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Solubility and spectroscopic study of An^{III}/Ln^{III} in dilute to concentrated Na–Mg–Ca–Cl–NO_3 solutions

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Introduction

- Long-term performance assessment of deep geological nuclear waste repositories → prediction of chemical behavior of An and long lived FP in aqueous solutions needed.
- Waste disposal in rock-salt formations: WIPP in USA, under consideration in Germany → high $[Na^+]$, $[Mg^{2+}]$ and $[Cl^-]$ expected in water intrusion scenarios.
- Nitrate can be found in high concentrations (≥ 1 M) as part of certain waste forms → i.e. waste originated from reprocessing facilities.
- Previous complexation studies with nitrate focused on acidic conditions; no $MgCl_2$ systems considered.

Objectives of this work

- **Assessment of NO_3^- effect on Ln(III)/An(III) solubility under repository relevant conditions.**
- **Development of chemical, thermodynamic and activity models for the system Ln(III)/An(III) in NaCl–$NaNO_3$, $MgCl_2$–$Mg(NO_3)_2$ and $CaCl_2$–$Ca(NO_3)_2$ solutions.**

Experimental

Solubility experiments

- Batch experiments in Ar atmosphere (22 ± 2°C)
- Undersaturation approach in 0.1–6.02 m NaCl–$NaNO_3$, 0.25–5.2 m $MgCl_2$–$Mg(NO_3)_2$ and 2.91–4.02 m $CaCl_2$–$Ca(NO_3)_2$ mixtures → **up to 8.0 m NO_3^-**
- pH range: $7.5 \le pH_m \le 13.2$
- 6–12 mg $Nd(OH)_3$(am) solid phase in each experiment
- Equilibration time: t ≤ 500 days
- pH measurements: $pH_m = -\log m_{H^+} = pH_{exp} + A_m$ [1]; A_m for Cl^-–NO_3^- mixtures determined in this study
- $m_{Nd(III)}$ measured by ICP-MS after 10 kD (2-3 nm) ultrafiltration
- Solid phase characterization: XRD, SEM-EDX

Nd–L_{III} EXAFS @ ANKA (Karlsruhe, Germany)

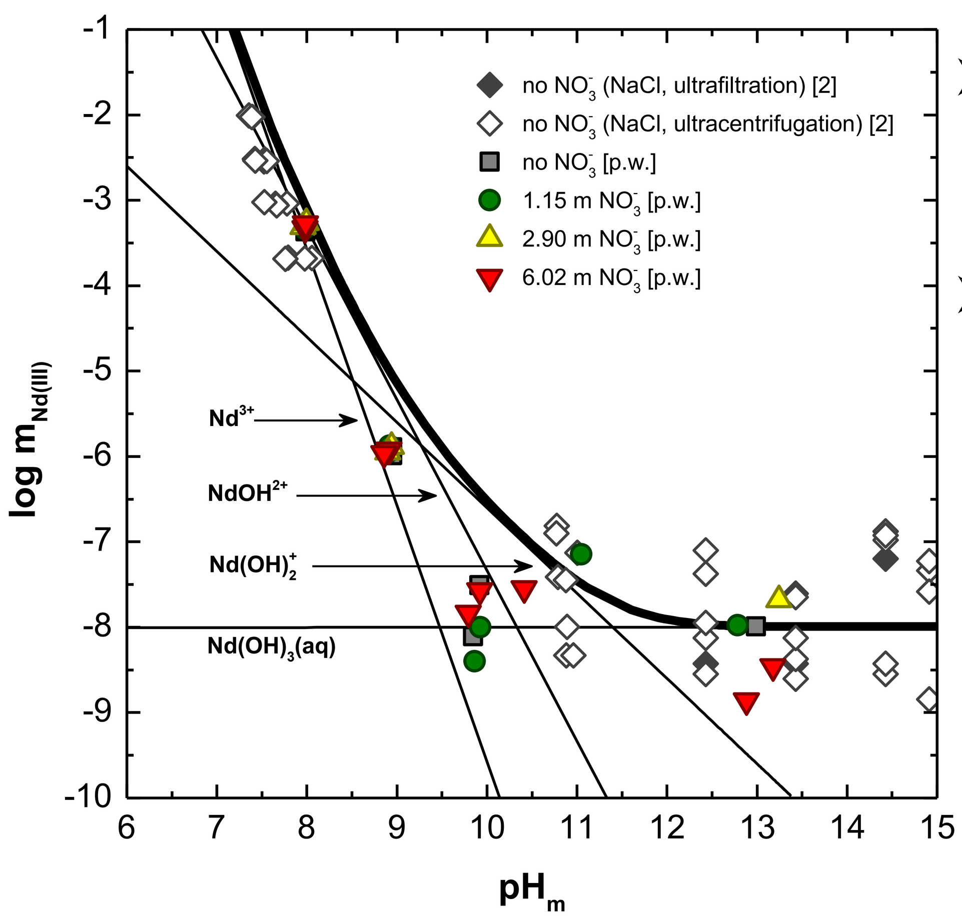
- 4.06 m $MgCl_2$–$Mg(NO_3)_2$ with 5.81 m NO_3^-; pH_m = 8.15
- $m_{Nd(III)} = 1.49\times10^{-3}$ m after 10 kD (2–3 nm) ultrafiltration

Cm(III)–TRLFS

- Sample preparation in Ar atmosphere (22 ± 2°C)
- TRLFS studies in 5.61/6.02 m NaCl–$NaNO_3$, 0.25/4.1 m $MgCl_2$–$Mg(NO_3)_2$ and 4.02 m $CaCl_2$–$Ca(NO_3)_2$ mixtures → **up to 8.0 m NO_3^-**
- pH range: $1 \le pH_m \le 9$
- $[Cm(III)] \sim 1\times10^{-7}$ M per sample

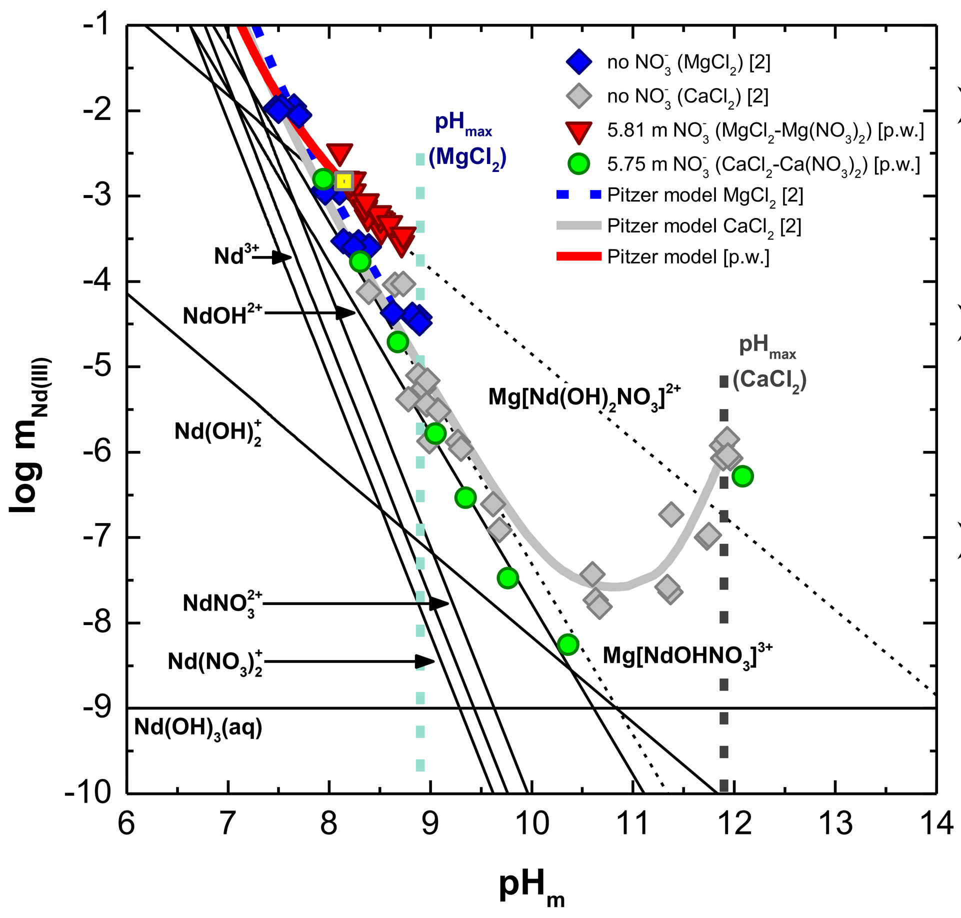
Results and discussion

Solubility of Nd(III) in 5.61 m NaCl–$NaNO_3$



- ➢ Very good agreement with nitrate-free solubility data reported in [2].
- ➢ No effect of NO_3^- on $Nd(OH)_3$(am) solubility in NaCl–$NaNO_3$ systems.

Solubility of Nd(III) in 4.06 m $MgCl_2$–$Mg(NO_3)_2$ & 4.02 m $CaCl_2$–$Ca(NO_3)_2$



- ➢ No effect of NO_3^- on $Nd(OH)_3$(am) solubility in $CaCl_2$–$Ca(NO_3)_2$ systems.
- ➢ Significant effect of $m_{NO_3^-}$ on $Nd(OH)_3$(am) solubility in $MgCl_2$–$Mg(NO_3)_2$ systems.
- ➢ Slope analysis indicates the formation of aqueous species Mg–Nd–OH–NO_3 with stoichiometries Nd:OH 1:1 ($pH_m \le 8.3$) and Nd:OH 1:2 (pHm > 8.3).

Chemical and thermodynamic model for the system Ln^{3+}/An^{3+}–H^+–Na^+–Mg^{2+}–Ca^{2+}–OH^-–Cl^-–NO_3^-

- ➢ Solid phase controlling solubility: $Nd(OH)_3$(am) (XRD, SEM-EDX).
- ➢ Ternary/quaternary species with slope −1 and −2 in $MgCl_2$–$Mg(NO_3)_2$ systems.
- ➢ Formation of $Mg[An^{III}/Ln^{III}OHNO_3]^{3+}$ and $Mg[An^{III}/Ln^{III}(OH)_2NO_3]^{2+}$ indicated by Cm(III)–TRLFS and Nd–L_{III} EXAFS.

$$An^{III}/Ln^{III}(OH)_3(am) + 2H^+ + NO_3^- + Mg^{2+} \Leftrightarrow Mg[An^{III}/Ln^{III}OHNO_3]^{3+} + 2H_2O$$

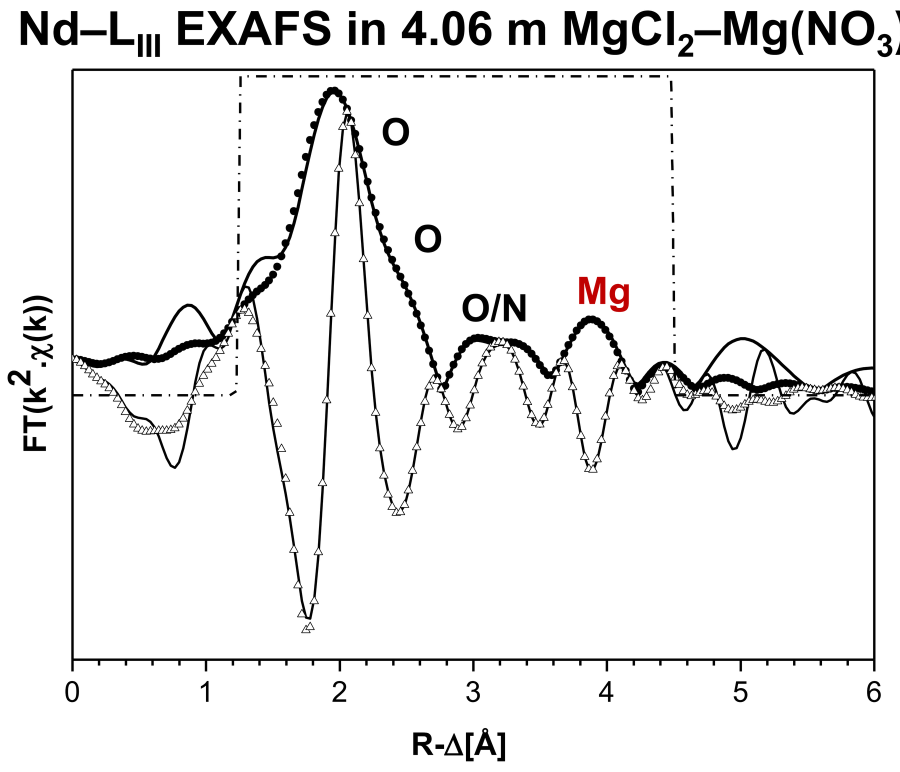
$$\log {}^*K^\circ_{s,(1,1,1,1)} = 10.80;\ \beta^{(0)} = 0.93;\ \beta^{(1)} = 4.30;\ C^\Phi = 0$$

$$An^{III}/Ln^{III}(OH)_3(am) + H^+ + NO_3^- + Mg^{2+} \Leftrightarrow Mg[An^{III}/Ln^{III}(OH)_2NO_3]^{2+} + H_2O$$

$$\log {}^*K^\circ_{s,(1,1,2,1)} = 1.56;\ \beta^{(0)} = 0.18;\ \beta^{(1)} = 1.60;\ C^\Phi = 0$$

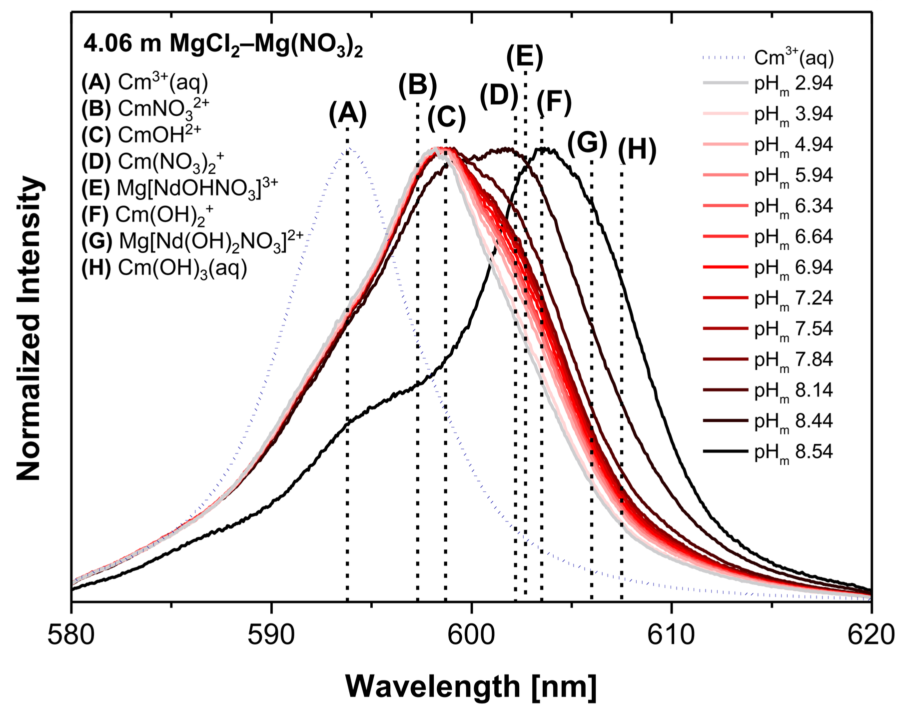
Ternary Pitzer paramter generally set to 0.
Interaction of the cation with the anion is assumed to be almost the same for chloride and nitrate.

Nd–L_{III} EXAFS in 4.06 m $MgCl_2$–$Mg(NO_3)_2$



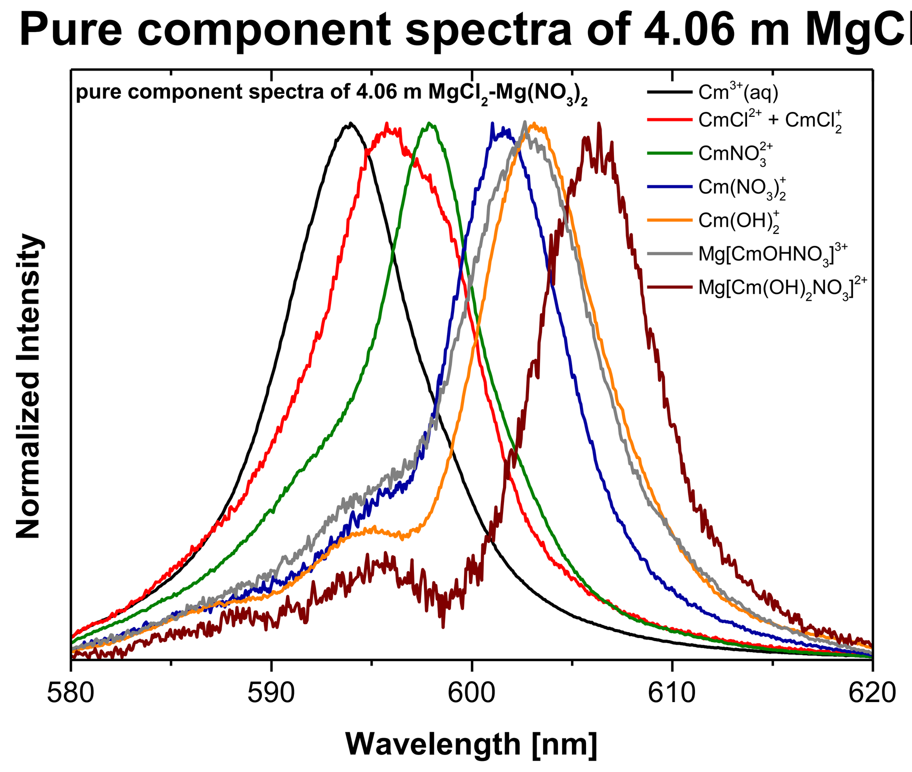
- ➢ Peak at ~4 Å is properly fitted with Mg as backscatterer.
- ➢ EXAFS evaluation shows no Nd–Nd interaction.

TRLFS of Cm(III) in Na–Mg–Ca–Cl–NO_3



- ➢ No ternary/quaternary species needed to explain TRLFS observations in NaCl–$NaNO_3$ and $CaCl_2$–$Ca(NO_3)_2$ (data not shown).
- ➢ Ternary/quaternary species do form in $MgCl_2$–$Mg(NO_3)_2$ with $pH_m \ge 4.94$.

Pure component spectra of 4.06 m $MgCl_2$–$Mg(NO_3)_2$



- ➢ Nitrate effect → genuine complexation reaction!
- ➢ Very complex Cm(III) speciation found in $MgCl_2$–$Mg(NO_3)_2$ mixtures.

Conclusion

- ✓ **Nitrate significantly influences solubility of $Nd(OH)_3$(am) in concentrated and weakly alkaline $MgCl_2$–$Mg(NO_3)_2$ solutions at $m_{Mg^{2+}} \ge 2.83$ m, $m_{NO_3^-} \ge 1.13$ m and pH_m 8–9.**
- ✓ **No effect of nitrate in NaCl–$NaNO_3$ and $CaCl_2$–$Ca(NO_3)_2$ solutions hinting towards the participation of Mg^{2+} in the complex formation reaction.**
- ✓ **Cm(III)–TRLFS and Nd–L_{III} EXAFS further confirm the participation of Mg^{2+}.**
- ✓ **The chemical model proposed includes the formation of the quaternary aqueous species $Mg[An^{III}/Ln^{III}OHNO_3]^{3+}$ and $Mg[An^{III}/Ln^{III}(OH)_2NO_3]^{2+}$ in equilibrium with solid $Nd(OH)_3$(am).**
- ✓ **Thermodynamic and activity models (Pitzer) derived for the system Nd^{3+}/Cm^{3+}–H^+–Mg^{2+}–OH^-–Cl^-–NO_3^-.**

References:
[1] M. Altmaier et al. *Geochim. Cosmochim. Acta* **67**, 3595 (2003).
[2] V. Neck et al. *Pure Appl. Chem.* **81**, 1555 (2009).
[3] A. Skerencak et al. *Radiochim. Acta* **97**, 385 (2009).