Complexation of Nd(III) with Tetraborate Ion and Its Effect on Actinide (III) Solubility in WIPP Brine

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Abstract

The potential importance of tetraborate complexation on lanthanide (III) and actinide (III) solubility is recognized in the literature but a systematic study of f-element complexation has not been performed. In neodymium solubility studies in WIPP brines, the carbonate complexation effect is not observed since tetraborate ions form a moderately strong complex with neodymium (III). The existence of these tetraborate complexes was established for low and high ionic strength solutions. Changes in neodymium (III) concentrations in undersaturation experiments were used to determine the neodymium with tetraborate stability constants as a function of NaCl ionic strength. As very low Nd(III) concentrations have to be measured, it was necessary to use an extraction pre-concentration step combined with ICP-MS analysis to extend the detection limit by a factor of 50.

The determined Nd(III) with borate stability constants at infinite dilution and 25 °C using the SIT is equal to log β₁ = 4.55 ± 0.06, using the Pitzer approach is equal to log β₁ = 4.99 ± 0.30, and apparent log β₁ = 4.06 ± 0.15 (in molal units) at I = 5.6 m NaCl. Pitzer ion-interaction
parameters for neodymium with tetraborate and SIT interaction coefficients were also determined and reported.

**Keywords:** borax, borate complexation, Nd-tetraborate stability constant, Nd-borate Pitzer parameter, neodymium-borate SIT coefficients.

**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 (Na₂B₄O₇·10H₂O) and other boron minerals were discovered in California and Nevada in the mid 1800’s. Today, borax is used in hundreds of applications [1-2].

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 $^{10}$B (19.6%) and $^{11}$B (80.4%) are NMR-active,
- Incorporation of $^{17}$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 (Na₂B₄O₇·10H₂O) in natural inclusion in Salado Formation salt been found at the Waste Isolation Pilot Plant (WIPP) and also in 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 [3]. 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.

Sodium tetraborate has a limited solubility in water and the 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 (ERDA-6 brine). While performing neodymium solubility experiments in 5 M NaCl solution, the effect of carbonate ion complexation on neodymium solubility could be easily seen. While performing the same experiments in WIPP brines, the effect of enhanced solubility of neodymium with carbonate was invisible. The cause of such behavior was formation of a strong neodymium (III) complex with borate ions. Using the current WIPP Performance Assessment assumptions about the concentration of carbonate ions, expected at the level of 10⁻³ M, borate ions had the effect of masking carbonate ion complexation [4, 5]. The tetraborate ion is a contributor in actinide (III) speciation in the WIPP but knowledge
about its coordination chemistry in weakly basic media with actinides, in particular, was not reported.

The goal of the present work was to determine the neodymium (III) ion (an analog for actinide (III)) stability constant with tetraborate ion and to determine Pitzer parameters allowing for modeling of the behavior of actinides with tetraborate ion in high ionic strength solutions. The experiments were performed under the Actinide Repository Science Program (ACRSP) in Carlsbad, New Mexico, to support the WIPP performance assessment.

Experimental

Chemicals

Pure Na₂B₄O₇·10H₂O was supplied by Acros. NaOH solid and standardized 0.10 N HCl solutions were analytical grade supplied by Fisher. Neodymium and indium standard solutions used for ICP-MS calibration were supplied by High Purity Standards. High purity HNO₃ concentrated solution (6N) was obtained from Fisher Optima, ICP-MS tuning solution supplied by Agilent, Nd(OH)₃ solid produced by Alfa Aesar, di(2-ethylhexyl)phosphoric acid, HDEHP, made by Aldrich and n-heptane provided by Fisher.

Sample preparation

Samples of 1, 2, 3, 4 and 5 M NaCl containing sodium tetraborate concentrations ranging from 0 to 0.04 M were prepared by weight. The pC⁺₃ (negative logarithm of a hydrogen ion concentration) was determined by a nondestructive method, commonly applied in
high ionic strength solutions using pH measurements appropriately corrected with the NaCl ionic strength. The pCH$^+$ was calculated using an experimentally established relationship between pCH$^+$, pH measured and NaCl concentration given by the following equation:

$$pCH^+ = pH_{meas} + 0.2 \times M_{NaCl}$$

where pH$_{meas}$ denotes the measured pH and $M_{NaCl}$ the molarity of NaCl solution.

The pCH$^+$ was maintained at a constant value equal to $\sim 8.59 \pm 0.04$.

Large excess, about 10 mg of Nd(OH)$_3$ solid, was added to each sample and the samples were equilibrated for 90-120 days. The equilibrium pH was measured in each sample at the end of the experiment after 120 days of equilibration. The neodymium concentration was determined in each sample using the following pre-concentration procedure and an Agilent ICP-MS 7500ce mass spectrometer.

**Pre-concentration procedure**

Neodymium concentrations were measured in all samples after 90 and 120 days of equilibration. ICP-MS measurements in high ionic strength require 100 fold dilution of brine to keep the recovery of indium internal standards in the acceptable range and to avoid instrumental saturation by sodium. However, after the 100-fold dilution, the neodymium concentrations in the samples were close to or below the neodymium detection limit. In order to improve the overall sensitivity of the neodymium analysis, an extraction method was deployed. The idea of improvement was to eliminate sodium cations maintaining high ionic strength by extracting/re-extracting the neodymium
quantitatively from the brine. The resultant low ionic strength solution needed to be
diluted only by a factor of 2, giving a net gain of ~50 times improvement in our overall
neodymium concentration sensitivity. 0.1 M HDEHP in n-heptane was used as the first
extractant at pH ~2-3 and re-extraction was performed using ~2 M HNO₃. This method
was tested on several samples containing a known amount of neodymium and varied
NaCl and Na₂B₄O₇ concentrations. The average neodymium recovery after extraction and
re-extraction steps was equal to 103.8% ± 4.8% and was assumed to be quantitative. No
correction for the neodymium concentration was applied.

For the overall procedure, about 2.3 mL of brine solution was filtered using a 30,000
nominal molecular weight limit (NMWL) filter, which is equivalent to a 5 nm pore size.
The solution was centrifuged for 30 minutes at 9000 rpm. An 2.00 mL aliquot of filtered
brine solution containing neodymium was introduced to an extraction vial and 0.20 mL of
0.10 M HCl was added. 2.00 mL 0.1M HDEHP in n-heptane was added as the organic
phase to the extraction vial and was shaken for 45 min using mechanical shaker. 1.80 mL
of the organic phase was transferred to a clean vial containing 1.80 mL of ~2 M HNO₃
(high purity, 6N). The re-extraction time was 20 minutes. Duplicate aliquots of 0.75 mL
of the aqueous phase were moved to 0.75mL of 2% HNO₃ containing an indium internal
standard. Total neodymium concentrations were determined in these solutions using
ICP-MS. The ICP-MS detection limit for neodymium determination was on the level
~10⁻¹⁰ M.
Results and Discussion

Tetraboric acid dissociation constant

Boron can link either three oxygen atoms to form a triangle or four oxygen atoms to form a tetrahedron. Boric acid, B(OH)₃, is a very weak acid and acts exclusively by hydroxyl-ion acceptance rather than proton donation. Tetraboric acid, which is a polymeric form of boric acid, should have similar chemical properties compared to the monomer. The pKₐ of boric acid is well known in the literature [6] and the pKₐ of tetraboric acid was measured for comparison. To perform this measurement, a solution with a known concentration of sodium tetraborate containing a small addition of sodium hydroxide was titrated with standarized 0.10 M HCl. The measured dissociation constant was equal to pKₐ = 8.95. The result of the sodium tetraborate titration indicated that the pKₐ of tetraboric acid is the same as monoboric acid and that tetraboric acid is a diprotic acid. Both protons are far away each other and do not influence each other’s dissociation behavior, leading to effectively the same dissociation constants. Taking into consideration the structure of the boric acid molecule and the fact that both protons have the same dissociation constants, it may be assumed that each end of this molecule behaves as single molecule of monoboric acid. The dissociation constants of boric acid as a function of NaCl ionic strength are reported in the literature [6]. The distribution of tetraborate species shown in Figure 1 was calculated for the pH range of 7 to 11 and the pKₐ value for 5 M NaCl. The concentrations of HB₄O₇⁻ species were calculated the same method for each NaCl concentration used in these experiments.
Interaction of neodymium with tetraborate ion

During the neodymium solubility measurements in GWB and ERDA-6 brines, the effect of carbonate complexation on neodymium solubility was invisible, but in the \( \text{pC}_{11+} \) range of 8.5-9.5 an increase in neodymium solubility was observed. The concentration of tetraborate in both GWB and ERDA-6 brines is 45 and 13 mM, respectively. Under repository conditions, e.g. \( \text{pC}_{11+} \sim 8.5-9.5 \), complexation of trivalent cations (lanthanides and actinides) with tetraborate anions is the only possible explanation of this effect. The effect of the tetraborate complexes on neodymium solubility was tested for in low ionic strength solution by measuring the solubility of solid \( \text{Nd(OH)}_3 \) in high purity water as a function of tetraborate concentration. The primary impact on neodymium solubility is pH, therefore, the pH in all these solutions was kept constant, equal to 8.60. The results of these measurements are presented in Figure 2.

According to the data in Figure 1, the dominating species of the tetraboric acid dissociation at pH = 8.6 is the \( \text{HB}_4\text{O}_7^- \) anion. The neodymium complexation reaction with this tetraborate species at \( \text{pC}_{11+} = 8.6 \) in water and WIPP brine might be given by the following reaction:

\[
\text{Nd}^{3+} + \text{HB}_4\text{O}_7^{1-} \rightleftharpoons \text{NdHB}_4\text{O}_7^{2+}
\]  

(1)

On the basis of the prior argument about tetraboric acid behavior, we could assumed that 1) each end of the tetraboric acid molecule behaves as a single molecule of monoboric acid, 2) with the long distance between the donor atoms, the tetraborate molecule cannot interact with \( \text{Nd}^{3+} \) as a bidentate ligand, 3) interaction with each site has a similar
strength or the same effective pKa and 4) among other cationic species present in the solution the interaction of the dominating tetraboric species with 3+ cation is the most probable reaction, however formation of ternary complexes cannot be excluded. Therefore, reaction (1) should correctly describe the acid-base chemistry of the tetraborate species. The apparent stability constant, $\beta_1$, for reaction (1) is given by the following equation:

$$\beta_1 = \frac{[\text{NdHB}_4\text{O}_7^{2+}]}{[\text{Nd}^{3+}][\text{HB}_4\text{O}_7^{1-}]}$$

The square brackets indicate equilibrium concentrations. The increase of neodymium concentration with increasing tetraborate concentration in Figure 2 was assigned to neodymium-tetraborate complexation.

The goal of this work was to determine the stability constant for reaction (1) as a function of NaCl ionic strength, which is necessary to perform a Pitzer ion-interaction parameter calculation. To provide a workable concentration range matrix, NaCl solutions of 1, 2, 3, 4 and 5 M, containing varied concentrations of sodium tetraborate, were equilibrated with Nd(OH)$_3$ solid for 120 days with Nd concentrations measured periodically using the pre-concentration procedure and ICP-MS analysis until steady state was achieved. Neodymium concentrations measured after 90 days and 120 days were essentially the same within the experimental error. Neodymium concentrations versus total tetraborate concentrations measured in 1, 2, 3, 4 and 5 M NaCl are presented in Figure 3.

The p$C_{H^+}$, equal to $8.59 \pm 0.04$, was adjusted and kept constant in these samples for the duration of the experiment. For each NaCl concentration, the increase of the neodymium
concentration was assigned to tetraborate complexation only, because other parameters affecting the neodymium solubility and speciation, such as pCH⁺, ionic strength and chloride concentration, were kept constant.

The formation constant of the neodymium with tetraborate complex in each NaCl ionic strength solution was calculated using the following formalism. The concentration of the neodymium-tetraborate complex was calculated as a difference between neodymium concentration at the given tetraborate concentration and the neodymium concentration in sample without tetraborate for the same NaCl concentration. The tetraborate species concentration taking part in the complexation reaction was calculated using the pKa corresponding to the NaCl concentration, pCH⁺ and total borate concentration as described in the Section Tetraboric Acid Dissociation Constant. The amount of tetraborate used out for the neodymium complexation was neglected because this amount was three or more orders of magnitude smaller than the dissociated fraction of the tetraborate concentration.

The free (uncomplexed) neodymium concentration was calculated from the solubility model using the FMT (Fracture-Matrix Transport) computer code [7, 8], considering the presence of Nd(OH)₃(s), Nd³⁺, NdOH²⁺, Nd(OH)₂⁺ and NdCl²⁺ species by using Am(III) analog species. In references [7 and 8], the origin of the all thermodynamic data used for the database is detailed. The calculated fractions of free Nd³⁺ species in the samples of 1, 2, 3, 4 and 5 M NaCl without tetraborate present were 7.20, 5.11, 4.40, 1.60 and 1.88 % respectively.
The apparent stability constant was calculated for single data points using Eq. 2 and the methodology described above. The average stability constants with standard deviations were calculated for each concentration of NaCl solution and are shown in Figure 4. Relatively small changes in the stability constants as a function of NaCl ionic strength were found. The greater increase of neodymium concentration observed for the highest borate concentration in 4 and 5 M NaCl presented in Figure 3 and may suggest a formation of the higher neodymium tetraborate complexes. These points were treated equally with other points and included to the overall apparent stability constants presented in Figure 4.

The stability constant for the neodymium (III) with tetraborate anion was not reported in literature. Measurements of stability constants for borate-complexes of metal ions reported in the literature [9, 10] have been largely restricted to Group I and II metals. Bousher critically reviewed data reported in the literature [9] suggesting unidentate complexation involving the borate ion. This approach is consistent with the approach applied and justified in the present work. Among trivalent cations, the only available stability constants are for Al(III) and Fe(III). Shchigol [10] reported a value of log K = 8.6 for borate with Fe(III) complexation at I = 0.7 M with this value being corrected to 5.5 by Bousher due to the significant amount of oxalate present in the Shchigol experiment. By comparison, the NIST Database [6] reports a value of 6.58 for I = 0.7 M published by Byrne [11]. Stability constants of Fe(III) with inorganic and organic ligands are usually greater than those for trivalent lanthanides and actinides. Shchigol also measured the stability constant for aluminum complexation with borate using competition
with iron(III). Since the Fe(III) with borate constant was erroneously determined by him, this error was transferred to the aluminum with borate stability constant. Bousher corrected this constant to the value of log $K = 4.5 \pm 0.4$. Aluminum stability constants with many anions are very close to those of neodymium. Therefore, the constant measured in the present work is in reasonable agreement with the stability constants for other metals available in literature.

These determined apparent stability constants were then used for the Pitzer ion-interaction parameter calculation that can be used in modeling the trivalent actinide behavior in the high ionic strength brine in WIPP conditions.

**Calculation of Pitzer parameters**

In this study, the Pitzer interaction parameters of the neodymium-tetraborate complex $\text{NdHB}_4\text{O}_7^{2+}$ with $\text{Cl}^-$ are obtained by fitting the experimental data using the NONLIN computer code. In order to perform the modeling, the concentrations of supporting NaCl solutions on molar scale are converted to those on molal scale using the conversion factors tabulated in [12]. In the modeling, the Pitzer interaction parameters of $\text{Na}^+$ with $\text{B}_3\text{O}_5(\text{OH})_4^{-}$ are used as analogs to the interaction between $\text{Na}^+$ and $\text{HB}_4\text{O}_7^-$ [13]. Also in this modeling, the $\beta^{(1)}$ parameter for $\text{NdHB}_4\text{O}_7^{2+}$ with $\text{Cl}^-$ interaction is set to 1.74 as it was done before for 2-1 electrolytes [14]. Ion interaction parameters used in these calculations are listed in Table 1. Then, the experimental data were fitted using the Pitzer
approach in order to obtain $\mu^0/RT$ for NdHB$_4$O$_7^{2+}$, $\beta^{(0)}$ and $C^\phi$. Figure 4 illustrates the comparison of experimental values with the predicted values by using the Pitzer parameters calculated in this work. The values predicted by our model appear to be in good agreement with the experimental values.

Based on the standard dimensionless chemical potential of NdHB$_4$O$_7^{2+}$ obtained in this study (Table 2) in combination with those for Nd$^{3+}$ and HB$_4$O$_7^-$ from [15], the formation constant of NdHB$_4$O$_7^{2+}$ at infinite dilution is calculated as 4.99 ± 0.30 in logarithmic units (Table 2). This value is close to the value of 4.55 ± 0.06 when the Specific Interaction Theory (SIT) is applied for the extrapolation of experimental values of 1-4 M NaCl to infinite dilution (Table 3). In addition, $\varepsilon$(NdHB$_4$O$_7^{2+}$, Cl$^-$) is also derived in this study (Table 3) by using $\varepsilon$(Sm$^{3+}$, Cl$^-$) = 0.211 from [16] as an analog to $\varepsilon$(Nd$^{3+}$, Cl$^-$), and $\varepsilon$(Na$^+$, B(OH)$_4^-$) = −0.07 from [17] as an analog to $\varepsilon$(Na$^+$, HB$_4$O$_7^-$).

**Conclusions**

The tetraborate ion is a contributor in actinide (III) speciation in the WIPP. It was found that tetraborate ion, under repository conditions, competes with carbonate for An(III) complexation. Under WIPP-relevant conditions, i.e. $p_{H^+}$ ranging from 8.5 to 9.5, the concentration of undissociated acid is rapidly reduced to form two anionic species: HB$_4$O$_7^{1-}$ and to a smaller extent, B$_4$O$_7^{2-}$ at $p_{H^+} = 8.6$.

Neodymium is complexed by tetraborate with logarithm of the apparent stability constant ranging from 3.5 to 4.1 (depending on ionic strength). The Pitzer parameters for
Nd(III), and by analogy for An(III) interaction with tetraborate ion, were determined and will be introduced to the WIPP database used for performance assessment.

Taking into consideration the limited solubility of sodium tetraborate in brine, for \( pC_{H^+} \) lower than 8.0, the concentration of the species available for complexation is not high enough to have an effect on the overall neodymium solubility. For \( pC_{H^+} \) higher than 10.0, hydrolysis overwhelms all other complexation reactions. This trend in neodymium solubility was observed in the WIPP specific brine ERDA-6.

References


Figure Captions

Figure 1. Tetraborate speciation in 5 M NaCl solution under basic conditions as a function of pH showed that the dominating species at pH=8.59 is HB₄O₇⁻.

Figure 2. The results of the undersaturation solubility experiment conducted in water at constant pH=8.6 and low but varied ionic strength solution (supporting electrolyte was not added) provided evidence of neodymium with tetraborate complexation.

Figure 3. Neodymium concentrations measured in solubility experiments after 120 days of equilibration as a function of tetraborate concentration in 1, 2, 3, 4 and 5 M NaCl solutions at pH=8.59, normalized for constant free neodymium concentration equal to 1x10⁻⁹ M.

Figure 4. Neodymium-tetraborate stability constants experimentally determined in different NaCl ionic strength solutions (points) and model fit calculated (line) using the Pitzer parameters determined in this study.
5 M NaCl
\[ \text{pK}_a = 9.02 \]

Figure 1.
Figure 2.
Figure 3.
Figure 4.
Table 1. Binary Pitzer parameters used and calculated in the present work for neodymium complexation with teraborate anion.

<table>
<thead>
<tr>
<th>Species $i$</th>
<th>Species $j$</th>
<th>$\beta_{ij}^0$</th>
<th>$\beta_{ij}^1$</th>
<th>$\beta_{ij}^2$</th>
<th>$c_{ij}^+$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>Cl$^-$</td>
<td>0.178</td>
<td>0.295</td>
<td>0</td>
<td>0.008</td>
<td>[7]</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>Cl$^-$</td>
<td>0.0765</td>
<td>0.266</td>
<td>0</td>
<td>0.00127</td>
<td>[7]</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>OH$^-$</td>
<td>0.0864</td>
<td>0.253</td>
<td>0</td>
<td>0.0044</td>
<td>[7]</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>Cl$^-$</td>
<td>0.612</td>
<td>5.4</td>
<td>0</td>
<td>-0.0184</td>
<td>[8]</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>B$_3$O$_3$(OH)$_4^+$</td>
<td>-0.056</td>
<td>-0.91</td>
<td>0</td>
<td>0</td>
<td>[13]$^A$</td>
</tr>
<tr>
<td>NdHB$_4$O$_7^{2+}$</td>
<td>Cl$^-$</td>
<td>-0.0352</td>
<td>1.74</td>
<td>0</td>
<td>-0.0130</td>
<td>Present work</td>
</tr>
</tbody>
</table>

$^A$ Used as an analog to the interaction of Na$^+$ with HB$_4$O$_7^-$
Table 2. Standard dimensionless chemical potential and formation constant of NdHB₄O₇²⁺ at infinite dilution and 25 °C.

<table>
<thead>
<tr>
<th>Species or Formation Reaction</th>
<th>( \mu^0/RT ) for Species or log ( \beta_1 ) for Formation Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdHB₄O₇²⁺</td>
<td>(-1365.508 \pm 0.72 ) (2σ)</td>
</tr>
<tr>
<td>( \text{Nd}^{3+} + \text{HB}_4\text{O}_7^- \rightleftharpoons \text{NdHB}_4\text{O}_7^{2+} )</td>
<td>( 4.99 \pm 0.30 ) (2σ)</td>
</tr>
</tbody>
</table>

Table 3. Formation constant of NdHB₄O₇²⁺ at infinite dilution and 25 °C using the SIT model for extrapolation.

<table>
<thead>
<tr>
<th>Formation Reaction and SIT Interaction Coefficient</th>
<th>log ( \beta_1 ) and the Value of SIT Interaction Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Nd}^{3+} + \text{HB}_4\text{O}_7^- \rightleftharpoons \text{NdHB}_4\text{O}_7^{2+} )</td>
<td>( 4.55 \pm 0.06 ) (2σ)</td>
</tr>
<tr>
<td>( \Delta \varepsilon ) (Eq. 1)</td>
<td>( -0.189 \pm 0.015 ) (2σ)</td>
</tr>
<tr>
<td>( \epsilon(\text{NdHB}_4\text{O}_7^{2+}, \text{Cl}^-) )</td>
<td>( -0.048^\text{A} \pm 0.023 ) (2σ)</td>
</tr>
</tbody>
</table>

\(^\text{A} \) Calculated by using \( \epsilon(\text{Sm}^{3+}, \text{Cl}^-) \) as an analog to \( \epsilon(\text{Nd}^{3+}, \text{Cl}^-) \), and \( \epsilon(\text{Na}^+, \text{B(OH)}_4^-) \) as an analog to \( \epsilon(\text{Na}^+, \text{HB}_4\text{O}_7^-) \).