

# Complexation of Eu(III) and Cm(III) with phosphates: a luminescence, thermodynamic, and theoretical study

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The environmental fate of radionuclides (RN), such as actinides and fission products, disposed of in underground nuclear waste repositories is a major concern. Long-term safety assessments of these disposal sites depend on the ability of geochemical models and thermodynamic databases (TDBs) to predict the mobility of RNs over very long time scales. One example where TDBs still have large data gaps is related to the complexation of trivalent lanthanides and actinides with aqueous phosphates. Indeed, solid phosphate monazites are one of the candidate phases for the immobilization of specific high-level waste streams for future safe storage in deep underground disposal facilities, therefore potentially and locally increasing the presence of phosphate at the final disposal site.

Recent work [1-3] obtained reliable complexation constants and thus, closed some knowledge gaps. Laser-induced luminescence spectroscopy was used to study the complexation of Eu(III) and Cm(III) as a function of total phosphate concentration in the temperature regime 25-90 °C, using NaClO<sub>4</sub> as a background electrolyte. These studies were conducted in the acidic pH range to avoid precipitation of solid Eu and Cm rhabdophane. In addition to the presence of the EuH<sub>2</sub>PO<sub>4</sub><sup>2+</sup>/CmH<sub>2</sub>PO<sub>4</sub><sup>2+</sup> species [1-3], the formation of Eu(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub><sup>+</sup> [2] and Cm(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub><sup>+</sup> [3] was unambiguously established from the luminescence spectroscopic data. The conditional complexation constants of all aqueous complexes were extrapolated to infinite dilution with the Specific ion Interaction Theory. The molar enthalpy of reaction  $\Delta_r H_m^\circ$  and entropy of reaction  $\Delta_r S_m^\circ$  were derived with the integrated van't Hoff equation.

Monodentate or bidentate Cm(III)/Eu(III) phosphate complexes form with different overall coordination numbers (8,9), but obtaining such information from spectroscopic data only is challenging. Thus, the structural properties, electronic structures, and thermodynamics of the 1:1 and 1:2 Eu(III) and Cm(III) phosphate complexes were solved using state-of-the-art relativistic quantum chemical (QC) calculations. The QC methods allowed i) to investigate the complexation strength of Eu(III) and Cm(III) with aqueous phosphate, ii) to understand the changes of the coordination number with increasing temperature and iii) to decipher the nature (ionic/covalent) of the Eu/Cm bonds with water and phosphate.

Combining quantum chemical calculations with the observed spectral changes facilitates the decisive determination of the structures of the formed phosphate complexes and their overall coordination [2,3].

[1] N. Jordan et al., *Inorganic Chemistry* 57, 7015 (2018).

[2] I. Jessat et al., *Inorganic Chemistry* (in preparation).

[3] N. Huittinen et al., *Inorganic Chemistry* 60, 10656 (2021).