Solubility and Speciation of Cm(III) and Nd(III) in borate rich NaCl and $CaCl_2$ solutions

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Introduction

•Nuclear waste disposal in deep underground facilities requires detailed understanding of aqueous actinide (geo)chemistry in order to assess the long-term performance of a repository. Considering waste disposal in rock salt formations, dedicated studies at high ionic strength conditions are mandatory.

• Batch solubility studies allow robust predictions on radionuclide solubility limits as function of key geochemical parameters (pH, E_h, I) and potentially complexing ligands like borate. Nd(III) is used as a well-established analog for trivalent actinides.

• Detailed analysis of actinide speciation using advanced spectroscopic tools like TRLFS (Time Resolved Laser Fluorescence Spectroscopy) is advised as basis for correct and trustworthy chemical and thermodynamic models.

• Actinide–borate complexation has recently become a focus of research attention following the pioneering study of Borkowski et al. [10BOR/RIC]. Boron can be present a salt-based repository as a component of intruding brines, relict borate phases in rock salt or as part of the emplaced waste.

• Part of the studies on Cm(III)-TRLFS in NaCl performed in cooperation with LANL-CO.

• Focus of the present study is to:

1. Derive experimental solubility data for $Nd(OH)_3$(am) in dilute to concentrated NaCl at 7 < pH_c < 13 and total boron concentrations from 4 mM < $[B]_{tot}$ < 40 mM.

2. Derive experimental solubility data for $Nd(OH)_3$(am) in dilute to concentrated $CaCl_2$ at 8 < pH_c < 12 and total boron concentrations from 4 mM < $[B]_{tot}$ < 40 mM.

3. Perform systematic Cm(III)-TRLFS studies in the NaCl- and $CaCl_2$ - borate system.

4. Get information about the speciation of boron in solution by ^{11}B-NMR studies in NaCl and $CaCl_2$ solutions.

Experimental

Solubility experiments with Nd(III)

- **Experiments conducted in Ar-glovebox**
- ***ca.* 10 mg $Nd(OH)_3$(am) per experiment** (characterized by XRD)
- **$[B_4O_7^{2-}]_{init.}$ = 1 mM and 10 mM**
  => $[B]_{tot}$ = 4 mM and 40 mM
- **Background electrolytes:** NaCl 0.1 M to 5.0 M
  $CaCl_2$ 0.25 M to 3.5 M
- **Equilibration time:** 7d - 140 d
- **Phase separation:** 10 kD (2-3 nm) ultrafiltration
- **Reference system without borate [09NEC/ALT]**

TRLFS experiments with Cm(III)

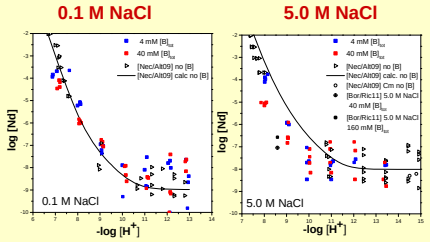
- **Samples prepared in Ar-glovebox**
- **[Cm] = $1\cdot10^{-7}$ M per sample**
- **$[B_4O_7^{2-}]_{init.}$ = 1 mM and 10 mM,**
  => $[B]_{tot}$ = 4 mM and 40 mM
- **Background electrolytes:** NaCl 0.1 M to 5.0 M
  $CaCl_2$ 0.25 M to 3.5 M
- **Equilibration time:** spectra taken at < 1 d
- **TRLFS data collection:** single emission spectra
- **Reference system for TRLFS without borate [08RAB/ALT]**

^{11}B-NMR experiments

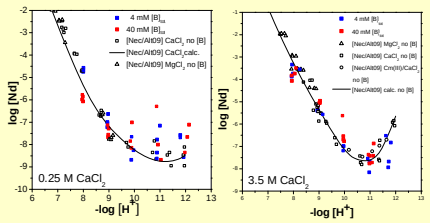
- **Background electrolytes:** NaCl 0.1 M to 5.0 M
  $CaCl_2$ 0.25 M to 3.5 M
- **$[B]_{tot}$ = 40 mM**
- **Equilibration time:** > 1 month

Solubility in Na-Ca-Nd(III)-borate systems

NaCl system



$CaCl_2$ system

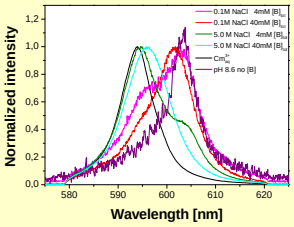


- **No significant effect of borate on $Nd(OH)_3$(am) solubility in dilute to concentrated NaCl and $CaCl_2$ solutions.**

TRLFS of Ca-Cm(III)-borate systems

Cm(III) emission spectra NaCl

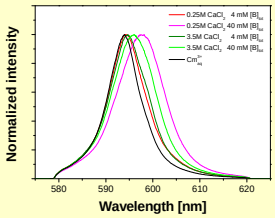
-log[H+] = 8



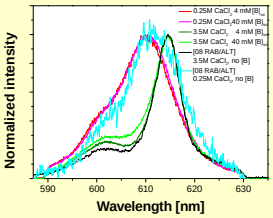
- **At low borate concentration only slight peak shifts → very weak borate complexation.**
- **At higher borate concentration: peak shifts compared to the low borate concentration indicate increasing borate complexation.**

Cm(III) emission spectra $CaCl_2$

-log[H+] = 8



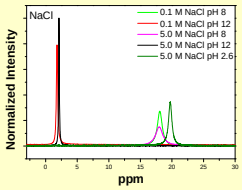
-log[H+] = 12



- **At low borate concentration: similar spectra, no significant borate complexation.**
- **At higher borate concentration: peak shifts compared to the low borate concentration indicate increasing borate complexation.**
- **Increasing borate concentration does not affect peak position and peak shape.**
- **Similar spectra in the present and absence off borate → in agreement with solubility experiment, no hint on significant borate complexation.**

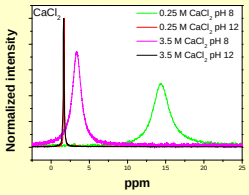
^{11}B-NMR

NaCl system



- **One single peak detected →no or few polyborates in solution.**
- **At pH_c = 2.6 boric acid expected, at pH_c = 8 detected peak slightly shifted → boric acid is dominating species.**
- **At pH_c = 12 tetraborate ion dominating species.**

$CaCl_2$ system



- **One single peak detected →no or few polyborates in solution.**
- **compared to NaCl-System very broad peaks observed.**
- **pH_c = 8: peak at high ionic strength is shifted.**

Conclusions

- **The speciation of boron in aqueous systems is highly complicated and potentially affected by pH, ionic strength and total boron concentration → mandatory information required for comprehensive thermodynamic description of An-borate complexation.**
- **^{11}B-NMR studies only give limited information on the boron speciation in solution.**
- **$Nd(OH)_3$(am) solubility studies in NaCl or $CaCl_2$ solution at the investigated pH, I and borate concentrations do not indicate a pronounced solubility enhancement due to strong borate complexation.**
- **TRLFS-studies in NaCl or $CaCl_2$ solutions with trace amounts of Cm(III) indicate weak borate complexation at pH_c 8-9 and no borate complexation at high pH_c (>10).**
- **Borate complexation seems to compete with hydrolysis at pH_c 8-9 and is out-competed at higher pH conditions. Evaluation of TRLFS data affected by uncertainties regarding Cm-hydrolysis scheme.**
- **Following the evaluation of the Nd(III) solubility data and TRLFS in NaCl and $CaCl_2$ solution we conclude that the contribution from An(III)-borate complexation to a solubility based An(III) source term at the investigated borate concentrations is limited.**
- **Studies are currently being extended to (i) even higher borate concentrations (160 mM) in NaCl solution, (ii) investigations of An(III)-borate interactions in $MgCl_2$ solutions and (iii) similar studies on Th(IV) solubility in borate systems. Studies aim at a comprehensive assessment of borate complexation for tri- and tetravalent Actinides in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions.**

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References

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