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Introduction

Carbonate complexation data are needed to predict the speciation of radionuclides in natural environments. Indeed, carbonate is one of the most complexing inorganic ligands present in groundwater. Pu, Am and Cm can be stable at the +3 oxidation state in the anoxic chemical conditions of the Callovo-Oxfordian geological formation studied in France for a possible radioactive waste repository.

Although a large number of studies were performed, the stoichiometry of the limiting carbonate complexes of actinides(III) (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.

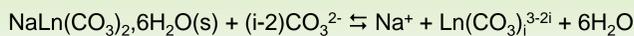
In this study, Ln(III)/H₂O/HCO₃⁻/CO₃²⁻/OH⁻ aqueous system was investigated since, in a first approximation, Ln can be considered as chemical analogues of An. The aims of this study are:

- > to check the stoichiometries of the limiting carbonate complexes of Ln(III),
- > to determine the equilibrium constant corresponding to its formation.

Method

Various experimental techniques can be used in order to determine the stoichiometry of aqueous complexes: ultraviolet-visible spectrophotometry, electrochemistry, potentiometric measurement, extended X-ray absorption fine structure... Nevertheless, information about the aqueous complex can rarely be obtained (stoichiometry, charge...). To elucidate the stoichiometries of the Ln(III) limiting carbonate complexes, solubility measurements were carried out. Solubility was chosen since information on both the solid phase and the aqueous complexes can be obtained simultaneously.

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]. The studied reaction is then:



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

$$\lg S \approx \lg \{\text{Ln}(\text{CO}_3)_i^{3-2i}\} = (i-2) \lg \{\text{CO}_3^{2-}\} - \lg \{\text{Na}^+\} + \lg K_{\text{msi}}$$

The specific interaction theory (SIT) was used to extrapolate the values of the formation constants to other ionic conditions. It is particularly useful to compare literature data and to extract standard values at zero ionic strength (typically K⁰) from experimental ones (typically K_m).

$$\lg K_m = \lg K^0 + \Delta z^2 D - (\Delta \epsilon_{\text{ClO}_4^-} \{\text{ClO}_4^-\} + \Delta \epsilon_{\text{Cl}^-} \{\text{Cl}^-\} + \Delta \epsilon_{\text{CO}_3^{2-}} \{\text{CO}_3^{2-}\} + \Delta \epsilon_{\text{HCO}_3^-} \{\text{HCO}_3^-\} + \Delta \epsilon_{\text{OH}^-} \{\text{OH}^-\} + \Delta \epsilon_{\text{Na}^+} \{\text{Na}^+\} + \lg a_{\text{H}_2\text{O}}$$

Results and discussion

Solubility measurements are time consuming due to:

- > the synthesis and the characterization of the most stable solid phase under the solubility conditions,
- > the few weeks needed to reach the equilibrium between the solid and liquid phases.

Therefore, solubility measurements were performed only on 4 NaLn(CO₃)₂.6H₂O(s) (with Ln=La, Nd, Eu and Dy).



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.

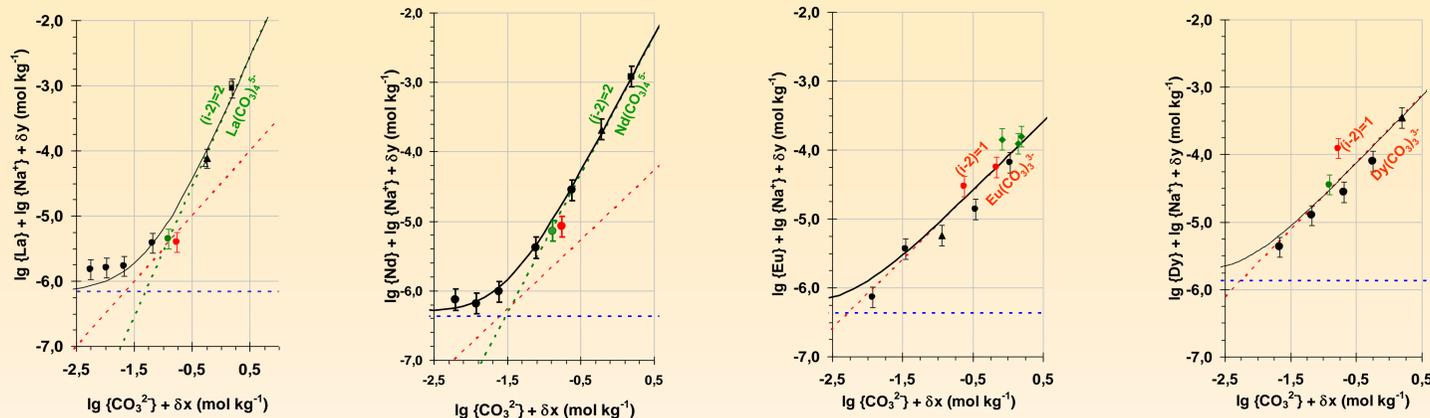


Fig. 1: Corrected solubilities measured after 70 to 120-day equilibration periods. (●) [Na⁺]=3M, (○) [Na⁺]=1M, (◐) [Na⁺]=0.5M, for different holding electrolytes (▲) NaCl, (●) NaClO₄, (■) Na₂CO₃ (no holding electrolyte). The concentrations are extrapolated to 3M NaClO₄ aqueous conditions to minimize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

The classical lg-lg plot of the experimental solubilities shows a slope of 2 in limiting conditions for NaLa(CO₃)₂.6H₂O(s) and NaNd(CO₃)₂.6H₂O(s); whereas a slope of 1 gives the best fit for NaEu(CO₃)₂.6H₂O(s) and NaDy(CO₃)₂.6H₂O(s). Those different slopes evidence two different stoichiometries among the Ln series: Ln(CO₃)₄⁵⁻ and Ln(CO₃)₃³⁻. The Ln(CO₃)₄⁵⁻ stoichiometry was evidenced for the lightest (hence largest) lanthanides (La and Nd), whereas the heaviest (Eu and Dy) form Ln(CO₃)₃³⁻ limiting complexes.

	La	Nd	Eu	Dy
lg K _{m3} ^{NaClO4 3M}	1.7 0.1	1.6 0.1	2.3 0.1	2.2 0.1
lg K ₃ ⁰	0.6 0.2	0.5 0.2	1.2 0.2	1.2 0.2
lg K _{m4} ^{NaClO4 3M}	0.9 0.1	1.5 0.1		
lg K ₄ ⁰	-2.5 0.2	-2.0 0.2		

Concerning the complex formation equilibrium constants, they have been extrapolated to zero strength. The variation of the lg K₃⁰ value is not smooth. When a tetracarbonato compound can form, it seemed that the predominant field of Ln(CO₃)₃³⁻ is very narrowed. As well as for the stoichiometry, two distinct behaviours can be highlighted

The radii of those 4 lanthanides are quite different (for 8-coordination) [12]: r_{La3+}} = 1.16 Å, r_{Nd3+}} = 1.12 Å, r_{Eu3+}} = 1.07 Å, r_{Dy3+}} = 1.03 Å.

Therefore, the hypothesis explaining the stoichiometry of the limiting carbonate complex with ionic radius seems to be validated. Knowing their ionic radius, it may be possible to propose a stoichiometry for the limiting carbonate complex of Pu³⁺, Am³⁺ and Cm³⁺: r_{Pu3+}} = 1.12 Å, r_{Am3+}} = 1.09 Å and r_{Cm3+}} = 1.09 Å.

It appears that, if Ln and An behaviour concerning carbonate complexation is analogue, Pu³⁺ would form a tricarbonato compound. No assumption can be made for Am³⁺ and Cm³⁺ since their ionic radius is smaller than Nd³⁺ radius but larger than Eu³⁺ radius.

Conclusion

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 counter-ions.

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