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Complexation of gluconate with An(III)/Ln(III) in diluted to concentrated $MgCl_2$ solutions: Mg(II)–gluconate and Mg(II)–An(III)/Ln(III)–gluconate systems

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Introduction

In the long term safety assessment of repositories for radioactive waste disposal, the event of water intrusion and consequent formation of aqueous systems needs to be evaluated. In the case of repositories in rock salt formations, brine solutions are dominated by NaCl and $MgCl_2$. The use of brucite-based backfill material in such repository concepts is responsible for the buffering of pH_m to ~9. Gluconic acid ($C_6H_{12}O_7$) is a poly–hydroxycarboxylic acid expected in repositories for low and intermediate–level radioactive waste as a component in the formulation of cement.

Formation of stable An(III)/Ln(III)–gluconate(/GLU) binary complexes has been reported in the literature [1]. The presence of Ca(II) enhances complex stability through formation of ternary species with An(III)/Ln(III) in the hyperalkaline pH range [2]. Despite the relevance of Mg(II) in several repository concepts for radioactive waste disposal, no studies assessing the role of Mg(II) in An(III)/Ln(III)–gluconate complexation have been conducted so far. In $MgCl_2$–rich brines, the formation of highly stable Mg(II)–gluconate complexes may outcompete the formation of An(III)–gluconate complexes.

Objectives

- **Evaluation of the binary Mg(II)–gluconate (GLU) system, deriving the corresponding thermodynamic and activity models**
- **Assessing the solubility and aqueous speciation of Ln(III)/An(III) in the presence of gluconate and dilute to concentrated $MgCl_2$ solutions in alkaline media**
- **Deriving comprehensive thermodynamic and activity models for Mg(II)–Ln(III)/An(III)–gluconate systems under repository-relevant conditions**
- **Providing a sound basis to interpret An(III) behavior in saline systems in the presence of gluconate**

Experimental conditions

NMR experiments

- ^1H and ^{13}C NMR spectra recorded at 25.0 ± 0.2 °C
- Bruker Avance DRX-500 spectrometer operating at 499.9 MHz for ^1H and 125.7 MHz for ^{13}C
- $[GLU]_{tot}$ = 0.20 M, pH_c = 8 (TRIS)
- NaCl and $MgCl_2$ as background electrolytes:
  - 0.03 M ≤ $[MgCl_2]_{tot}$ ≤ 0.27 M
  - I = 1.00, 2.00 M (NaCl–$MgCl_2$–NaGLU)

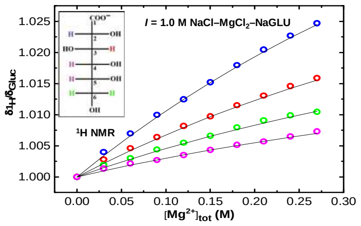
Nd(III) – solubility experiments

- Samples prepared and stored at 22 ± 2 °C in Ar-gloveboxes (O_2 content < 2 ppm)
- Undersaturation solubility experiments with $Nd(OH)_3$(am) (7–15 mg per batch experiment)
- pH_m = 8 (TRIS/MES), 9 ($Mg(OH)_2$ or $Mg_2(OH)_3Cl\cdot 4H_2O$(cr)) (with $pH_m = pH_{exp} + A_m$)
- BGE: 0.25 M – 4.50 M $MgCl_2$
- 10^{-4} M ≤ $[GLU]_{tot}$ ≤ 0.10 M
- Equilibration time: ≤ 360 days
- $[Nd(III)]_{tot}$ determined by ICP-MS after 10 kD ultrafiltration
- Solid phase characterization: XRD

^{248}Cm(III)–TRLFS measurements

- Excitation at λ = 396.6 nm
- $[Cm(III)]_{tot} = 1\cdot 10^{-7}$ M
- 0.25 M, 4.50 M $MgCl_2$ and 0.10 M, 4.50 M NaCl as background electrolyte
- pH_m = 6 (MES), 8, 8.7 (MOPS/TRIS),
- 10^{-4} M ≤ $[GLU]_{tot}$ ≤ 0.10 M, or
- 5 ≤ pH_m ≤ 8.7 ($pH_m = pH_{exp} + A_m$)

Mg(II)–GLU

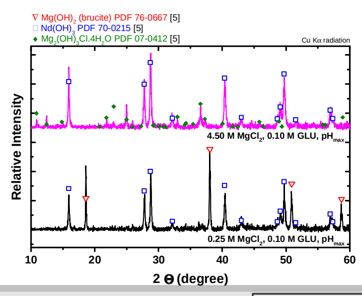


- Mg(II)–GLU interaction is weaker than for the Ca(II)–GLU system [4]
- → rigid coordination structure (octahedral) of Mg(II) aq
- Formation of $MgGLU^+$ proposed
- Apparent stability constant in I = 1.00 M in NaCl–$MgCl_2$–NaGLU-system:

M^{2+} + GLU ⇔ MGLU

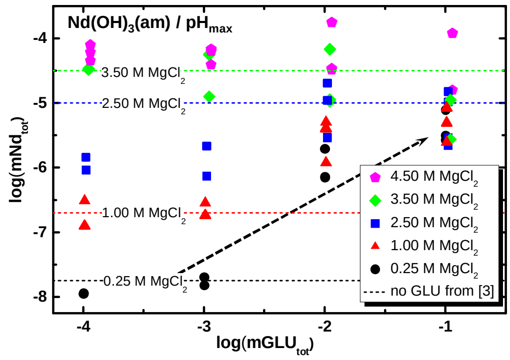
M = Mg → log K' (I = 1 M) **= 0.18 ± 0.41** (^1H, ^{13}C NMR)
log K' (I = 2 M) **= 0.49 ± 0.06** (^1H, ^{13}C NMR)
M = Ca → log K' (I = 1 M) **= 1.02 ± 0.05** [4]

XRD



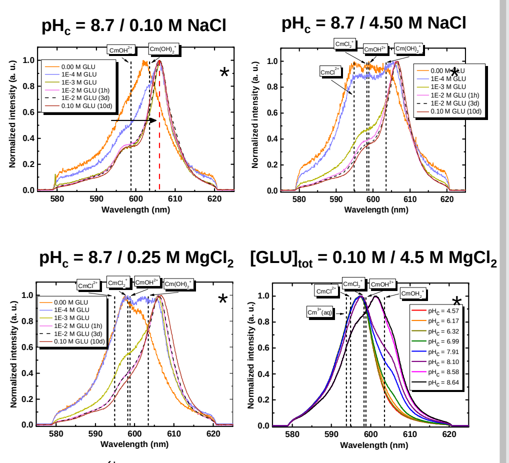
Mg(II)–An(III)/Ln(III)–GLU

Solubility–Nd(III)



- Strong increase in Nd(III) solubility with increasing $[GLU]_{tot}$ in 0.25 and 1.0 M $MgCl_2$ solutions
- Minor (or no effect) of GLU at higher $MgCl_2$ concentration
  → likely competition between Mg(II) and Nd(III) for GLU
- XRD shows the predominance of $Nd(OH)_3$(am) in all the investigated systems (from **0.25 M**, 4.50 M $MgCl_2$, with $[GLU]_{tot}$ ≤ 0.10 M)

TRLFS–Cm(III)



(* peak positions for Cm(III)-Cl-OH species as reported in [3])

- Series in NaCl and 0.25 M $MgCl_2$ at pH_c = 8.7:
  - large increase of intensity and red-shift in wavelength with increasing $[GLU]_{tot}$
  - single isobestic point observed → spectra deconvolution indicates one new Cm(III)–GLU species at ~606.2 nm
  - → Stoichiometry of the complex: 1:1 or 1:2 (see also [2])
- Spectra series from 4.50 M $MgCl_2$ at pH_c = 8.7:
  - less pronounced changes in the speciation
  - no direct evidence for the presence of ternary species
- Spectra collected at pH_c = 6 (0.10 M NaCl and 0.25 M $MgCl_2$):
  - complicated speciation scheme
  - continuous shift of peak maxima
  - → Step-wise formation of binary Cm(III)-GLU species (?)

References

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Summary and conclusions

- **GLU forms weak complexes with Mg^{2+} at pH_c = 8. Binary Mg(II)–gluconate species may become relevant in concentrated $MgCl_2$ brines**
- **GLU importantly increases the solubility of Nd(III) in diluted $MgCl_2$ solutions at pH_{max}, in good agreement with the binary Cm(III)-GLU complex observed by TRLFS**
- **Solubility and aqueous speciation of Ln(III)/An(III) are less impacted by GLU in concentrated $MgCl_2$ systems:**
  - **→Likely competition between Mg(II) and Ln(III)/An(III) for GLU complexation**
  - **→No exp. evidence on the formation of ternary Mg(II)–Nd(III)–GLU species**
- **Further exp. studies needed to gain insight on the Mg(II)–Nd(III)–GLU speciation and derive the corresponding thermodynamic and activity models**