EVIDENCE OF DIFFERENT STOICHIOMETRIES FOR THE LIMITING CARBONATE COMPLEXES OF LANTHANIDES(III)

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Context and goals of the study

The nature of the limiting carbonate complex of An^{3+} and Ln^{3+} cations is still debated in the literature: both $M(CO_3)_3^{3-}$ and $M(CO_3)_4^{5-}$ stoichiometries have been used, by different laboratories, to interpret measurements on M^{3+} f-block cations [1]. We have investigated the aqueous speciation of the lanthanides at the +3 oxidation state for CO_3^{2-} concentrations ranging from 10^{-3} to 2.5 mol L^{-1} at room temperature, atmospheric pressure and high ionic strengths by different techniques : **solubility**, **capillary electrophoresis** (CE) and **time-resolved laser fluorescence spectroscopy** (TRLFS), to study the **influence of the ionic radius of the lanthanides** on the limiting complex formed. The **influence of the alkali metal counter-ions** (Alk^+ = Li^+, Na^+, K^+, Cs^+), has also been investigated since solubility measurements of hydrated $AlkEu(CO_3)_2$ were interpreted with $Eu(CO_3)_4^{5-}$ in concentrated potassium carbonate solutions (supporting electrolyte: KCl 4.2 mol L^{-1}) [2], whereas $Eu(CO_3)_3^{3-}$ was evidenced in concentrated sodium carbonate solutions (supporting electrolyte: $NaClO_4$ 3 mol L^{-1}) [1]. The aqueous alkali metal counter-ions may favor a more anionic complex by **ion pairing**.

Experimental techniques

Solubility : $NaLn(CO_3)_2,xH_2O$ are equilibrated in carbonate solutions, a classical slope analysis allows to evidence the stoichiometry of the limiting carbonate complexes ($NaLn(CO_3)_2,xH_2O(s)$ + **(i-2)**$CO_3^{2-} \leftrightarrows Na^+ + Ln(CO_3)_i^{3-2i} + xH_2O$).

CE-ICP-MS : $Ln(CO_3)_3^{3-}$ and $Ln(CO_3)_4^{5-}$ are separated by their charge to hydrodynamic radius ratio, in an high electric field, in 0.15 and 0.5 mol L^{-1} Alc_2CO_3 solutions (Alc^+ = Li^+, Na^+, K^+, Cs^+).

SLRT : Fluorescent Eu(III) is excited in carbonate solutions by a pulsed laser beam. The analysis of its fluorescence spectra enables to measure K_3 in $[Alc^+]$ = 3 mol L^{-1} solutions (Alc^+ = Na^+, K^+, Cs^+).

Results and discussion

The **La and Nd** solubility data approached accurately a limiting **slope of 2** in the region of high carbonate concentration, whereas **Eu and Dy** approached a limiting **slope of 1**, indicating the formation of **$Ln(CO_3)_4^{5-}$** and **$Ln(CO_3)_3^{3-}$** respectively.

The **measurements of Vercouter** [1], who dealt with the solubility of $NaEu(CO_3)_2,6H_2O$ in $NaClO_4$ supporting electrolyte, are indicated by blue solid circles, they **coincide with our data fairly well**.

⇒ **The stoichiometry of the limiting carbonate complex changes among the lanthanide series.**

$\mu^I = \sum \Phi_i \mu_i^I$ and $\mu_i^I = f(\eta, \varepsilon, I, pH, T, V, z_i/r_i)$

μ^I: global electrophoretic mobility, η: viscosity, ε: dielectric constant I: ionic strength, pH, T: temperature of the experimental medium, z_i, r_i, Φ_i and μ_i^I: charge, radius, molar fraction and electrophoretic mobility of each ion i, V: voltage during the electrophoretic separation
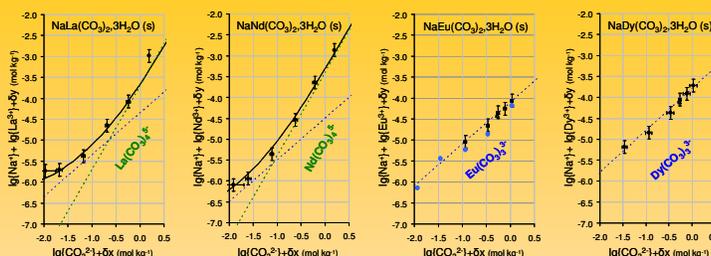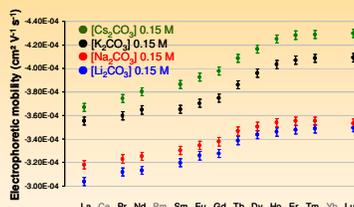

The curves are S shaped whatever the counter-ion indicating that La→ Nd and Dy→ Lu have a similar aqueous speciation.

The most anionic species are slower than the least anionic ones, and the variations of η, ε and I are not sufficient to explain the difference of mobility.

⇒ **$Ln(CO_3)_i^{3-2i}$ are stabilized by ion-pairing and the association increases from Cs^+ to K^+ to Na^+ to Li^+.**

The **fluorescence spectra superimposed** whatever the experimental medium.

The intensity of the fluorescence spectra decreases for $[CO_3^{2-}]<0.3$ mol L^{-1} indicating the **dissociation of the limiting carbonate complex**. The stepwise formation constant of $Eu(CO_3)_3^{3-}$ is determined : **$K_3 \approx 1.7 \pm 0.2$** and **$K_3^0 = 0.6 \pm 0.5$** (extrapolated to zero ionic strength with the SIT formula).

$Eu(CO_3)_2^- + CO_3^{2-} \leftrightarrows Eu(CO_3)_3^{3-}$ (K_3)
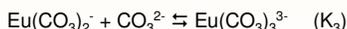
⇒ **The ion pairs are solvent-shared or solvent-separated ion pairs since there is no modification of the inner sphere of the complexes.**
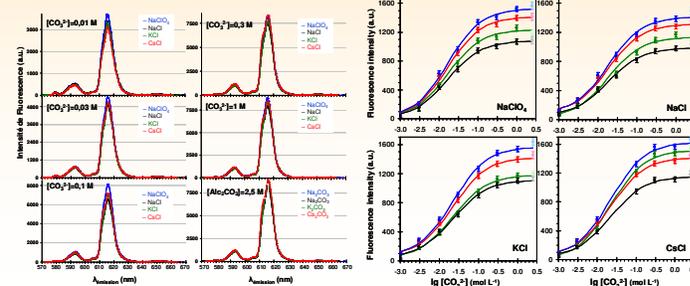
Conclusion

The stoichiometry of the carbonate limiting complexes of lanthanides(III) changes among the 4f-block; but the counter-ion is not able to modify the stoichiometry of the complex nor its inner-sphere. Alkali metal form solvent-shared or solvent-separated ion pairs with $Ln(CO_3)_i^{3-2i}$, and the association increases from Cs^+ to K^+ to Na^+ to Li^+.

References

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