

Evidence of Different Stoichiometries for the Limiting Carbonate Complexes Among the Lanthanide(III) Series by Capillary Electrophoresis-Mass Spectrometry

Violaine Philippini¹, Thomas Vercouter¹, Chrystel Ambard², Sylvain Topin², Jean Aupiais², Pierre Vitorge^{1,3}, Annie Chaussé³

¹CEA SACLAY DEN/DANS/DPC/SECR, 91191 Gif-sur-Yvette, France

²CEA BRUYERES-LE-CHATEL DAM/DIF/DASE/SRCE BP12, 91680 Bruyères-le-Châtel, France

³UMR 8587 (Evry University-CEA-CNRS), Boulevard François Mitterrand, 91025 Evry, France

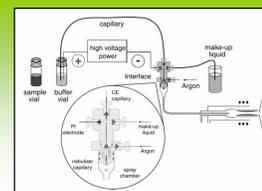
Context and goals of the study

The stoichiometry of the carbonate limiting complex of lanthanides (Ln) or actinides (An) is still discussed, even after the review of the published thermochemical data by the Nuclear Energy Agency. **Two stoichiometries** have been reported for the limiting complexes of these trivalent cations: $M(CO_3)_3^{3-}$ and $M(CO_3)_4^{5-}$. $Am(CO_3)_3^{3-}$ and $Cm(CO_3)_4^{5-}$ have been proposed as limiting complexes by the NEA whereas Am(III) and Cm(III) are known as analogs [1]. The small difference of **ionic radii** would explain the difference of stoichiometry. Since the Ln crystal ionic radii smoothly varies along the series ($r_{La(III)} = 1.016 \text{ \AA}$ to $r_{Lu(III)} = 0.908 \text{ \AA}$), the same difference could exist. Solubility measurements have been performed on $NaLn(CO_3)_2 \cdot xH_2O$ (cr) (Ln=La, Nd, Eu and Dy). They evidenced that La and Nd form the aqueous limiting carbonate complex $Ln(CO_3)_4^{5-}$ whereas Eu and Dy form $Ln(CO_3)_3^{3-}$. Two different stoichiometries actually exist and are not only the result of various interpretations from several laboratories. Moreover, solubility measurements of hydrated $AlkLn(CO_3)_2$ were interpreted with $Ln(CO_3)_4^{5-}$ ($Ln^{3+} = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}$) in concentrated potassium carbonate solutions (**KCl 3.8 to 4.2 M**) [2] whereas $Eu(CO_3)_3^{3-}$ was evidenced in concentrated sodium carbonate solutions (**NaClO₄ 3 M**) [3]. The aqueous alkali metal counter-ions, which interact with highly negatively charged Ln complexes, could favor a more charged complex by **ion-pairing**. This work intends to determine where the stoichiometry break occurs and to test the formation of ion pairs.

CE-ICP-SFMS

Capillary Electrophoresis-Inductively Coupled Plasma-Sector Field Mass Spectrometry

- ⊗ Efficient physical separation of the aqueous species
- ⊗ Low detection limits (U.V. detection non adapted, Ln ~ insoluble, Ln ~ non chromophore)
- ⊗ Multi-element monitoring
- ⊗ Flow rate discrepancy between the both instruments
- ⊗ High salinity and basic pH of the samples



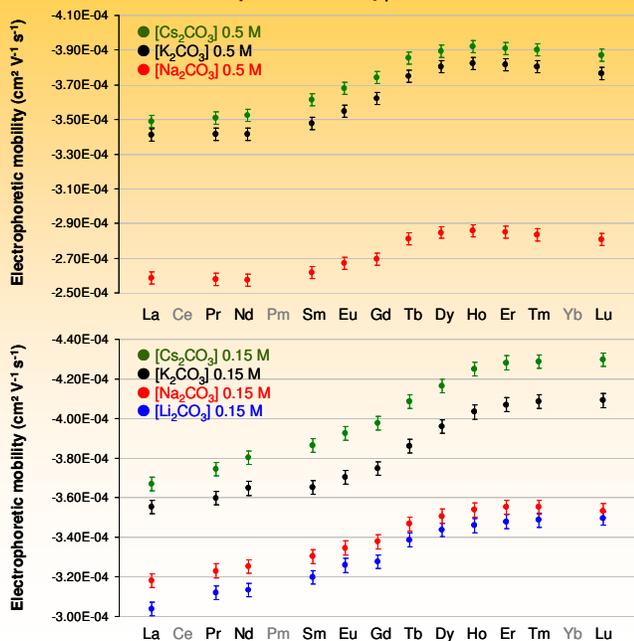
Results and discussion

Mobility measurements on 12 Ln(III) in concentrated carbonate solutions have been performed, varying the alkali metal counter ions (Li⁺, Na⁺, K⁺, Cs⁺)

$$\mu_i^0 = \Sigma \Phi_i \mu_i^0 \text{ and } \mu_i^0 = f(\eta, \epsilon, I, pH, T, V, z_i/r_i)$$

μ_i^0 : 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^0 : charge, radius, molar fraction and electrophoretic mobility of each ion i ; V : voltage during the electrophoretic separation

but no theoretical nor empirical law for μ_i^0 when $I \geq 0.1 \text{ M}$



➤ In a given medium: $\mu_i^0 = f(z_i/r_i)$:

- ✓ S shaped curves whatever the counter-ion:
 - La → Nd: similar speciation (mixture of ~50% $Ln(CO_3)_4^{5-}$ and 50% $Ln(CO_3)_3^{3-}$)
 - Dy → Lu: similar speciation (100% $Ln(CO_3)_3^{3-}$)
 - Sm, Eu, Gd, Tb (mixture of $Ln(CO_3)_3^{3-}$ and $Ln(CO_3)_4^{5-}$; predominance of $Ln(CO_3)_3^{3-}$)
- ✓ The most anionic species are slower than the least anionic ones, this tendency is unexpected. It may mean that $Ln(CO_3)_4^{5-}$ is stabilized by ion-pairing and the charge of the aqueous analyzed species is not -5.

*From the formation constants determined by solubility measurements extrapolated to the experimental ionic strengths

➤ Varying the counter-ion: $\mu_i^0 = f(\eta, \epsilon, I, z_i/r_i)$:

- ✓ Variations of η , ϵ , and I are not sufficient to explain the huge difference of mobility between Na⁺ and K⁺ media, for example.
- ✓ Spectroscopic measurements on Eu(III) show the same spectra, whatever the counter-ion, suggesting that the inner-sphere of the complexes are identical.
- ✓ The difference of electrophoretic mobility can be explained by ion-pairing (solvent-shared ion pairs or solvent-separated ion-pairs). Cs and K are "structure breakers" [4], their affinity for water molecules is weak, their Stokes radii are smaller than those of Li and Na. Thus, the electrophoretic mobility of the complexes are bigger in K and Cs media. Since the analyzed species remain anionic, less than 3 and 5 alkali metal ions stabilized the complexes.

➤ Varying the ionic strength of the background electrolyte:

- ✓ The mobility is higher in $[Alk_2CO_3] = 0.15 \text{ M}$ than in $[Alk_2CO_3] = 0.5 \text{ M}$ due to the decrease of the viscosity and the ionic strength, as expected.
- ✓ No plateau was observed for the lightest Ln, the aqueous speciation of each Ln is quite different, indicating that the formation constant of the limiting complex varies slightly with the atomic number.

Conclusion

The existence of two distinct stoichiometries for Ln carbonate limiting complexes, as a function of the atomic number, has been confirmed by CE-ICP-MS, which is a powerful tool to study the aqueous speciation of metals, even in highly concentrated solutions. The break occurs between Sm and Dy as for the aquo ions. The variation of electrophoretic mobility can be correlated to ion-pairing.

References

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