Impact of α–D–gluconic acid on the solubility and speciation of An(III)/Ln(III) in dilute to concentrated NaCl/$MgCl_2$ solutions

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Gluconic acid (GLU) is a poly–hydroxocarboxylic acid expected in repositories for low and intermediate–level radioactive waste as a component of cementitious materials. Formation of stable An(III)/Ln(III)-GLU complexes has been reported in the literature for dilute systems, but the knowledge lacks for more concentrated salt media expected in specific clays or in rock-salt formations. The presence of Ca(II) is known to enhance the stability of such complexes, however, analogous studies investigating the role of Mg(II) in An(III)/Ln(III)-GLU systems are so far missing.

All experiments were performed at T = (22 ± 2) °C under Ar atmosphere. Undersaturation solubility experiments with $Nd(OH)_3(s)$ were conducted in 0.1–5.0 M NaCl and 0.25–4.5 M $MgCl_2$ solutions with $6 \leq pH_m \leq 13$ and 10^{-4} M < $[GLU]_{tot}$ < 0.1 M. TRLFS measurements were performed under analogous conditions with $[Cm(III)]_{tot} \approx 10^{-7}$ M.

A distinct increase in the solubility of $Nd(OH)_3(am)$ with respect to the GLU-free systems is only observed for NaCl and less concentrated (< 2 M) $MgCl_2$ solutions, whereas the effect becomes negligible at higher $MgCl_2$ concentrations. Complementary TRLFS data indicates the formation of a single Cm(III)–GLU species in NaCl and diluted $MgCl_2$ solutions. A more complex Cm(III)-GLU speciation arises in alkaline NaCl solutions, most likely resulting from the deprotonation of the α-hydroxil group of gluconate. Results show the formation of stable binary An(III)/Ln(III)-GLU complexes, but the absence of ternary Mg(II)–Cm(III)–GLU species, due to the competitive behavior between Mg(II) and Nd(III) towards GLU-complexation. These results allow the development of thermodynamic and activity models for the system Na-Mg-An(III)/Ln(III)-GLU to be implemented in geochemical calculations of relevance in the context of nuclear waste disposal.

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