Lanthanide and actinide inorganic complexes in natural waters. TRLFS and ESI-MS studies

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Abstract *– Aqueous complexes of M(III) f-element ions with the inorganic ligands* CO_3^{2-} *and* SO_4^{2-} *have been investigated using the highly-sensitive speciation techniques TRLFS and ESI-MS. The* $Eu(CO_3)_i^{3-2i}$ *(i=1-3) species have been characterized by TRLFS, and the stoichiometry of the limiting complex* $Eu(CO_3)_3^{3-}$ *have been confirmed by solubility measurements of* $NaEu(CO_3)_2(s)$ *at high ionic strength. Temperature effect on Cm(III) carbonate complexes is evidenced by the TRLFS technique. Investigation on sulphate complexation has been done at various ionic strengths by TRLFS on Eu(III) and by ESI-MS on La(III). New thermodynamic data are obtained by both techniques, which are consistent with literature data.*

INTRODUCTION

Actinide chemistry in natural environments is of great interest to predict radionuclide migration from possible radioactive waste repositories. Interactions with inorganic ligands such as the hard anions carbonate and hydroxide should play an important role in actinide speciation ; however actinide complexes can as well be formed in groundwaters with sulphate, phosphate, silicate, chloride, and fluoride anions [1]. Many data on their stoichiometries and thermodynamic stabilities have been validated by the NEA-TDB critical reviews (Thermodynamic Data Base project of the Nuclear Energy Agency OECD) [2-5]. Beside the lack of available data at temperatures above 25°C, the NEA-TDB have pointed out discrepancies in the literature. Typically supplementary experimental work is still needed to find out whether other stoichiometries of actinide species could be stable under environmental conditions, particularly bicarbonate, hydroxocarbonate and hydroxosulphate mixed complexes. Interestingly analogies between actinides and with lanthanides may be used to implement databases [6]. Whereas the stoichiometry of the Am(III) limiting carbonate complex, $Am(CO_3)_3^{3-}$, seems well established, $M(CO_3)_4^{5-}$ has been proposed for M = Cm [7], Ce [8], and Eu [9(e-f)].

Our laboratory has developed time-resolved laser-induced fluorescence spectroscopy (TRLFS) and electrospray-ionisation mass spectrometry (ESI-MS) for speciation analysis purposes. TRLFS has been first dedicated to elemental detection of uranium [10(a)] ; it is now more often used as a speciation technique with much lower detection limits than classical ones to study fluorescent f-elements such as Eu(III), U(VI) and Cm(III) [10(b-f)]. ESI-MS enables detection of species of any lanthanide with a soft ionisation mode of a liquid at atmospheric pressure. It has been particularly used to study interactions of lanthanides with organic compounds [11(a-b)], and also to characterize the hydrolysis of U(VI) [11(c)] and Th(IV) [11(d)]. In the present work, ESI-MS is used as a new tool for speciation analyses of lanthanides with small inorganic ligands.

DESCRIPTION OF THE ACTUAL WORK

TRLFS analyses and solubility measurements have been carried out on aqueous bicarbonate and carbonate solutions of Eu(III). According to a sensitivity analysis based on Am(III) data, carbonate complexes $Eu(CO_3)_i^{3-2i}$ are found to be the major species under our experimental conditions. TRLFS data are consistent with the stability of carbonate complexes and give confidence for the limiting complex $Eu(CO_3)_3^{3-}$. Solubility measurements of $NaEu(CO_3)_2(s)$ in concentrated Na_2CO_3 solutions have been carried out to confirm the stoichiometry of the limiting complex. Experimental values of the stepwise complex formation constants are obtained. Temperature effect on the fluorescence spectra of Cm(III) solutions from 10 to 50°C is discussed according to changes in Cm(III) spectroscopy and in its speciation.

Eu(III) and La(III) have been selected to investigate the complexation of trivalent

lanthanide ions with sulphate ligand using TRLFS and ESI-MS techniques respectively. Stability constants of the first and second sulphate complexes are extracted from these experimental data.
This study is part of a PhD work : the numerical values will be given in the thesis document [12] and in forthcoming publications.

EXPERIMENTAL RESULTS AND DISCUSSION

Carbonate Complexes of Eu(III) and Cm(III)

Sensitivity Analysis

Equilibrium constants are expressed in concentration ratios rather than activity ratios, and activity coefficients are taken into account via the Specific ion Interaction Theory (SIT) as proposed by the NEA-TDB reviews [2-5] :

$$\lg K_m - \Delta z^2 D_m = \lg K^\circ - \Delta\varepsilon\, m \qquad (1)$$

where K_m is the equilibrium constant, Δz^2 is the sum of the squared charge of each species with the sign - for reactants and + for products, D_m is the Debye-Hückel term, K° is the equilibrium constant at zero ionic strength, $\Delta\varepsilon$ is the difference between specific ion interaction coefficients, ε, of products and reactants, and m the molal concentration of the added inert salt, used to fix the ionic strength. The subscript m refers to the molal unit.
Discrepancies in literature data reveal the difficulties to control the speciation in bicarbonate or carbonate solutions (Fig. 1). The choice of our experimental chemical conditions is based on the analogy with Am(III) for which data have been reviewed [3,5]. Solubility results from Robouch [13] obtained by using a correct protocol for $[H^+]$ measurements and carbonate concentration control are found to be relevant data and utilized for our sensitivity analysis since we have used similar experimental protocols. The speciation of Am(III) is then calculated on the basis of validated thermodynamic data for hydrolysis, solubility and ionic strength correction parameters [3,5], and carbonate complex formation constants from Robouch [13]. The stability domains of complexes and solid compounds are drawn on Fig. 2. One should notice that $Am(CO_3)_3^{3-}$ is the stable species at high $[CO_3^{2-}]$.

Experimental Details

Several sets of solutions have been prepared by titration techniques at either controlled carbon dioxide pressure or dissolved bicarbonate or carbonate salts. The Na^+ concentration in each solution was fixed by adding adequate amounts of $NaClO_4$. Experimental conditions for the study of Eu(III) complexation by TRLFS are reported on Fig. 2. A wide range of $[CO_3^{2-}]$ is investigated to observe the formation of all the carbonate complexes of Eu(III) and assess the possible formation of bicarbonate or mixed hydroxo-carbonate complexes.

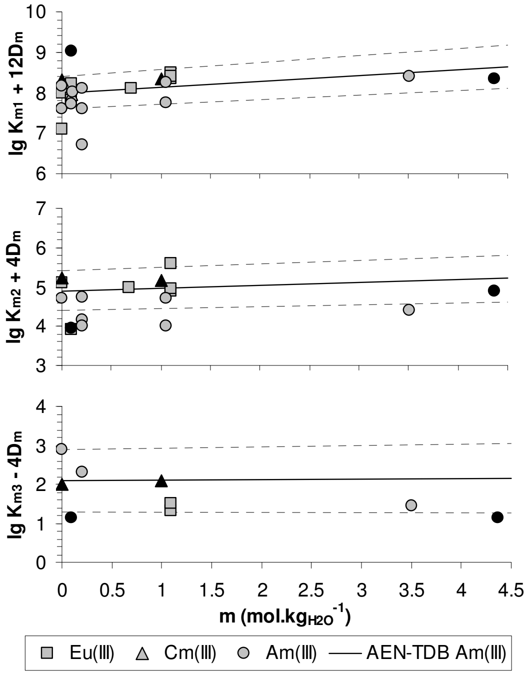

Fig. 1. Equilibrium constants K_{mi} for $M(CO_3)_{i-1}^{5-2i} + CO_3^{2-} \rightleftharpoons M(CO_3)_i^{3-2i}$ determined for M = Eu [9], Cm [5] and Am [3,5] and plotted according to equation (1). Grey and black symbols corresponds to $NaClO_4$ and NaCl ionic media respectively.

TRLFS Measurements

The fluorescence emission of Eu^{3+} in solution can be described with several transitions in particular from the $^5D_0$ excited state to the ground ^7F_j (j=0-6) manifold [14]. The $^5D_0 \rightarrow {}^7F_2$ transition occurring at about 618 nm is known as a hypersensitive transition that is highly affected by the environment of Eu(III). Fig. 3 contains fluorescence spectra measured in bicarbonate solutions at controlled $CO_2(g)$ pressure. The observed changes in intensity and shape of the peaks are characteristic of the complexation of Eu^{3+} by CO_3^{2-} to form the first carbonato complex $EuCO_3^+$. As the carbonate concentration increases, the overall intensity also increases and the symmetrical shape of the peaks at 592 and 618 nm of the measured fluorescence spectrum is lost, revealing an envelop of fine structures due to splitting. The growth of an emission peak at 580 nm that corresponds to the $^5D_0 \rightarrow {}^7F_0$ transition is also observed. This transition is forbidden by both electrical dipole and magnetic dipole selection rules [14], and is particularly absent in the Eu^{3+} spectrum. The detection of this emission band for solutions equilibrated with 1-atm $CO_2(g)$ indicates a loss of centrosymmetry in the complex in agreement with a monocarbonato complex (Fig. 3). Neither bicarbonate nor hydroxocarbonate complexes seem to significantly influence the data fit and are therefore considered as minor species under our experimental conditions. In bicarbonate and carbonate media for which $[CO_3^{2-}]$ is more important, changes of the fluorescence signature of the solutions are observed and interpreted with the formation of further carbonate complexes $Eu(CO_3)_i^{3-2i}$ (i=1-*n*). The value of *n* cannot be determined unequivocally since both interpretations with *n* = 3 or 4 may explain the changes of the fluorescence spectra. However we have observed that when four carbonate complexes are invoked, the spectrum that is attributed to $Eu(CO_3)_3^{3-}$ can be reproduced by a linear combination of the spectrum attributed to $Eu(CO_3)_2^-$ and $Eu(CO_3)_4^{5-}$. Thus the existence of four complexes remains doubtful.

Solubility Measurements

To confirm the species $Eu(CO_3)_3^{3-}$ as the limiting carbonate complex of Eu(III), solubility measurements of $NaEu(CO_3)_2(s)$ in $Na_2CO_3/NaClO_4$ solutions have been carried out. This solid compound is the one that is stable in concentrated carbonate solutions [8] giving little chance for phase transformation during the experiments. The X-ray diffraction (XRD) technique has been used to characterize the solid phases in the batch solutions. The diffraction peaks compared well with the XRD powder pattern of $NaEu(CO_3)_2{,}xH_2O(s)$ obtained by Runde *et al.* [15]. This phase is observed in all our solutions whatever the equilibrium time and carbonate concentrations. Inductively coupled plasma optical emission spectroscopy (ICP-OES) has been used to measure the solubility $m_{Eu,T}$. $[Na^+]$ was kept constant in the batch solutions to control ionic pair interactions of negatively-charged Eu(III) complexes that should be the major Eu(III) species under these conditions.

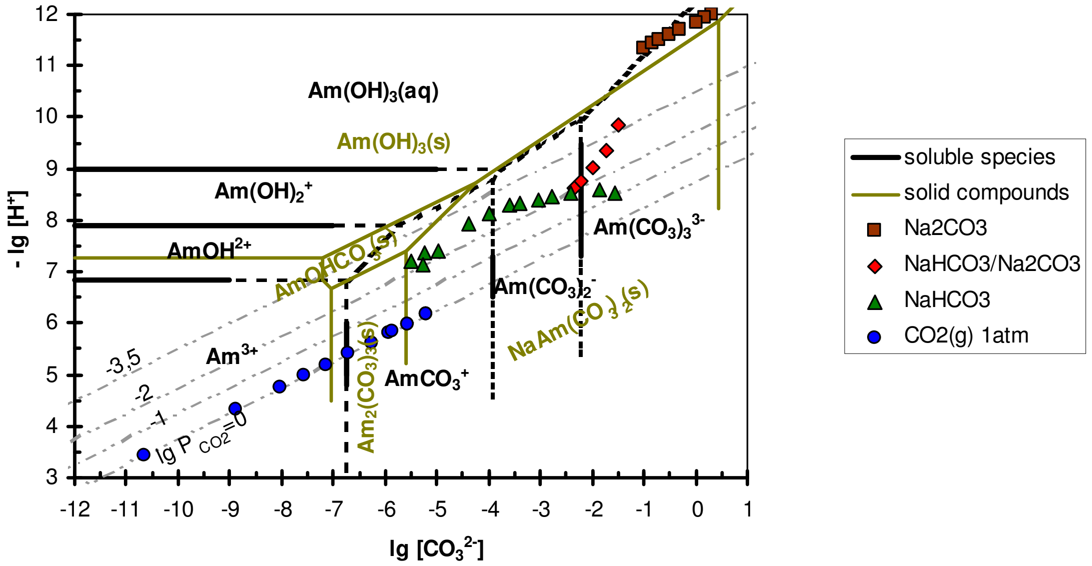

Fig. 2. Stability diagram for Am(III) species with $-\lg [H^+]$ and $\lg [CO_3^{2-}]$ at I = 0.1M calculated with equation (1) and data from [3,5,13]. Symbols denote our experimental conditions for TRLFS measurements on Eu(III) solutions.

When $Eu(CO_3)_i^{3-2i}$ is the major aqueous species, its molality is actually the measured solubility $m_{Eu,T}$ and

$$\lg m_{Na^+} + \lg m_{Eu,T} - \Delta z^2 D_m + \Delta\varepsilon\, m_{Na^+} = \lg K_{s,i}{}^\circ + (i-2)\lg m_{CO_3{}^{2-}} \qquad (2)$$

is deduced from equation (1), where $\Delta z^2 = (1 + (3-2i)^2 - (i-2)*2^2$, $K_{s,i}$ is the equilibrium constant for the reaction

$$NaEu(CO_3)_2(s) + (i\text{-}2)\, CO_3^{2-} \rightleftharpoons Na^+ + Eu(CO_3)_i^{3-2i} \qquad (3)$$

Fig. 4 shows the interpretation of our solubility measurements. The sum of the logarithms of the measured solubility and the Na^+ molality increases linearly with the logarithm of the CO_3^{2-} molality with a slope +1, which confirms that $Eu(CO_3)_3^{3-}$ is the main species in solution (see the plot of $\lg m_{Na+} + \lg m_{Eu,T}$ in blue). For the highest value of m_{CO32-}, $[Na^+]$ equals 4M and the slight increase in the solubility is taken into account by ionic strength corrections (see the plot of $\lg m_{Na+} + \lg m_{Eu,T} - 6D_m + \Delta\varepsilon\, m_{Na+}$ in red). This interpretation leads to larger uncertainties as the value for Δε calculated from analogies with Am(III) [5] could be slightly different. One should notice that the ionic strength for the solution with $\lg m_{CO32-} = -1$ is fixed with NaCl ; no significant influence of possible Cl^- complexation is observed as the solubility is not increased, and specific anion-anion interaction terms are not needed for activity coefficients calculation.

The presence of the species $Eu(CO_3)_3^{3-}$ in all the solutions is also verified by recording the TRLF spectra of the solutions after filtration. The same shape and relative intensity peak ratio are observed confirming that only one major complex is stable.

TRLFS Measurements at Different Temperatures

The stability of carbonate complexes of Cm(III) is also investigated by TRLFS at various temperatures from 10 to 50°C. Carbonate solutions with $[Cm(III)]=10^{-8}M$, $[Na^+]=3M$ and $[Na_2CO_3] > 10^{-3}M$ have been prepared. The fluorescence spectra measured at 25°C are given in Fig. 6. Not only the fluorescence intensity is affected by $[CO_3^{2-}]$, but also the maximum of the peak is shifted toward the red wavelengths when $\lg [CO_3^{2-}]$ increases. This suggests the presence of two or more Cm(III) species.

In 1M Na_2CO_3 solution, one may expect a unique aqueous complex of Cm(III) that could be $Cm(CO_3)_3^{3-}$ by analogy with our results on Eu(III), or $Cm(CO_3)_4^{5-}$ according to Fanghänel *et al.* [7]. The corresponding fluorescence spectra at different temperatures are shown on Fig. 7. It is likely that no significant change with temperature in Cm(III) speciation occurs, and the decrease of the measured fluorescence intensities must rather be due to an increase of non-radiative relaxation processes.

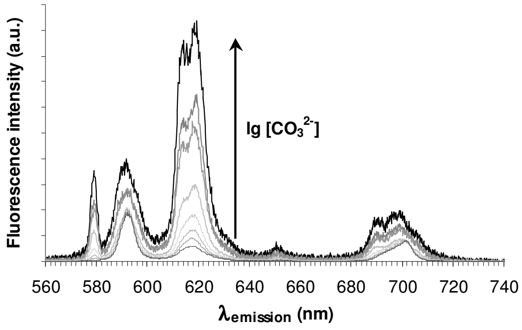

Fig. 3. Measured fluorescence spectra of Eu(III) in $NaHCO_3$ solutions equilibrated with $CO_2(g)$ 1 atm ($-10.65<\lg [CO_3^{2-}]<-5.21$).

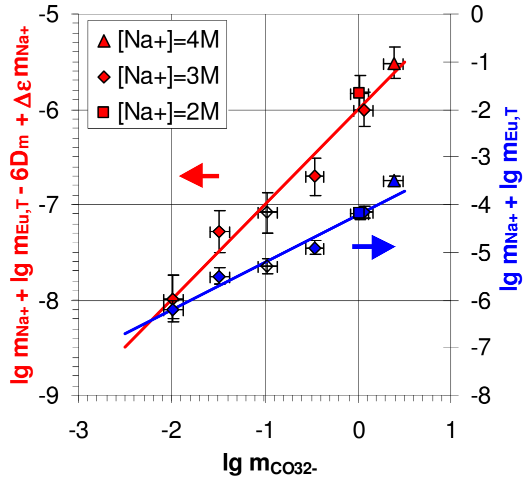

Fig. 4. Measured solubility of $NaEu(CO_3)_2(s)$ in $Na_2CO_3/NaClO_4$ solutions with fixed $[Na^+]$ plotted according to equation (2). Open symbols are used for the $Na_2CO_3/NaCl$ solution.

Sulphate Complexes of La(III) and Eu(III)

According to literature trivalent actinides and lanthanides may form complexes in sulphate media with the general formula MSO_4^+ and $M(SO_4)_2^-$ [3-6]. Similar values of stability constants are published for actinides and lanthanides, giving confidence for analogies [6]. However it still remains difficult to accurately determine the ionic strength dependency of the constants since there are discrepancies in the values from various authors and techniques [5].

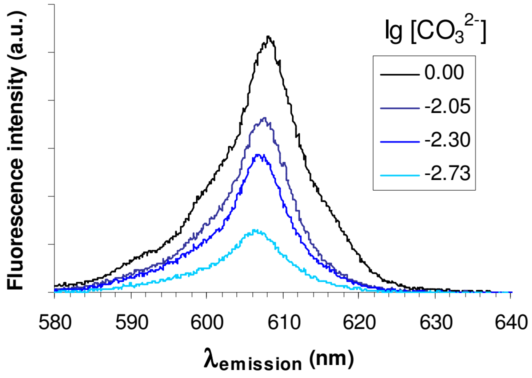

Fig. 6. Measured fluorescence spectra of Cm(III) in Na_2CO_3 solutions with [Cm(III)]=10^{-8}M and [Na^+]=3M at 25°C.

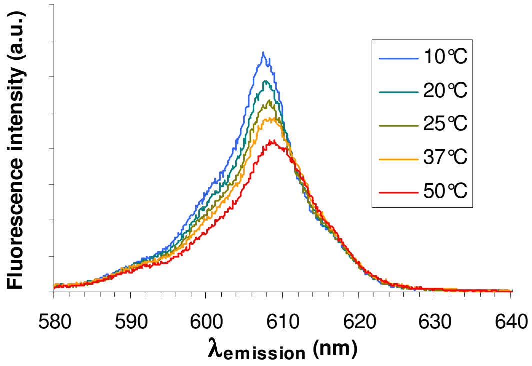

Fig. 7. Measured fluorescence spectra of Cm(III) in a 1M Na_2CO_3 solution with [Cm(III)]=10^{-8}M and [Na^+]=3M at various temperatures.

TRLFS has been here chosen to measure lg β_1 and lg β_2 from Eu(III) solutions at different ionic strengths. A comparison with another technique is very useful to check the confidence level of our determination. ESI-MS has proven good capabilities for speciation works [11], but rarely on inorganic systems since complexation of metal ions by inorganic ligands is usually weaker than by organic ones, and chemical conditions are often limited by low solubility.

TRLFS Measurements

Complexation of Eu(III) by SO_4^{2-} is characterized from acidic solutions at pH 2 and 3 fixed using $HClO_4$ to prevent from hydrolysis. Ionic strength is controlled by adding adequate amounts of $NaClO_4$, so that three titration series at different ionic strengths have been carried out. An increase of the hypersensitive transition intensity at 618 nm is observed with the increase of [SO_4^{2-}]. The equation

$$\frac{I_{mes}}{[Eu]_T} = \frac{\sum_i (I_i^0 \beta_i [SO_4^{2-}]^i)}{\sum_i (\beta_i [SO_4^{2-}]^i)} \qquad (4)$$

where I_{mes} is the measured fluorescence intensity and I_i^0 the fluorescence intensity of the species $Eu(SO_4)_i^{3-2i}$ per M, is used for the interpretation of the spectra. This is consistent with the formation of $EuSO_4^+$ and $Eu(SO_4)_2^-$. Values for lg K_{m1} and lg K_{m2} are adjusted by using equation (4) to fit the experimental data. A very good agreement is found between theoretical curves and experimental measurements (Fig. 8).

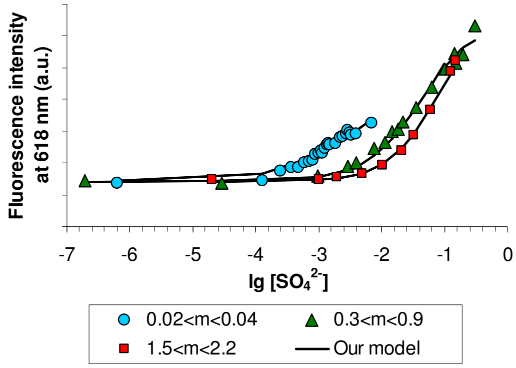

Fig. 8. Fitted curves on the fluorescence intensities of Eu(III) measured at 618 nm in $HClO_4/H_2SO_4$ and $NaClO_4/Na_2SO_4$ solutions at various ionic strengths.

ESI-MS Analyses

Eu(III) is known to be easily reduced in the electrospray-ionization source, and La(III) has been preferred in this study since its redox potential is much lower [16]. In the present work ESI-MS analyses are carried out on La(III) acidic solutions. No addition of inert salt to fix the ionic strength have been made to prevent the formation of ionic aggregates that would scatter the signal. Therefore HNO_3/H_2SO_4 mix solutions at pH 1 and 2 with low ionic strength (usually less than 0.1M) have been prepared for this investigation. Many ionic species are observed in the positive mode with m/z values ranging from 50 to almost 1200. Identification of each peak is made with help from MS-MS measurements. It is possible to define a few groups of gas-phase species with various solvation molecules such as H_2O, HNO_3, H_2SO_4 ; oxides, hydroxide, nitrate, and sulphate complexes of La(III) are observed on the spectra.

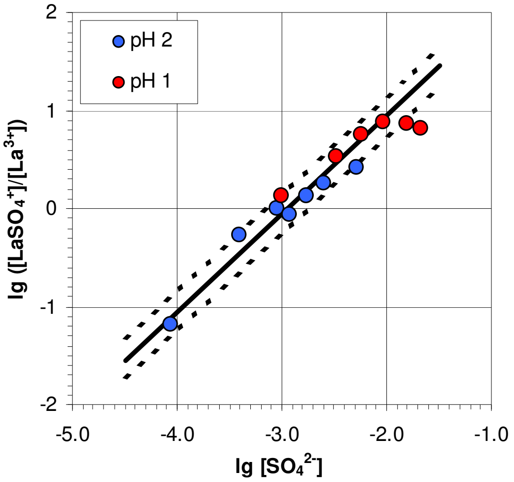

Fig. 9. Logarithm of the ratio of the La(III) aqueous species concentrations measured by ESI-MS against the logarithm of free sulphate concentration (equation (6)).

These species may be reasonably attributed to ionization of initial $La^{3+}{}_{(aq)}$ and $LaSO_4{}^{+}{}_{(aq)}$ that should be the major species in the solution under our chemical conditions. Note that the subscript (aq), which was so far omitted, is added for clarity in the ESI-MS discussion and refers to initial aqueous species. Ionic currents, $I_{m/z}$, of all the detected gaseous species corresponding to La(III) are measured and, assuming the same ionization rates, used for the calculation of the concentrations in the initial aqueous solutions :

$$\frac{[LaSO_4{}^{+}{}_{(aq)}]}{[La^{3+}{}_{(aq)}]} = \frac{\sum\limits_{m/z} I_{m/z}(LaSO_4{}^{+})}{\sum\limits_{m/z} I_{m/z}(La^{3+})} \qquad (5)$$

Applying the mass action law,

$$\lg\left(\frac{[LaSO_4{}^{+}{}_{(aq)}]}{[La^{3+}{}_{(aq)}]}\right) = \lg K_1 + \lg[SO_4{}^{2-}{}_{(aq)}] \qquad (6)$$

is obtained. The results are shown on Fig. 9. A linear increase of the quantity lg ($[LaSO_4{}^{+}]/[La^{3+}]$) with lg $[SO_4{}^{2-}]$ is observed with a slope +1. These results agree well with the speciation model of the formation of $LaSO_4{}^{+}$ from La^{3+}. The value of lg β_1 is in good agreement with literature data [17] taking into account activity coefficients. For lg $[SO_4{}^{2-}] > -2$, a significant deviation can be noted and suggests the formation of $La(SO_4)_2{}^{-}$ which is actually observed with the ESI-MS negative detection mode.

CONCLUSION

The carbonate complexes $Eu(CO_3)_i{}^{3-2i}$ (i=1-3) have been characterized in bicarbonate and carbonate media by TRLFS and solubility measurements. Particularly the identification of the limiting complex $Eu(CO_3)_3{}^{3-}$ is of great interest since $Eu(CO_3)_4{}^{5-}$ has also been proposed from solvent extraction methods [9(e-f)]. The effect of temperature on analogous Cm(III) solutions is currently being studied by TRLFS. Sulphate complexes of Eu(III) in solutions have been observed by TRLFS. Formation constants for $EuSO_4{}^{+}$ and $Eu(SO_4)_2{}^{-}$ have been obtained at various ionic strengths. A successful use of ESI-MS for quantitative measurements of the analogous $LaSO_4{}^{+}$ formation in aqueous solutions has been presented. The results agree well with our data for Eu(III) and with the literature.

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