

## 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<sub>2</sub>. The use of brucite-based backfill material in such repository concepts is responsible for the buffering of pH<sub>m</sub> to ~9. Gluconic acid (C<sub>6</sub>H<sub>12</sub>O<sub>7</sub>, HG<sub>5</sub>) 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 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<sub>2</sub>-rich brines, the formation of highly stable Mg(II)–gluconate complexes may outcompete the formation of An(III)–gluconate complexes.

## Objectives:

- Evaluating the formation of binary Mg(II)–gluconate complexes, and deriving the corresponding thermodynamic and activity models, as basis for the interpretation of the ternary system Mg(II)–An(III)–gluconate
- Assessing the solubility and aqueous speciation of Nd(III)/Cm(III) in the presence of gluconate and dilute to concentrated MgCl<sub>2</sub> solutions in alkaline media
- Deriving comprehensive thermodynamic and activity models for Mg(II)–Nd(III)/Cm(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

### Mg(II)–GH<sub>5</sub><sup>-</sup> system

#### NMR experiments

- <sup>1</sup>H and <sup>13</sup>C NMR spectra recorded at 25 °C
- Bruker Avance DRX-500 spectrometer operating at 499.9 MHz for <sup>1</sup>H and 125.7 MHz for <sup>13</sup>C
- [GH<sub>5</sub><sup>-</sup>]<sub>tot</sub> = 0.20 M, pH<sub>m</sub> = 8 (TRIS)
- NaCl and MgCl<sub>2</sub> as background electrolytes:
  - 0.03 M ≤ [MgCl<sub>2</sub>]<sub>tot</sub> ≤ 0.27 M
  - I = 1.0, 2.0 M (NaCl)

### Mg(II)–An(III)/Ln(III)–GH<sub>5</sub><sup>-</sup> system

#### Nd(III) – solubility experiments

- Samples prepared and stored at 22 ± 2 °C in Ar-gloveboxes (O<sub>2</sub> content < 2 ppm)
- Undersaturation solubility experiments with Nd(OH)<sub>3</sub>(am) (ca. 7 mg per batch experiment)
- pH<sub>m</sub> = 8 (TRIS), 9 (Mg(OH)<sub>2</sub> or Mg<sub>2</sub>(OH)<sub>3</sub>Cl·4H<sub>2</sub>O(cr)) (with pH<sub>m</sub> = pH<sub>exp</sub> + A<sub>m</sub>)
- Background electrolyte: 0.25 M, 1.00 M, 2.50 M, 3.50 and 4.50 M MgCl<sub>2</sub>
- 10<sup>-4</sup> M ≤ [GH<sub>5</sub><sup>-</sup>]<sub>tot</sub> ≤ 0.1 M
- Equilibration time: 16 days (on-going)
- Phase separation: 10 kD ultrafiltration
- [Nd(III)]<sub>tot</sub> determined by ICP-MS
- Reference system without GH<sub>5</sub><sup>-</sup> available from [3]
- Solid phase characterization (on-going): XRD, SEM-EDS, XPS, chemical analysis

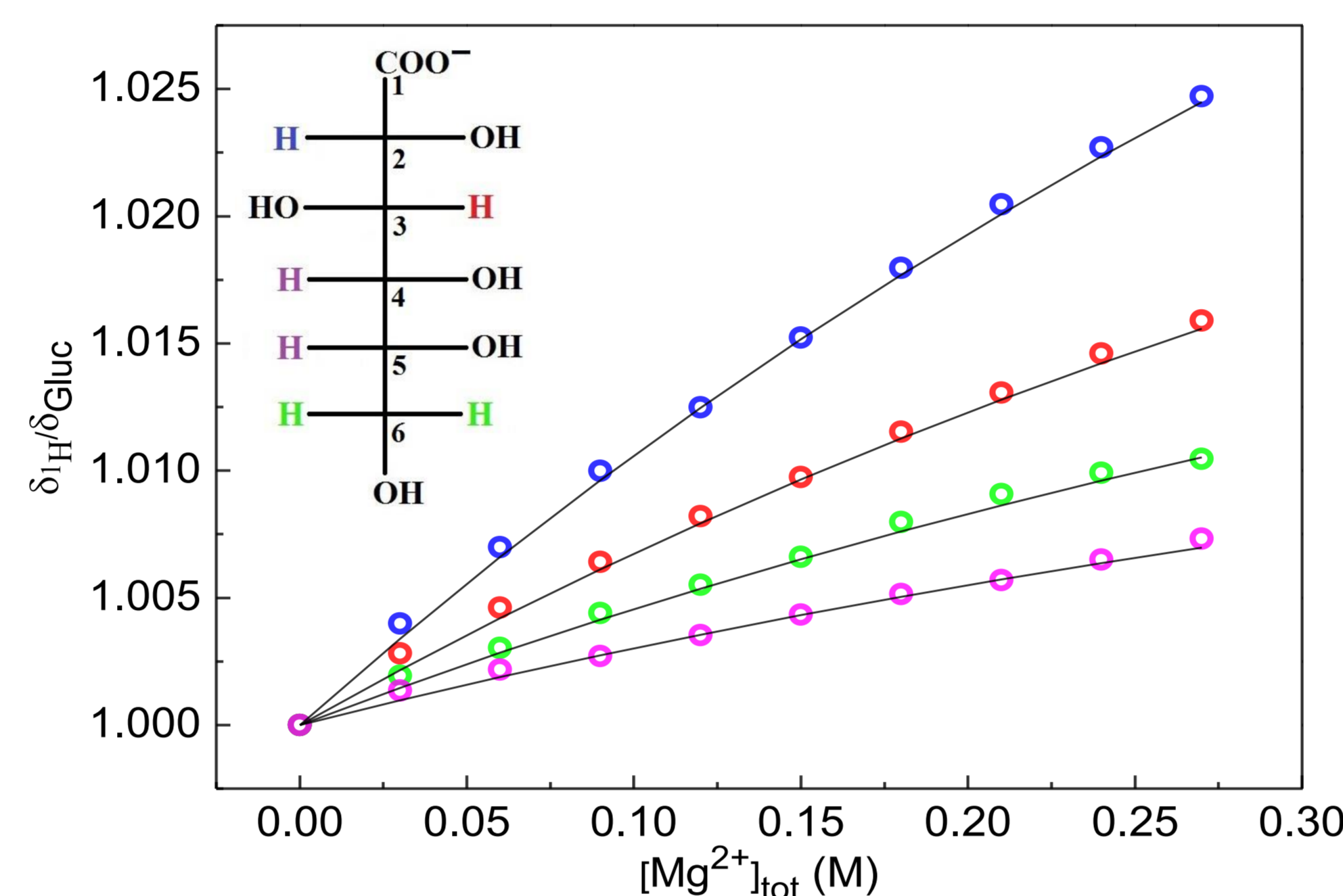
#### Cm(III)–TRLFS measurements

- Excitation at λ = 396.6 nm
- [Cm(III)]<sub>tot</sub> = 1·10<sup>-7</sup> M
- 0.25 M and 4.50 M MgCl<sub>2</sub> as background electrolyte
- 10<sup>-5</sup> M ≤ [GH<sub>5</sub><sup>-</sup>]<sub>tot</sub> ≤ 0.1 M, by step-wise addition of concentrated NaGH<sub>5</sub> stock solution

## Results and discussion

### Mg(II)–GH<sub>5</sub><sup>-</sup> : <sup>1</sup>H, <sup>13</sup>C NMR

Differences in <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (δ) upon increasing [Mg(II)]<sub>tot</sub> were used to assess the complex formation in the binary system Mg(II)–GH<sub>5</sub><sup>-</sup> system:



- Mg(II)–gluconate interaction is weaker than for the Ca(II)–gluconate system [4]
  - Hypothesis: rigid coordination structure (octahedral) of Mg(II)-complexes
- Formation of MgGH<sub>5</sub><sup>+</sup> proposed
- Apparent stability constant in I = 1.0 M (NaCl–MgCl<sub>2</sub>–NaGH<sub>5</sub>):
 
$$M^{2+} + GH_5^- \rightleftharpoons MGH_5^+$$

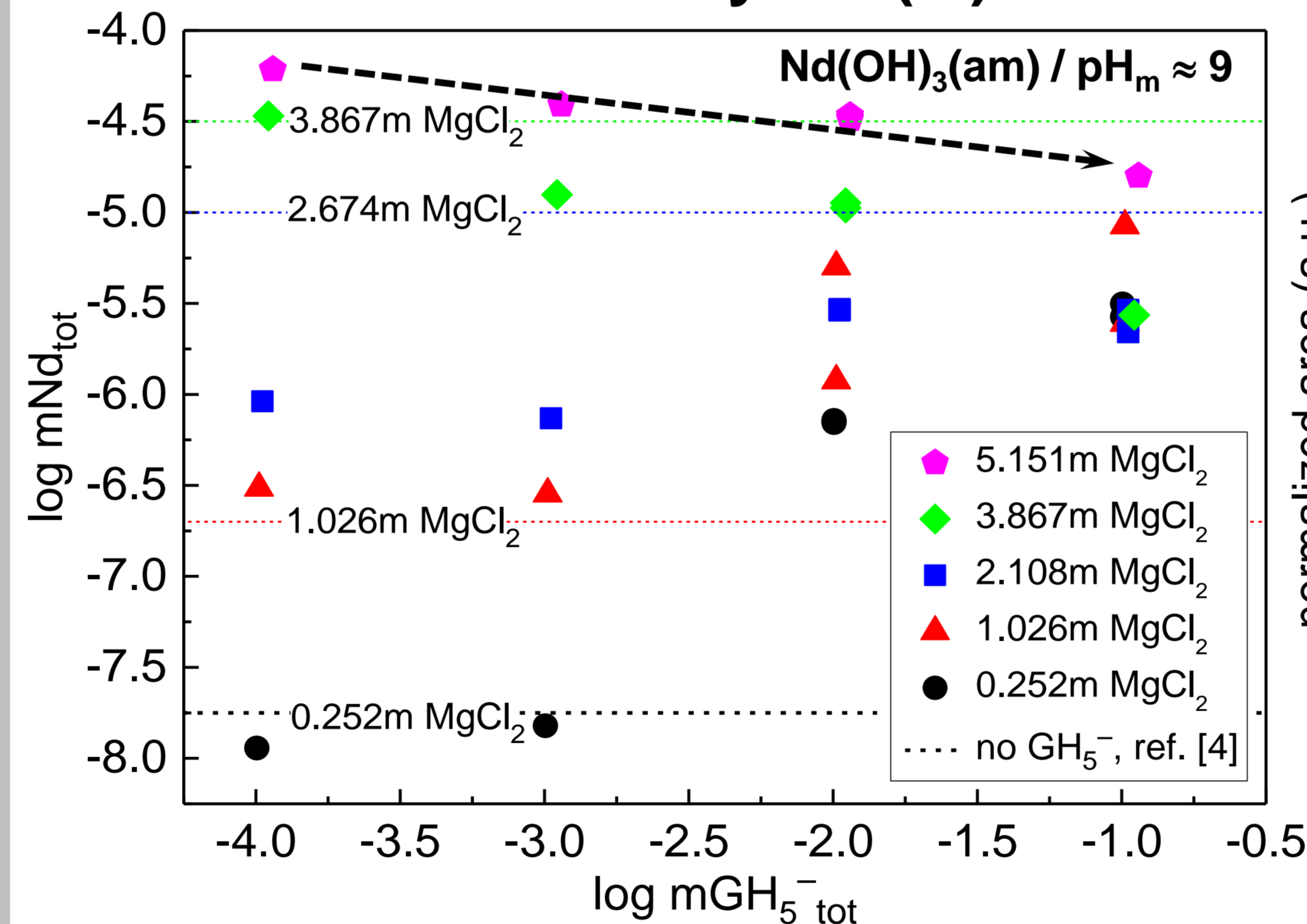
$$M = Mg \rightarrow \log K' (I = 1 M) = 0.15 \pm 0.20 \text{ (p.w.) } (^1H + ^{13}C \text{ NMR})$$

$$M = Ca \rightarrow \log K' (I = 1 M) = 1.02 \pm 0.05 [3]$$

On-going <sup>25</sup>Mg 1D and <sup>25</sup>Mg <sup>1</sup>H 2D NMR measurements, coupled with quantumchemical calculations

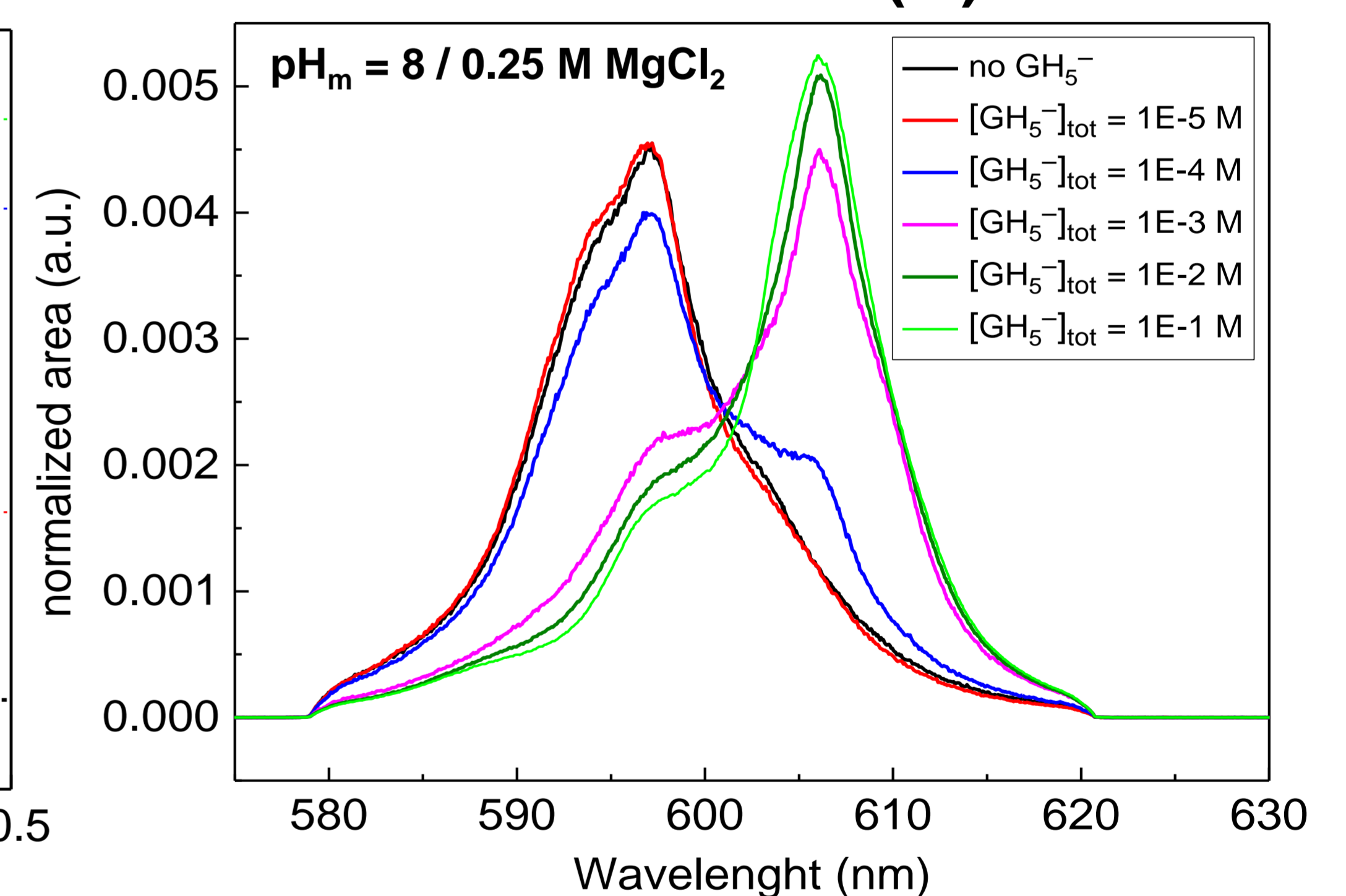
### Mg(II)–An(III)/Ln(III)–GH<sub>5</sub><sup>-</sup> :

#### Solubility–Nd(III)



- Strong increase in Nd(III) solubility in 0.25 and 1.0 M MgCl<sub>2</sub> solutions with increasing gluconate concentration
- No (or weak) complexation at higher MgCl<sub>2</sub> concentration
  - competition between Mg(II) and Nd(III) for gluconate
- Decrease of m<sub>Nd</sub> at high MgCl<sub>2</sub> and GH<sub>5</sub><sup>-</sup> concentration
  - formation of a Mg(II)–Nd(III)–gluconate solid phase (?)

#### TRLFS–Cm(III)



- Single isosbestic point found in 0.25 M MgCl<sub>2</sub> and pH<sub>m</sub> = 8
- Large red-shift in wavelength: ~9 nm
  - indicating the formation of one Cm(III)–gluconate species with 1:2 stoichiometry (analogy with Ca(II)–Cm(III)–GH<sub>5</sub><sup>-</sup> [2])
- More complex speciation scheme observed at higher MgCl<sub>2</sub> concentrations

## Summary and conclusions

- GH<sub>5</sub><sup>-</sup> forms weak complexes with Mg<sup>2+</sup> at pH<sub>m</sub> ≤ 9. Binary Mg(II)–gluconate species may become relevant in concentrated MgCl<sub>2</sub> brines
- GH<sub>5</sub><sup>-</sup> importantly increases the solubility of Nd(III) in diluted MgCl<sub>2</sub> solutions, but has a minor impact on the solubility in concentrated MgCl<sub>2</sub> brines:
  - competition of Mg(II) with Nd(III) and possible formation of Mg(II)–Nd(III)–gluconate solid phases
- TRLFS data show distinct Cm(III) spectra in the absence and presence of gluconate, clearly hinting towards the formation of Cm(III)–gluconate complexes
- Sampling at longer equilibration times and accurate solid phase characterization planned before development of thermodynamic and activity models

## References

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