

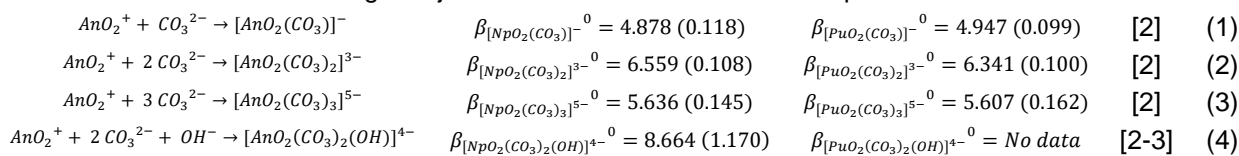
# Determination of the stability constant of $[\text{NpO}_2(\text{CO}_3)_2(\text{OH})]^{4-}$ by capillary electrophoresis coupled with an ICP-MS (CE-ICP-MS)

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Ternary complexes are little studied species, as they are less easy to study than binary complexes. These reactions were initially considered negligible in speciation studies until the mid-90s with the discovery of calcium uranium carbonate complexes by Bernhard *et al.* [1] which are the predominant species of uranium in aquatic environments. Determining the thermodynamic constants of these reactions is therefore essential for studying the migration and toxicity of elements in the environment. Plutonium is an extremely toxic element present at the ultra-trace scale in the environment. Its behavior is different at this scale, making it stable at an oxidation state of V. The study of complexes of this element therefore requires highly sensitive equipment, capable of distinguishing changes in plutonium species as a function of variations in ligand concentration.

Capillary electrophoresis coupled with ICP-MS can meet these needs. Carbonates are strong ligands found in significant quantities in the environment. Plutonium and neptunium V behave similarly, forming mono (1), di (2) and tri carbonates (3) complexes, as well as carbonate hydroxide ternary complexes (4) at alkaline pH. This study focuses on neptunium V, before applying a similar methodology to plutonium V. Measurements are taken at different pH values with a total carbonate concentration of  $0.1 \text{ mol}\cdot\text{L}^{-1}$  and an ionic strength adjusted to  $0.37 \text{ mol}\cdot\text{L}^{-1}$  with sodium perchlorate.



The different charged species have different electrophoretic mobility, and since chemical kinetics are rapid, the mobility measured is linked to the stability constants of the species (5).

$$\mu_{ov} = \frac{\mu_{\text{AnO}_2^+} + \sum_{0 \leq m \leq 3} \sum_{0 \leq n \leq 2} (\mu_{[\text{AnO}_2(\text{CO}_3)_m(\text{OH})_n]^{(2m+n-2)-}} \times [\text{CO}_3^{2-}]^m \times [\text{OH}^-]^n \times \beta_{[\text{AnO}_2(\text{CO}_3)_m(\text{OH})_n]^{(2m+n-2)-}})}{1 + \sum_{0 \leq m \leq 3} \sum_{0 \leq n \leq 2} ([\text{CO}_3^{2-}]^m \times [\text{OH}^-]^n \times \beta_{[\text{AnO}_2(\text{CO}_3)_m(\text{OH})_n]^{(2m+n-2)-}})} \quad (5)$$

The species stability constants can therefore be determined by mathematical adjustment to match the mobility curve obtained (Figure 1). Preliminary results show formation constants in agreement with the literature data with a lower uncertainty than the reference value.

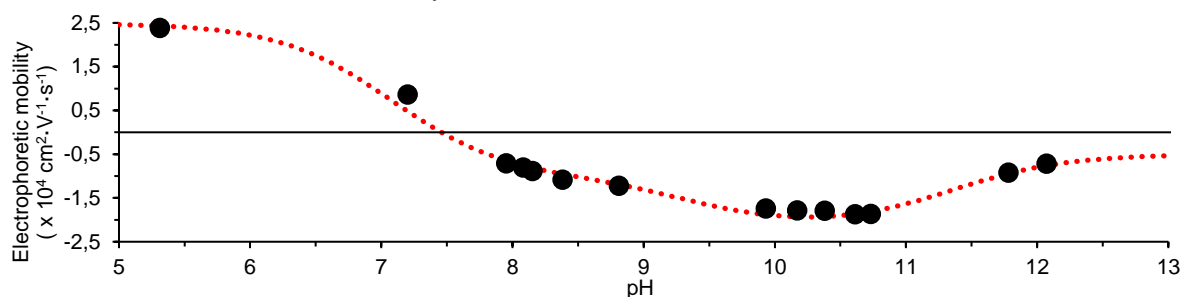


Figure 1 : Evolution of the electrophoretic mobility of neptunium depending of pH with  $[\text{CO}_3^{2-}]_{\text{total}} = 0.1 \text{ mol}\cdot\text{L}^{-1}$  and ionic strength adjusted to  $0.37 \text{ mol}\cdot\text{L}^{-1}$  with sodium perchlorate, black circles are measured data and the red dotted line is the mathematical adjustment

[1] Bernhard G., Geipel G., Brendler V., Nitsche H. « Speciation of Uranium in Seepage Waters of a Mine Tailing Pile Studied by Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS) ». *Radiochimica Acta* 74, no s1 (December 1996): 87-92. <https://doi.org/10.1524/ract.1996.74.special-issue.87>.

[2] Topin S., Aupiais J., Moisy P. « Direct Determination of Plutonium(V) and Neptunium(V) Complexation by Carbonate Ligand with CE-ICP-sector Field MS ». *ELECTROPHORESIS* 30, no 10 (May 2009): 1747-55. <https://doi.org/10.1002/elps.200800656>

[3] Guillaumont R., Fanghänel T., Neck V., Fuger J., Palmer D. A., Grenthe I., Rand M. H., Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier B.V., Amsterdam, 2003