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# Complex Formation of Ln(III) with Borate Ion

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## INTRODUCTION

Although not a particularly abundant element, boron is found in many rocks, soils, and natural waters in the western United States, Argentina, and in extensive areas from the Mediterranean to Kazakhstan. Vast deposits of Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and other boron minerals were discovered in California and Nevada in the mid 1800's. Today, borax is used in hundreds of applications.<sup>1-2</sup>

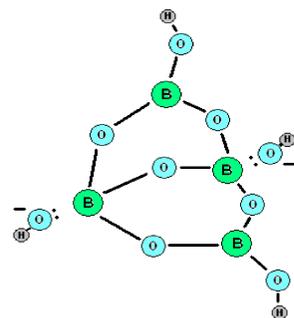
Borates have many interesting properties for studying *f*-electron element solution chemistry:

- Borate buffer solutions provide a wide range of pH values (pH ~5-12),
- Borate compounds are soluble in water,
- Borates provide a wide spectroscopic window for UV-VIS-NIR spectroscopy,
- Naturally occurring <sup>10</sup>B (19.6%) and <sup>11</sup>B (80.4%) are NMR-active,
- Incorporation of <sup>17</sup>O in the borate anion would also serve as an NMR probe,
- Borate oxy-anions provide a useful Raman-active probe,
- Borate solutions are good solvents for electrochemical studies.

Borates may provide an environmentally benign medium for processing, purification, recovery, and disposition of radioactive wastes. They have the potential of providing a viable, recyclable, recoverable matrix for nuclear waste containment. In this context a reprocessing approach using borate would be very compatible with final disposal in a salt-based repository. Borax has been found in Waste Isolation Pilot Plant (WIPP) inclusion and seepage brine (up to ~166 mM calculated as monoboric acid) and is currently present in the simulated brines used to establish actinide solubility in the WIPP.<sup>3</sup> Studies of borate complexation of selected lanthanides and actinides have been reported previously but a systematic study of *f*-electron element periodic trends has not been performed.

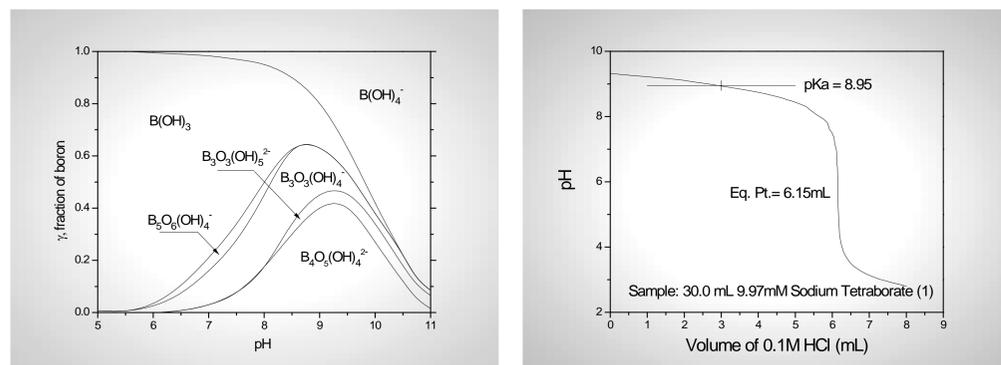
## TETRABORATE ANION

Boron can link either three oxygens to form a triangle or four oxygens to form a tetrahedron. Boric acid is a very weak acid and acts exclusively by hydroxyl-ion acceptance rather than proton donation. A structure of tetraborate anion in basic medium is presented on the right.



Titration of sodium tetraborate, that is present in WIPP brine, with hydrochloric acid indicated, that tetraboric acid is diprotic acid and both centers have the same pKa = 8.95, and are very similar to monoboric acid. Calculated distribution of possible tetraborate species as a function of pC<sub>H</sub> is presented in the figure below.

The solution chemistry of borates is a topic of current interest due to a history of conflicting report that are not yet totally resolved. A variety methods unequivocally established the existence of polyborate anions in aqueous solution. Aqueous polyborate equilibria were studied by <sup>11</sup>B NMR and by Raman Spectroscopy. On the basis of these data the formation constants for  $\text{B}(\text{OH})_3$ ,  $\text{B}_3\text{O}_3(\text{OH})_4^-$ ,  $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$  and  $\text{B}_5\text{O}_6(\text{OH})_4^-$  were reported. This speciation is function of pH and also boron concentration. The relative importance of the concentrations of various boric acid species over the 5 to 11 pH range and 0.4 M boric acid is presented in the figure below. The lengths of vertical line segments between the curves represent the fraction of boron present as a given species.



## RESULTS AND DISCUSSION

### Interaction of Tetraborate Anion with Neodymium (III) an Analog for An(III)

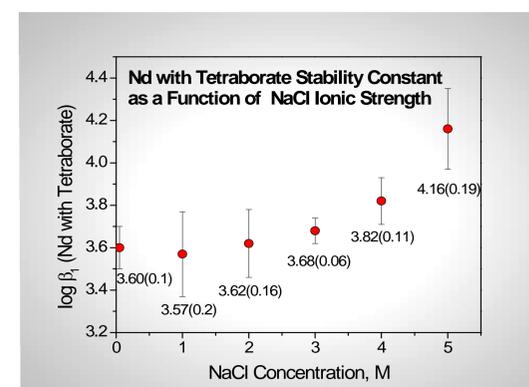
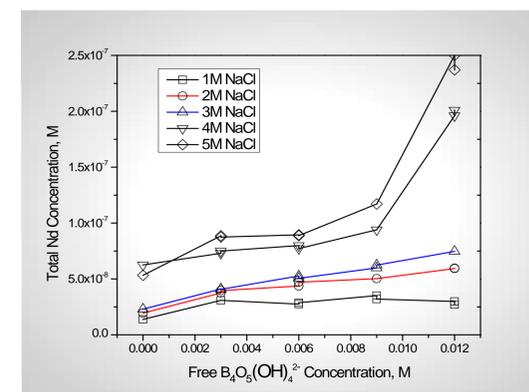
Sodium tetraborate has limited solubility in water. Maximum achievable concentration in the pH range from 7 to 9 is about 0.1 M. In the generic WIPP brines its concentration is equal to 45 mM (GWB brine) and 13 mM (ERDA6 brine). While performing neodymium solubility experiments in 5 M NaCl solution we could easily see effect of carbonate ion on neodymium solubility. While performing the same experiments in WIPP brines the effect of enhanced solubility of neodymium with carbonate was invisible. We found that borate ions formed a strong complex with neodymium (III). Using the current WIPP Performance Assessment assumptions about the expected concentration of carbonate ions, borate ions had the effect of masking carbonate ion complexation!<sup>4</sup> Lanthanide with tetraborate complexation experiments were performed under the Actinide Repository Science Program (ACRSP) in Carlsbad, New Mexico, to support the WIPP and other projects. The formation constant of neodymium with borate complex was measured in low ionic strength solutions<sup>5</sup> to establish a standard chemical potential for the species formed. Stability constants for Nd complexation with tetraborate were measured using the solubility approach from undersaturation. Neodymium hydroxide was used as the solid phase. Free neodymium concentrations were calculated from the solubility model. Pitzer parameters for Nd with tetraborate interactions are calculated from the Nd solubility data collected in 1, 2, 3, 4 and 5 M NaCl as a function of tetraborate concentrations. The experimental data for various NaCl concentrations is presented on the right (upper graph). Stability constants for Nd complexation with tetraborate as a function of NaCl concentrations are presented in the graph on the right (bottom graph). Calculations performed for 1-5 M NaCl at pH=8.5 show that neodymium, analog for An(III), exists in aqueous solution in form of five different hydroxo-chloro-borate species. The neodymium tetraborate complex is the major species in all the NaCl solutions.

Pitzer parameters are calculated on basis of these data using the NONLIN computer code are presented in Table (below).

Strong evidence of tetraborate interactions with neodymium, an analog for actinides (III) is provided by our data. Actinides (IV), (V) and (VI) should also form stable complexes with tetraborate ion. However, strong hydrolysis of actinide (IV) cations are expected to overwhelm borate complexation.

Binary Pitzer Parameters						
Species <i>i</i>	Species <i>j</i>	$\beta^0_{ij}$	$\beta^1_{ij}$	$B^2_{ij}^*$	$C^0_{ij}$	Reference
H <sup>+</sup>	Cl <sup>-</sup>	0.178	0.295	0	0.008	[6]
Na <sup>+</sup>	Cl <sup>-</sup>	0.0765	0.266	0	0.00127	[6]
Na <sup>+</sup>	OH <sup>-</sup>	0.0864	0.253	0	0.0044	[6]
Nd <sup>3+</sup>	Cl <sup>-</sup>	0.612	5.4	0	-0.0184	[7]
Na <sup>+</sup>	$\text{B}_3\text{O}_3(\text{OH})_4^-$	-0.056	-0.91	0	0	[8]
$\text{NdB}_4\text{O}_5(\text{OH})_4^+$	Cl <sup>-</sup>	-0.0352	1.74	0	-0.013	Present work

\* Parameter was set to zero.



## CONCLUSIONS

- Tetraborate ion, under repository conditions, successfully competes with carbonate for An(III) complexation.
- Neodymium is complexed by tetraborate with logarithm of stability constant equal to 3.6 – 4.2 (depends on ionic strength).
- Pitzer parameters for An(III) interaction with tetraborate ion are under the processing and will be introduced to the WIPP data base.
- An(IV) should also form even more stable complexes with tetraborate ion, however, strong hydrolysis may mask its formation and these complexes should have no impact on An(IV) solubility.

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