

Evidence of different stoichiometries for the limiting carbonate complexes of lanthanides(III) by solubility measurements.

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After the thorough review on thermochemical data on actinides (An) by the Nuclear Energy Agency, the stoichiometry of the limiting carbonate complexes of An(III) is still discussed. Two stoichiometries for An(III) and their lanthanides(III) (Ln(III)) chemical analogues are proposed: $M(\text{CO}_3)_3^{3-}$ and $M(\text{CO}_3)_4^{5-}$ ($M = \text{An}$ or Ln) [1-11]. We suggest that such differences can be correlated to the metal radii, and/or to interactions between the counter-ion and the highly negatively charged aqueous complexes.

Carbonate complexation data are needed to predict the speciation of radionuclides in natural environments. The Callovo-Oxfordian geological formation is studied in France for a possible radioactive waste repository. It is in anoxic chemical conditions, where Pu, Am and Cm can be stable at the +3 oxidation state. In this study, Ln(III)/H₂O/HCO₃⁻/CO₃²⁻/OH⁻ aqueous systems were investigated. When extracting thermodynamic formation constants from experimental data, considering erroneous species in the speciation model can affect the numerical values of the stability constants fitted for the other complexes. The aim of this study is to check the stoichiometries of the limiting carbonate complexes.

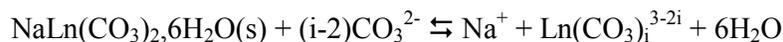
To elucidate the stoichiometries of the Ln(III) and An(III) limiting complexes, three complementary techniques are used: solubility, coprecipitation and capillary electrophoresis. Only the solubility results are presented here.

The limiting complexes are stable in concentrated Alk₂CO₃ aqueous solutions (Alk⁺=alkaline ions, *i.e.* Na⁺ in the present study), particularly when they are in equilibrium with the solid AlkM(CO₃)₂.xH₂O(s) [4-6]. We already reported synthesis methods at room temperature for NaLn(CO₃)₂.xH₂O(s) (Ln=La, Nd, Eu, Dy) [12], in chemical conditions close to those used for solubility measurements.

Several batches (containing NaOH, NaHCO₃, Na₂CO₃, NaClO₄, NaCl) were prepared with different [CO₃²⁻] and [Na⁺]. A few tens of milligrams of the NaLn(CO₃)₂.xH₂O(s) solid were added to the carbonate solutions, so that they were initially undersaturated. Comparing the Ln concentrations measured after various equilibration periods, a steady state was observed after a few days only.

The experimental solubilities are presented after ionic strength corrections. The experimental results were extrapolated to 3 M NaClO₄ by using the specific ion interaction (SIT) formula. The choice of this particular reference state minimizes the calculated corrections by comparison to the usual standard state of zero ionic strength.

Under these conditions, the main dissolution reaction is:



A classical log-log plot of the experimental solubilities against the CO₃²⁻ concentration (**fig. 1**) should draw a curve, built from linear straight lines, whose slopes are equal to (i-2). The

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values 2 and 1 give the best fit in limiting conditions for $\text{NaNd}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ and $\text{NaEu}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, respectively, which evidences the $\text{Nd}(\text{CO}_3)_4^{5-}$ and $\text{Eu}(\text{CO}_3)_3^{3-}$ stoichiometries. Similar experiments were performed for La and Dy. The $\text{Ln}(\text{CO}_3)_4^{5-}$ stoichiometry was evidenced for the lighter (hence bigger) lanthanides (La and Nd), whereas the heavier (Eu and Dy) form $\text{Ln}(\text{CO}_3)_3^{3-}$ limiting complexes.

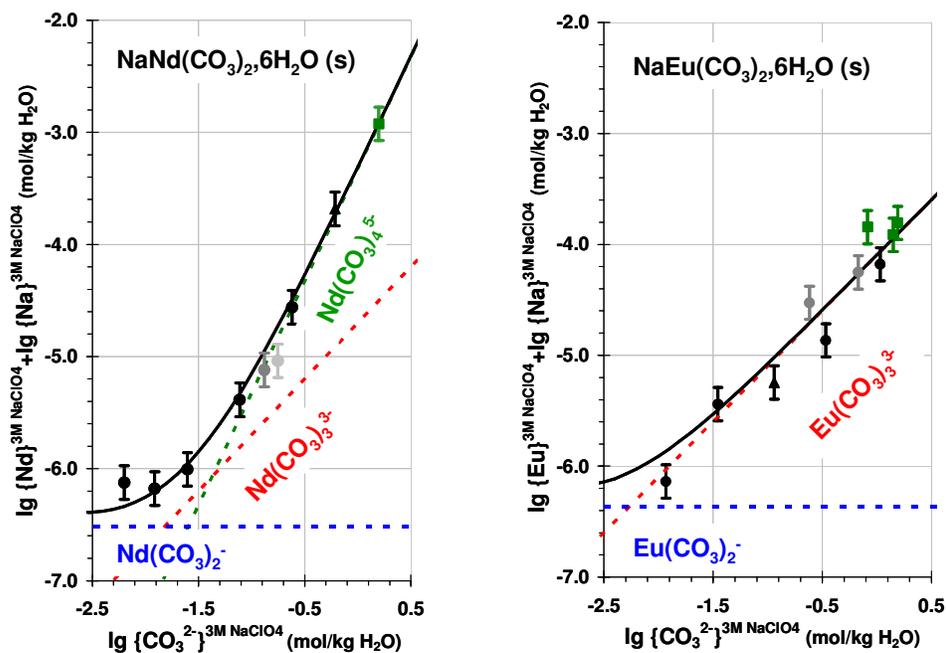


Fig. 1: Corrected Nd and Eu solubilities measured after 70 to 120-day equilibration periods. (●) $[\text{Na}^+]=3\text{M}$, (◐) $[\text{Na}^+]=1\text{M}$, (◑) $[\text{Na}^+]=0.5\text{M}$, for different holding electrolytes (▲) NaCl, (●) NaClO₄, (■) Na₂CO₃ (no holding electrolyte). The concentrations are extrapolated to 3M NaClO₄ aqueous conditions to minimize the ionic strength corrections (see text).

To our knowledge, it is the first time that two different stoichiometries are confirmed by the same laboratory, using the same experimental methodology. Further measurements using other techniques are in progress, in order to elucidate the stoichiometry for the whole series of lanthanides(III) (except Pm), Am(III) and Cm(III), in Na⁺ solutions and with other counterions.

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