

Determination of Formation Constants and Specific Ion Interaction Coefficients for Mg/Ca-UO₂-CO₃ Complexes in NaCl Solution by Time-Resolved Laser-Induced Luminescence Spectroscopy.

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The speciation of uranium is of great importance for a reliable prediction of its transport from disposal and storage site of radioactive waste into various geochemical environments. In particular, the ubiquitous presence of magnesium/calcium and carbonate in natural water systems renders the formation and chemical behaviour of uranium in Mg/Ca-CO₃ rich waters important to be elucidated. Since their first evidence in the 1990's, the Mg/Ca_nUO₂(CO₃)₃⁽⁴⁻²ⁿ⁾⁻ complexes have been the subject of several studies. Nevertheless, the evolution of the formation constants of at varying ionic strength has only been merely the subject of attention, which leaves the subject of the thermodynamic constants in the standard state a matter of debate. In this study, the formation constants of Mg/CaUO₂(CO₃)₃²⁻ and Ca₂UO₂(CO₃)₃(aq) were determined in varying ionic strength in NaCl and NaClO₄ media, using time-resolved laser-induced luminescence spectroscopy (TRLs). Spectroluminescence titration of UO₂(CO₃)₃⁴⁻ complex by Mg²⁺/Ca²⁺ were conducted at atmospheric CO₂(g) and varying pH values in order to avoid the precipitation of both schoepite (UO₃·2H₂O) and Mg/Ca carbonate minerals in aqueous solutions. The stoichiometry of Mg²⁺/Ca²⁺ was evidenced by the slope analyses corrected by the Ringböm coefficient of UO₂(CO₃)₃⁴⁻ relative to pH and CO₂(g), instead of the typical expression relative to UO₂²⁺ and CO₃²⁻. In the range of studied ionic strength, satisfactory linear fits assessed the stepwise formation constants, the values of which were in good agreement with literature data at comparable ionic strengths. Determination of the thermodynamic constants in the standard state were done through extrapolations to infinite dilution in the framework of the specific ion interaction theory (SIT), also providing the evaluation of the specific ion interaction coefficients $e(\text{Mg/CaUO}_2(\text{CO}_3)_3^{2-}, \text{Na}^+)$ and $e(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq}), \text{NaX})$, X being either Cl or ClO₄. The implications of this full set of data on the speciation of uranium in groundwaters representative of possible radioactive waste repositories in clayey environments and in seawater, providing different Mg-Ca-CO₃ and ionic strength conditions, will be discussed from geochemical modelling.

