

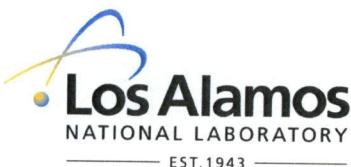
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Author(s): Marian Borkowski
Michael Richmann
Donald Reed
Xiong Yongliang

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

Marian Borkowski¹, Michael Richmann¹, Donald T. Reed¹, and Yongliang Xiong²

¹Earth and Environmental Sciences Division, Los Alamos National Laboratory, Carlsbad Operations, 115 Main St., Carlsbad, NM 88220

²Sandia National Laboratories, Carlsbad Program Group, 4100 National Parks Highway, Carlsbad, NM 88220

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 are equal to $\log \beta_1 = 4.55 \pm 0.06$ using the SIT approach, equal to $\log \beta_1 = 4.99 \pm 0.30$ using the Pitzer approach, with an apparent $\log \beta_1 = 4.06 \pm 0.15$ (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 ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and other boron minerals were discovered in California and Nevada in the mid 1800's. Today, borax is used in hundreds of applications [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 ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) 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 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ 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 HNO_3 concentrated solution (6N) was obtained from Fisher Optima, ICP-MS tuning solution supplied by Agilent, $\text{Nd}(\text{OH})_3$ 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_{H^+} (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 pC_{H^+} was calculated using an experimentally established

relationship between pC_{H^+} , pH measured and NaCl concentration given by the following equation:

$$pC_{H^+} = pH_{\text{meas}} + 0.2 \times M_{\text{NaCl}}$$

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

The pC_{H^+} was maintained at a constant value equal to $\sim 8.59 \pm 0.04$.

Large excess, about 10 mg of $\text{Nd}(\text{OH})_3$ 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% \pm 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 $\sim 10^{-10}$ 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, $\text{B}(\text{OH})_3$, 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 pK_a of boric acid is well known in the literature [6] and the pK_a 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 $\text{pK}_a = 8.95$. The result of the sodium tetraborate titration indicated that the pK_a of tetraboric acid is the same as monoboric acid and that tetraboric acid is a diprotic acid. Both protons are far away from 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 pK_a value for 5 M NaCl. The concentrations of HB_4O_7^- 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 pC_{H^+} 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. $pC_{H^+} \sim 8.5-9.5$, 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 $Nd(OH)_3$ 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 $HB_4O_7^{1-}$ anion. The neodymium complexation reaction with this tetraborate species at $pC_{H^+} = 8.6$ in water and WIPP brine might be given by the following reaction:



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 Nd^{3+} as a bidentate ligand, 3) interaction with each site has a similar strength or the same effective pK_a 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, β_1 , for reaction (1) is given by the following equation:

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

The square brackets indicate equilibrium concentrations. The increase of neodymium concentration with increasing tetraborate concentration in Figure 2 was assigned to neodymium-tetraborate complexation. At pC_{H^+} greater than pK_a of tetraboric acid, e.g. equal 9.5, the dominating species is $\text{B}_4\text{O}_7^{2-}$. Because of the long distance between the donor atoms, the tetraborate molecule can interact with Nd^{3+} as a monodentate ligand, therefore the stability constant should remain the same. This expectation needs experimental verification, however may be difficult due to the growing hydrolysis with pC_{H^+} .

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 $\text{Nd}(\text{OH})_3$ 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 pC_{H^+} , equal to 8.59 ± 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 pC_{H^+} , 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 pK_a corresponding to the NaCl concentration, pC_{H^+} 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 $Nd(OH)_3(s)$, Nd^{3+} , $NdOH^{2+}$, $Nd(OH)_2^+$ and $NdCl^{2+}$ 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 Nd^{3+} 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 greatest degree of deviation of neodymium concentration from ideality (i.e. straight-line behavior) is observed for the highest borate concentrations in 4 and 5 M NaCl and is presented in Figure 3. This 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 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 Na^+ with $\text{B}_3\text{O}_3(\text{OH})_4^-$ are used as analogs to the interaction between Na^+ and HB_4O_7^- [13]. Also in this modeling, the $\beta^{(1)}$ parameter for $\text{NdHB}_4\text{O}_7^{2+}$ with 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 μ^0/RT for $\text{NdHB}_4\text{O}_7^{2+}$, $\beta^{(0)}$ and C^ϕ . 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 $\text{NdHB}_4\text{O}_7^{2+}$ obtained in this study (Table 2) in combination with those for Nd^{3+} and HB_4O_7^- from [15], the formation constant of $\text{NdHB}_4\text{O}_7^{2+}$ 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, $\varepsilon(\text{NdHB}_4\text{O}_7^{2+}, \text{Cl}^-)$ is also derived in this study (Table 3) by using $\varepsilon(\text{Sm}^{3+}, \text{Cl}^-) = 0.211$ from [16] as an analog to $\varepsilon(\text{Nd}^{3+}, \text{Cl}^-)$, and $\varepsilon(\text{Na}^+, \text{B}(\text{OH})_4^-) = -0.07$ from [17] as an analog to $\varepsilon(\text{Na}^+, \text{HB}_4\text{O}_7^-)$.

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. pC_{H^+} ranging from 8.5 to 9.5, the concentration of undissociated acid is rapidly reduced to form two anionic species: $\text{HB}_4\text{O}_7^{1-}$ and to a smaller extent, $\text{B}_4\text{O}_7^{2-}$ at $\text{pC}_{\text{H}^+} = 8.6$.

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 and the SIT parameters for Nd(III), and by analogy for An(III) interaction with tetraborate ion were determined and can be used for modeling purposes.

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 low magnesium brine ERDA-6.

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Figure Captions

Figure 1. Tetraborate speciation in 5 M NaCl solution under basic conditions as a function of pC_{H^+} showed that the dominating species at $pH=8.59$ is $HB_4O_7^-$.

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 $pC_{H^+}=8.59$, normalized for constant free neodymium concentration equal to 1×10^{-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.

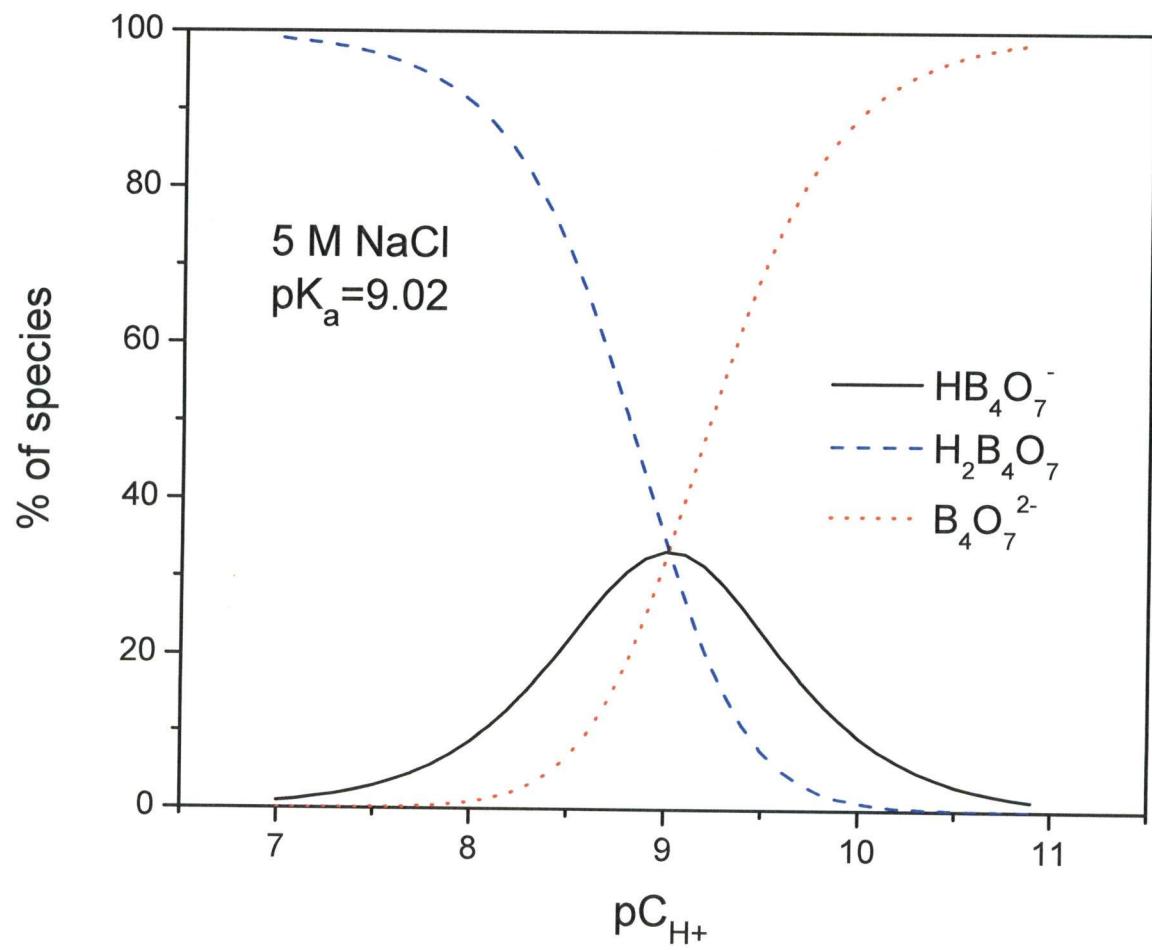


Figure 1.

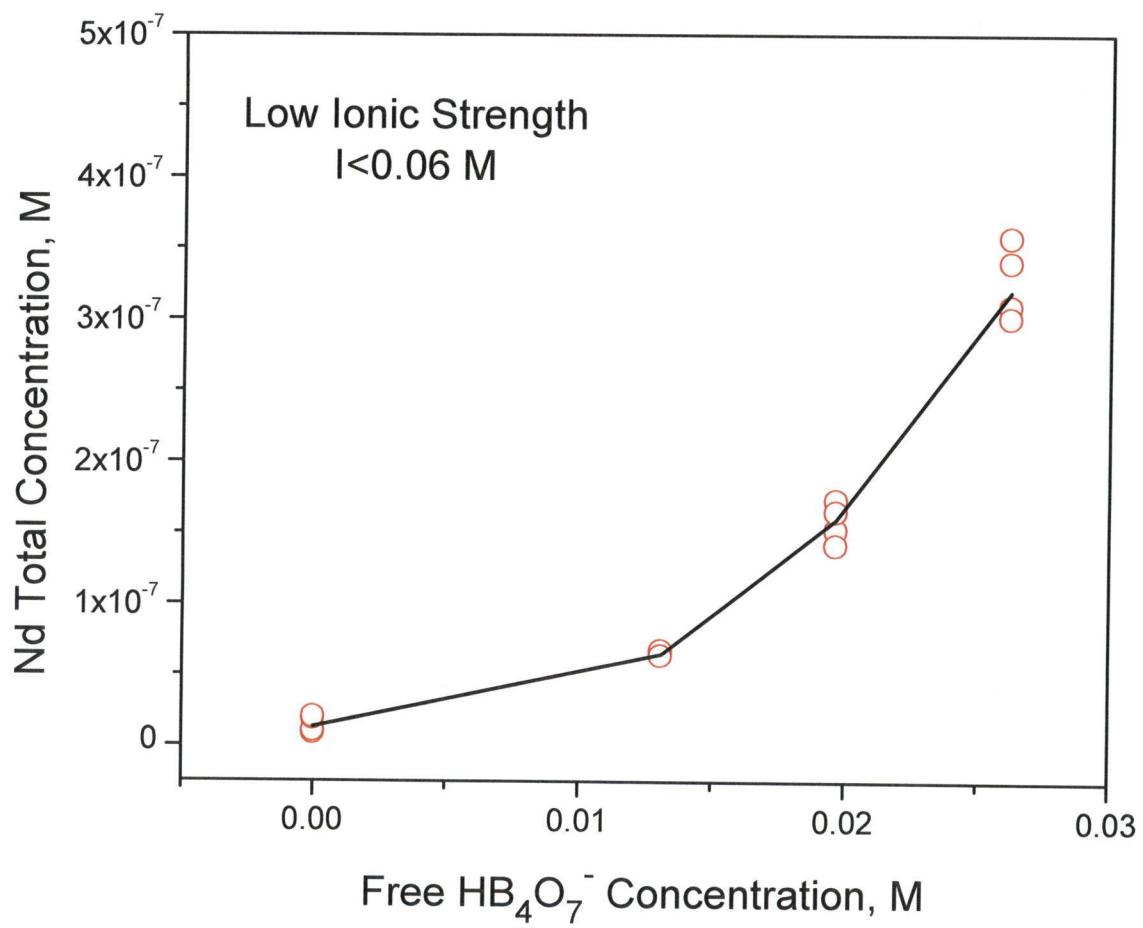


Figure 2.

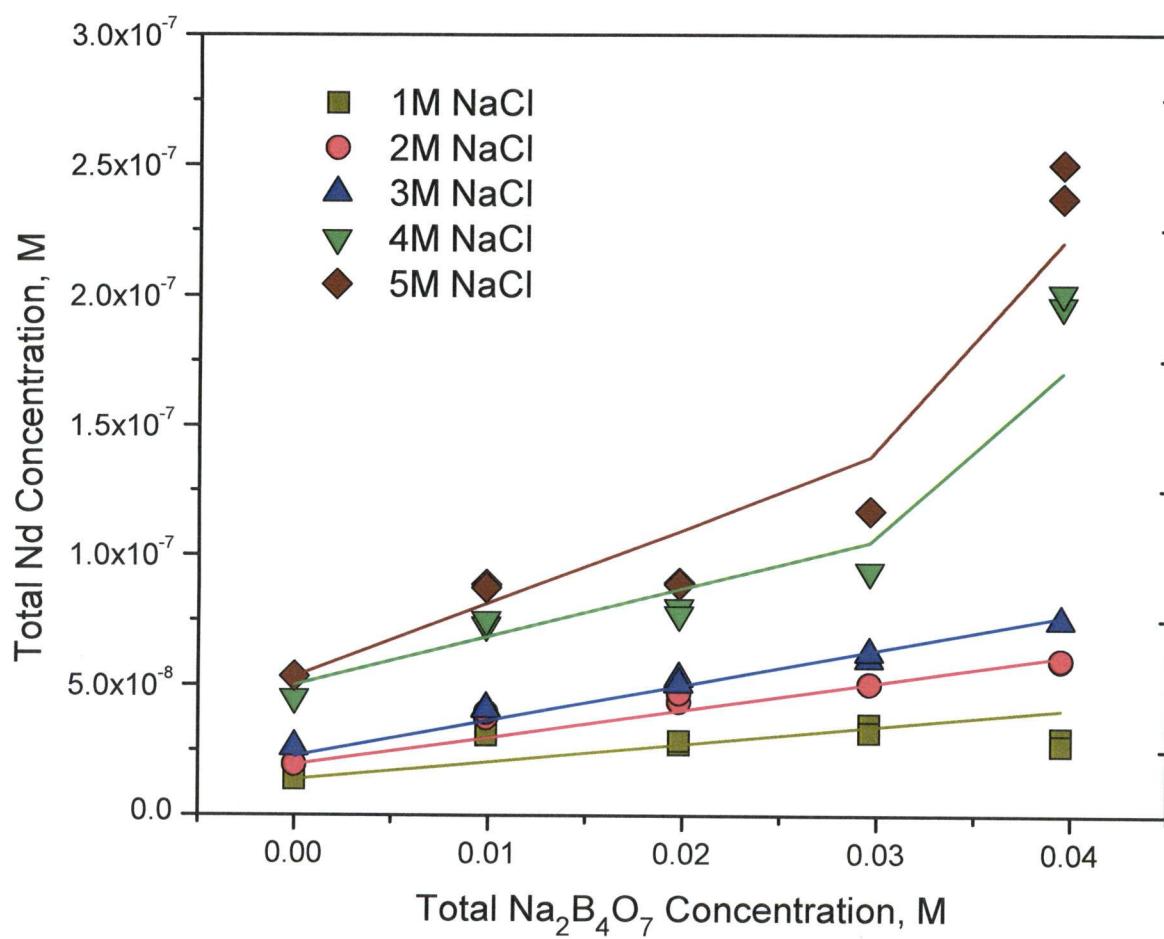


Figure 3.

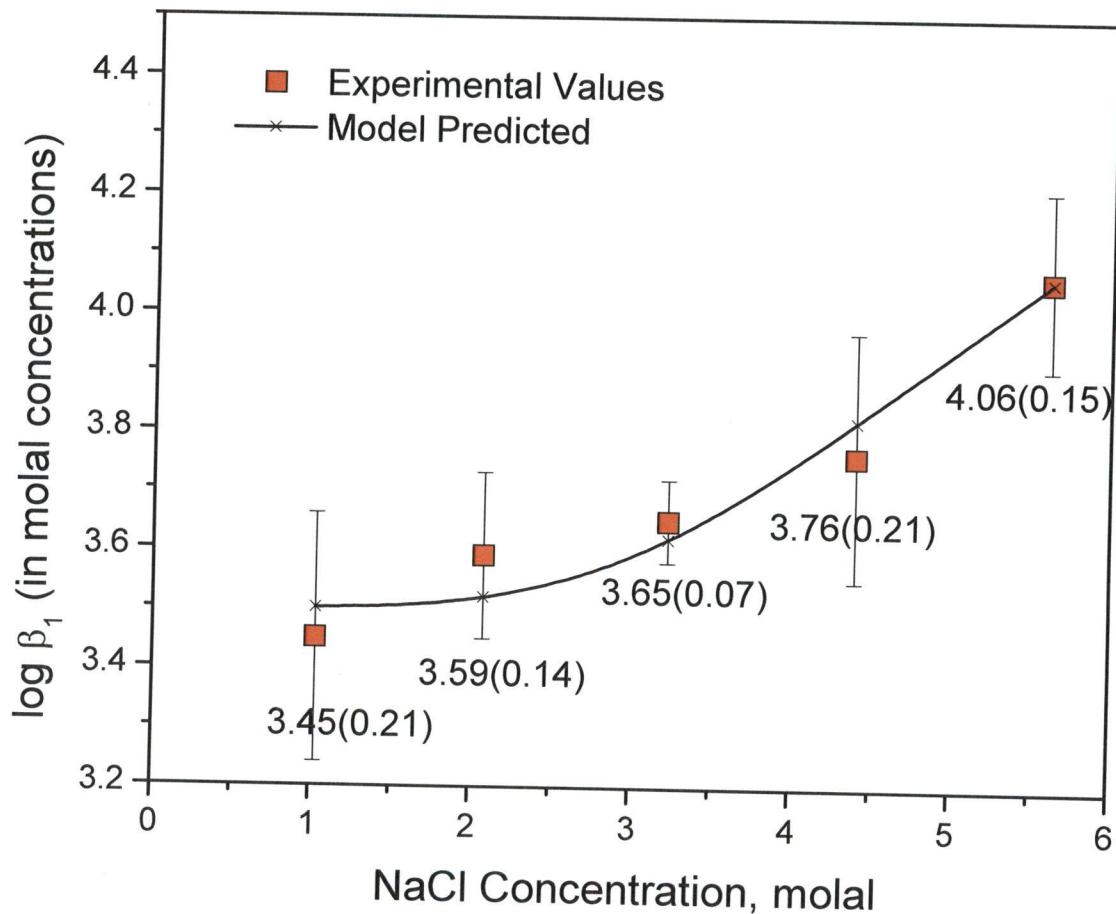


Figure 4.

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

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

^A Used as an analog to the interaction of Na^+ with HB_4O_7^-

Table 2. Standard dimensionless chemical potential and formation constant of $\text{NdHB}_4\text{O}_7^{2+}$ at infinite dilution and 25 °C.

Species or Formation Reaction	μ^0/RT for Species or $\log \beta_1$ for Formation Reaction
$\text{NdHB}_4\text{O}_7^{2+}$	-1365.508 ± 0.72 (2 σ)
$\text{Nd}^{3+} + \text{HB}_4\text{O}_7^{1-} \rightleftharpoons \text{NdHB}_4\text{O}_7^{2+}$	4.99 ± 0.30 (2 σ)

Table 3. Formation constant of $\text{NdHB}_4\text{O}_7^{2+}$ at infinite dilution and 25 °C using the SIT model for extrapolation.

Formation Reaction and SIT Interaction Coefficient	$\log \beta_1$ and the Value of SIT Interaction Coefficient
$\text{Nd}^{3+} + \text{HB}_4\text{O}_7^{1-} \rightleftharpoons \text{NdHB}_4\text{O}_7^{2+}$	4.55 ± 0.06 (2 σ)
$\Delta\epsilon$ (Eq. 1)	-0.189 ± 0.015 (2 σ)
$\epsilon(\text{NdHB}_4\text{O}_7^{2+}, \text{Cl}^-)$	$-0.048^{\text{A}} \pm 0.023$ (2 σ)

^A Calculated by using $\epsilon(\text{Sm}^{3+}, \text{Cl}^-)$ as an analog to $\epsilon(\text{Nd}^{3+}, \text{Cl}^-)$, and $\epsilon(\text{Na}^+, \text{B}(\text{OH})_4^-)$ as an analog to $\epsilon(\text{Na}^+, \text{HB}_4\text{O}_7^{1-})$.