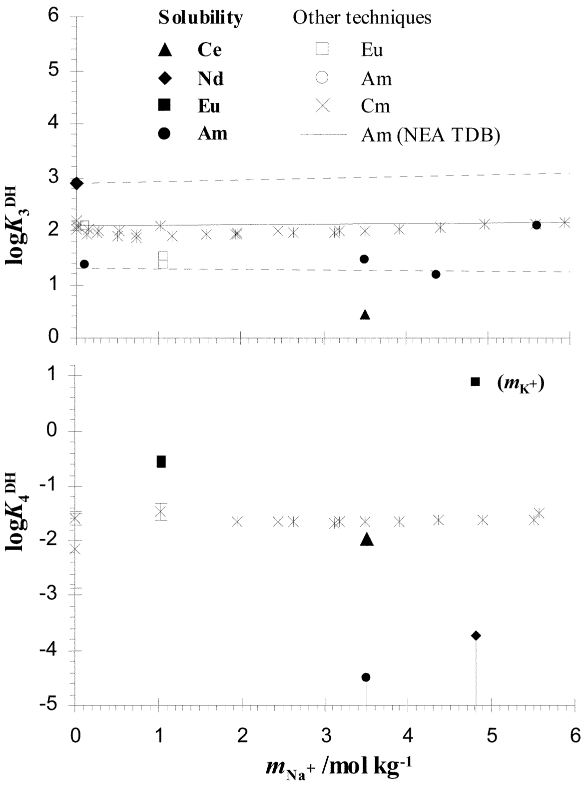

Fig. 6 SIT plots for comparison of the literature values of the stepwise formation constants K_3 and K_4 for M^{3+} f-ions in Na^+ aqueous solutions (except for some data in K^+ media, which are indicated on the figure). The straight line is the NEA-TDB correlation for Am(III).[5] K_4 data are considered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

Ln(III) and An(III) in Table 2. We used eqns. (20) and (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 logK_3 data for Am(III) had also been suggested by the NEA-TDB according to eqn. (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 eqn. (21) is not obvious because the values of logK_4^{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^+ media[17] (see Introduction). Maximum logK_4^{DH} values for Eu(III) determined in the present work and for Am(III),[6] both from solubility measurements, are represented with downward error bars. The elevated charge of the tetracarbonate complex can induce ion-pairing, which would explain the difference between Na^+ and K^+ aqueous media. A closer look at the data is necessary to understand the reason for such scatter.

In a few studies, tricarbonate complexes were characterised in limiting conditions. Rao *et al.* have measured the solubility of $NaNd(CO_3)_2 \cdot 6H_2O(s)$ 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 on the formation of $Nd(CO_3)_3^{3-}$ 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 log$K^0_{s,3}$ = −6.22 (no uncertainty was given with the original data). The analogous complex $Am(CO_3)_3^{3-}$ 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 $Am(CO_3)_3^{3-}$ in 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 report all the spectra. Although the initial solid, $Am_2(CO_3)_3(s)$, is not the thermodynamically stable solid in concentrated carbonate solutions with high [Na^+], both slope analysis and XRD analysis have shown that no phase transformation occurred in most of the batches, probably due to the slow kinetics of formation of $NaAm(CO_3)_2 \cdot xH_2O(s)$. However, precipitation of $NaAm(CO_3)_2 \cdot xH_2O(s)$ is suspected for [CO_3^{2-}] > 1 mol l^{-1}. Other studies were performed in NaCl solutions, but with carbonate concentrations less than 0.1 mol l^{-1}, which is too low to observe a possible $Am(CO_3)_4^{5-}$ in significant concentration.[7,8] Only measurements in 4 mol l^{-1} NaCl solutions were carried out with [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 tetracarbonate Am(III) complex even at high [CO_3^{2-}] and [Na^+].

These results might be balanced with determinations of the stability of tetracarbonate complexes. Faucherre *et al.* have admitted the existence of $Ln(CO_3)_4^{5-}$ for several lanthanide ions from solubility experiments and cryoscopic studies.[17] Solubility measurements of $KLn(CO_3)_2 \cdot xH_2O(s)$, 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 tetracarbonate 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 log[CO_3^{2-}] < −1.4; the authors attributed this deviation to inaccuracy of their Ln(III) titration method for concentrations less than about 5 × 10^{-4} mol l^{-1}. However, a nonrandom dispersion of the data points is observed and the deviation may very well be attributed to the dissociation of the tetracarbonate complexes into $Eu(CO_3)_3^{3-}$ (Fig. 4) and $Gd(CO_3)_3^{3-}$. Thus we re-interpreted these data and determined a value of K_4, the stepwise formation constant of $Eu(CO_3)_4^{5-}$ and $Gd(CO_3)_4^{5-}$ (Table 2). A cryoscopic method has also been applied to the lanthanides heavier than Gd, whose solubility is not high enough for accurate measurements; it consists in monitoring the lowering of temperature due to addition of a $Eu(NO_3)_3$ solution into a $KHCO_3$–K_2CO_3 buffer solution in the KNO_3–ice eutectic system. For all the studied Ln(III), tetracarbonate complexes were evidenced. These results are not necessarily inconsistent with our determination of the stoichiometry $Eu(CO_3)_3^{3-}$ for the limiting complex: The highly negative tetracarbonate complexes could very well be stabilised by ion-pairing with (less hydrated) K^+ more efficiently than with Na^+ ions. This type of difference between K^+ and Na^+ ions might also be at the origin of the difference in the solubility of $KEu(CO_3)_2 \cdot 3H_2O(s)$ and $NaEu(CO_3)_2 \cdot 5H_2O(s)$ (Fig. 4). Thus, the existence of highly charged $Ln(CO_3)_4^{5-}$ complexes could be favoured in concentrated K^+ ionic media. Similarly, tetracarbonate complexes could also be stabilised by the $C(NH_2)_3^+$ guanidinium cation, as observed by Dumonceau.[15]

The formation of $Ce(CO_3)_3^{3-}$ and $Ce(CO_3)_4^{5-}$ has been observed by Ferri *et al.* from solubility measurements of $NaCe(CO_3)_2 \cdot 2H_2O(s)$ 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 $Ce(CO_3)_4^{5-}$ by the Ce(IV) complex, $Ce(CO_3)_5^{6-}$, and assuming precipitation of $CeO_2(s)$; however the resulting formation constant of $Ce(CO_3)_5^{6-}$ would then be several orders of magnitude higher than the ones of analogous $M(CO_3)_5^{6-}$ for $M^{4+} = U^{4+}, Np^{4+}$ and Pu^{4+},[1,4,5] which is not realistic. The formation of $Ce(CO_3)_4^{5-}$, even in Na^+-based supporting electrolyte, may

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

M	Solid	Medium	m/kg mol^{-1}	$\log K_{s,3}$	$\log K_s$	$\log K^0_{s,3}$[a]	$\log K^0_s$[b]	Ref.
Ce	$NaCe(CO_3)_2 \cdot 2H_2O$	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	$NaNd(CO_3)_2 \cdot 6H_2O$	$I \rightarrow 0$	0	−6.22	−21.39	−6.22	−21.39	9
Eu	$NaEu(CO_3)_2 \cdot 5H_2O$	5 mol l^{-1} NaCl	5.60	—	−18.1 ± 0.2	—	−22.8 ± 0.3	8
Eu	$NaEu(CO_3)_2 \cdot 5H_2O$	3 mol l^{-1} $NaClO_4$	3.50	−4.2 ± 0.2	−17.5 ± 0.4[c]	−6.1 ± 0.3	−20.9 ± 0.5	This work
Am	$NaAm(CO_3)_2 \cdot 5H_2O$	5 mol l^{-1} NaCl	5.60	−3.6 ± 0.5	−16.5 ± 0.5	−6.0 ± 0.5	−21.2 ± 0.5	8

[a] $\log K^0_{s,3} = \log K^{DH}_{s,3} + (\Delta\varepsilon_{AX} + x\phi_{AX})m$, applied to $NaM(CO_3)_2 \cdot xH_2O(s) + CO_3^{2-} \rightleftharpoons Na^+ + M(CO_3)_3^{3-} + xH_2O$ with $\Delta\varepsilon_{NaCl} = -0.04$ kg mol^{-1}, $\Delta_{NaClO_4} = -0.06$ kg, $\phi_{NaClO_4} = -0.015_3$, and $\phi_{NaCl} = -0.019_4$. [b] $\log K_s^\circ = \log K^{DH}_s + (\Delta\varepsilon_{AX} + x\phi_{AX})m$, applied to $NaM(CO_3)_2 \cdot xH_2O(s) \rightleftharpoons Na^+ + M^{3+} + 2CO_3^{2-} + xH_2O$ with $\Delta\varepsilon_{NaCl} = 0.1$ kg mol^{-1}, $\Delta\varepsilon_{NaClO_4} = 0.34$ 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]

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 eight-coordinated Ce(III), Nd(III), Am(III) and Eu(III), respectively].[32] This trend suggests that the even larger La^{3+} can form a tetracarbonate complex in limiting Na_2CO_3 conditions, but to our knowledge, this has not been studied.

Another approach 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 $[C(NH_2)_3]_2CO_3$ solutions. From the positions of the oxygen atoms in the crystals, nine-coordinate Nd(III) and Sm(III) ions and an eight-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) tetracarbonate 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, that is, 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 with 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 tetracarbonate 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 $\log K_s$ and $\log K_{s,3}$ to assess whether the analogy between the M^{3+} f-elements ions is valid, it was necessary to extrapolate these data to zero ionic strength. Literature data and calculations are reported in Table 3. The most meaningful comparison is made by using $\log K^0_{s,3}$ values, since $\log K_{s,3}$ 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 footnote a of Table 3). The value of $\log K^0_{s,3}$ for Ce is significantly lower than the others and is probably correlated to the existence of a tetracarbonate limiting complex for this element. Note that extrapolation to zero ionic strength with the SIT formula may deviate for 5 mol l^{-1} NaCl since this formula is not very accurate for such a high ionic strength.

Another comparison was made with $\log K^0_s$ since more values are available. We deduced the solubility product of our $NaEu(CO_3)_2 \cdot 5H_2O(s)$ solid at 3 mol l^{-1} Na^+ by subtracting from $\log K_{s,3}$ the sum of $\log K_i$ (i = 1–3), determined by TRLFS after appropriate ionic strength corrections.[16] Interestingly, the solubility products of $NaAm(CO_3)_2 \cdot 5H_2O(s)$ and $NaEu(CO_3)_2 \cdot 5H_2O(s)$ have been directly measured by Runde and Kim at low $[CO_3^{2-}]$, 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 $\log K^0_s$ = −22.62 ± 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 an ionic strength correction, which would explain the large associated uncertainty. As reported by the author, $\log K^0_s$ was calculated for every measurement using an aqueous database that included $M(OH)_i^{3-i}$ (i = 1–3), MCO_3^+ and $M(CO_3)_2^-$, but not $M(CO_3)_3^{3-}$; hence, when using an NEA database for Am(III) that included $\log K^0_3$, Fannin adjusted $\log K^0_s$ 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 one log unit on the Eu solubility for solutions of the same pH and carbonate concentration, which could originate from differences in the crystallinity of the solids or from a poor 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 the uncertainties (Table 3). These data may be reduced to the four values that have been obtained from $\log K_{s,3}$, which is a more reliable determination; so a good agreement is observed for $\log K^0_s$ between Ce, Nd, Eu and Am, in accordance with $\log K^0_s$ = −21.0 ± 0.5, the value selected for Am(III) in the NEA-TDB Update.[5]

Conclusion

From solubility measurements of $NaEu(CO_3)_2 \cdot 5H_2O$ in concentrated carbonate solutions with high ionic strength (3 mol l^{-1} $NaClO_4$), we observed the limiting complex $Eu(CO_3)_3^{3-}$, 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 the 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 $Eu(CO_3)_3^{3-}$ has been confirmed by TRLFS, and we have estimated the coordination number of $Eu(CO_3)_3^{3-}$ 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 $Ce(CO_3)_4^{5-}$ preferentially forms in similar conditions, suggesting an effect of the larger ionic radius of Ce(III); tetracarbonate complexes of heavier Ln(III) can also form in K^+ solutions at high ionic strength, while this is not the case in Na^+ aqueous solutions.

Acknowledgements

We would like to thank ANDRA and CEA DEN/DSOE (R&D) for financial support. We are grateful to Michel Tabarant and Alex Chénière (CEA DEN Saclay DPC/SCP/LRSI) for their help with ICP-AES and DRX analyses. We also thank Craig Fannin for helpful communication of some of his thesis results.

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