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Sandia National Laboratories
Waste Isolation Pilot Plant

Thermodynamic Model for the Na–B(OH)$_3$–Cl–SO$_4$ system

Work Carried Out under Task 10 of AP-155: Analysis Plan for Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Borate.
To be included in the AP-155 records package

Author:	Yongliang Xiong, Org. 6212	August 16, 2012 Date
Technical Reviewer:	Greg Roselle, Org. 6212	8/20/2012 Date
QA Reviewer:	Shelly R. Nielsen, Org. 6210	8-16-12 Date
Management Reviewer:	Christi D. Leigh, Org. 6212	8-16-12 Date

WIPP:1.4.2.2:PA:QA-L:555261

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1 INTRODUCTION

This analysis report (AR) provides the results of derivation of thermodynamic properties including Pitzer parameters based on solubility of sodium tetraborate (borax) in NaCl and Na_2SO_4 solutions. Sodium tetraborate and borax are used interchangeably in this AR.

The computer code EQ3/6 Version 8.0a (Wolery, 2008; Wolery et al., 2010; Xiong, 2011) was used for this analysis. Wolery (2008), Wolery et al. (2010) and Xiong (2011b) completed the qualification of Version 8.0a of EQ3/6 according to Sandia National Laboratories' (SNL's) WIPP quality assurance (QA) procedures for WIPP compliance-related actinide solubility calculations, and US EPA approved it on September 27, 2011.

This analysis was carried out under Task 10 of AP-155 (Xiong, 2011c). There are two deviations from AP-155. The first deviation is that the literature data from Sborgi et al. (1924) and Reardon (1976) are also used for derivation of thermodynamic parameters, in addition to experimental data produced at SNL Carlsbad Facility. The second deviation is that the Python script developed by Kirchner (2012) is used instead of the one developed by Nemer (2010).

Table 1 (see next page) defines the generic abbreviations, acronyms, and initialisms used in this report and other analysis reports.

Table 1. Abbreviations, Acronyms, and Initialisms.

Abbreviation, Acronym, or Initialism	Definition
acetate	CH_3COO^- or $CH_3CO_2^-$
Am, Am(III)	americium, americium in the +III oxidation state
am	amorphous
anhydrite	$CaSO_4$
AP	analysis plan
aq	aqueous
aragonite	$CaCO_3$,a polymorph of $CaCO_3$ that is metastable with respect to calcite
atm	atmosphere(s)
B, B(III)	boron, boron in the +III oxidation state
Br, Br(−I)	bromine, bromine in the −I oxidation state
brucite	$Mg(OH)_2$
C	carbon
Ca, Ca(II), Ca^{2+}	calcium, calcium in the +II oxidation state, calcium ion
calcite	$CaCO_3$, the thermodynamically stable polymorph of $CaCO_3$
citrate	$(CH_2COO)_2C(OH)(COO)^{3-}$ or $(CH_2CO_2)_2C(OH)(CO_2)^{3-}$
Cl, Cl(−I), Cl^-	chlorine, chlorine in the −I oxidation state, chloride ion
CMS	(Sandia/WIPP software) Configuration Management System
CO_2	carbon dioxide
CO_3^{2-}	carbonate
CRA-2009	the second WIPP Compliance Recertification Application, submitted to the EPA in March 2009
DB	(thermodynamic) database
DOE	(U.S.) Department of Energy
dolomite	$CaMg(CO_3)_2$, a carbonate mineral that is nucleates and grows slowly under low-temperature conditions and is often suppressed (prevented from forming) in geochemical modeling calculations
DRZ	disturbed rock zone
EDTA	ethylenediaminetetraacetate, $(CH_2COO)_2N(CH_2)_2N(CH_2COO)_2)^{4-}$ or $(CH_2CO_2)_2N(CH_2)_2N(CH_2CO_2)^{4-}$
EPA	(U.S.) Environmental Protection Agency
EQ3/6	a geochemical software package for speciation and solubility calculations (EQ3NR) and reaction-path calculations (EQ6)

Table 1 continued on next page

Table 1. Abbreviations, Acronyms, and Initialisms (continued).

Abbreviation, Acronym, or Initialism	Definition
ERDA-6	Energy Research and Development Administration (WIPP Well) 6, a synthetic brine representative of fluids in Castile brine reservoirs
f_{CO_2}	fugacity (similar to the partial pressure) of CO_2
Fm.	Formation
FMT	Fracture-Matrix Transport, a geochemical speciation and solubility code
GWB	Generic Weep Brine, a synthetic brine representative of intergranular Salado brines at or near the stratigraphic horizon of the repository
gypsum	$CaSO_4 \cdot 2H_2O$
H or H_2, H^+	hydrogen or hydrogen ion
halite	NaCl
H_2O	water (aq, g, or contained in solid phases)
hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
I	ionic strength
K, K(I)	potassium, potassium in the +I oxidation state
kg	kilogram(s)
M	molar
m	meter(s) or molal
magnesite	$MgCO_3$
Mg, Mg(II)	magnesium, magnesium in the +II oxidation state
MgO	magnesium oxide, used to refer to the WIPP engineered barrier, which includes periclase as the primary constituent and various impurities
mM	millimolar
Na, Na(I), Na^+	sodium, sodium in the +I oxidation state, sodium ion
nesquehonite	$MgCO_3 \cdot 3H_2O$
Np, Np(V)	neptunium, neptunium in the +V oxidation state
O or O_2	oxygen
OH, OH^-	hydroxide or hydroxide ion
oxalate	$(COO)^{2-}$ or $C_2O_4^{2-}$
PA	performance assessment
PABC	Performance Assessment Baseline Calculations

Table 1 continued on next page

Table 1. Abbreviations, Acronyms, and Initialisms (continued).

Abbreviation, Acronym, or Initialism	Definition
periclase	pure, crystalline MgO, the primary constituent of the WIPP engineered barrier
pH	the negative, common logarithm of the activity of H^+
pcH	the negative, common logarithm of the molar concentration of H^+
phase 3	$Mg_2Cl(OH)_3 \cdot 4H_2O$
phase 5	$Mg_3(OH)_5Cl \cdot 4H_2O$
polyhalite	$K_2MgCa_2(SO_4)_4 \cdot 2H_2O$
QA	quality assurance
Rev.	revision
RH	relative humidity
S, S(VI), SO_4^{2-}	sulfur, sulfur in the +VI oxidation state, sulfate ion
s	solid
SCA	S. Cohen and Associates
SNL	Sandia National Laboratories
Th, Th(IV)	thorium, thorium in the +IV oxidation state
TIC	total inorganic C
WIPP	(U.S. DOE) Waste Isolation Pilot Plant
wt %	weight percent
μ^0/RT	dimensionless standard chemical potential

2 METHODS

The objective of this analysis was to derive thermodynamic properties in the Na^+–$B(OH)_3$–Cl^-–SO_4^{2-} system based on solubility data of sodium tetraborate in NaCl solutions produced at SNL (Xiong, 2012a) and in Na_2SO_4 solutions from the literature (Sborgi et al., 1924). Table 2 lists experimental data in NaCl solutions from Xiong (2012a), and Table 3 lists experimental data in Na_2SO_4 solutions from Sborgi et al. (1924).

Felmy and Weare (1986) developed a thermodynamic model concerning borate in the system Na—K—Ca—Mg—H—Cl—SO_4—CO_2—$B(OH)_4$—H_2O, based on literature data. This model will be abbreviated as the FW86 model hereafter. Their model is an extension of the Harvie et al. (1984) model to include borate species. In the FW86 model, the species, $NaB(OH)_4$(aq), was not explicitly considered. However, numerous researchers have suggested the existence of this complex in solutions containing sodium (e.g., Reardon, 1976; Corti et al., 1980; Rowe et al., 1989; Pokrowski et al., 1995; Akinfiev et al., 2006). Therefore, this complex could be important in Na-rich solutions.

In the work of Reardon (1976), the formation constants for the reaction,

$$Na^+ + B(OH)_4^- = NaB(OH)_4(aq) \qquad (1)$$

were determined in NaCl solutions with ionic strengths ranging from 0.165 m to 0.499 m at temperatures from 10 °C to 50 °C. To obtain the thermodynamic formation constants at infinite dilution, Reardon (1976) used the activity coefficients of HCO_3^- and H_3BO_3(aq) to approximate those of $B(OH)_4^-$ and $NaB(OH)_4$(aq), respectively. The thermodynamic formation constant at 25 °C for Reaction (1) obtained by Reardon (1976) was 0.22 ± 0.10.

In this study, conditional formation constants for Reaction (1) generated by Reardon (1976) are re-evaluated by using the specific ion interaction theory (SIT) model, following the methodology of Grenthe et al. (1992). The log β_1 at 25 °C obtained is 0.25 ± 0.01 (Figure 1 and Table 4). Based on $\Delta\varepsilon = -0.04 \pm 0.02$, the log β_1 at 10 °C, 40 °C and 50 °C are also obtained (Table 4). These values are in agreement with those of Pokrowski et al. (1995). The spreadsheet for calculation of these parameters is named XIONG_NaB(OH)4(aq)_SIT.xls and is located in the zip file Task10_DataPackage_Borate.zip.

The above log β_1 for $NaB(OH)_4$(aq), the experimental solubility data for borax in NaCl gathered under TP 10-01 and reported the milestone report (Xiong, 2012a), and solubility data of borax in Na_2SO_4 from Sborgi et al. (1924), are utilized to derive the Pitzer parameters and log K_{sp} for borax with the aid of the computer code EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011b). The essence of the modeling is to minimize the difference between experimental and model predicted values. The log K_{sp} for borax dissolution refers to the following reaction,

$$Na_2B_4O_7{\bullet}10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O\ (l) \qquad (2)$$

Using experimental solubility data of sodium tetraborate for NaCl solutions (Xiong, 2012a), log K_{sp} for sodium tetraborate and $\lambda_{Na^+-NaB(OH)_4(aq)}$ are obtained. The values for these two parameters are evaluated by using the Python script (Na2B4O7_NaCl_Brute_PSD.py) which runs the EQ3CodeModule optimization routine (Kirchner, 2012) with EQ3NR input files NaTC-1.3i through NaTC-85.3i. These files are located in the folder labeled as "EQ3_NaCl" in the zip file "Task10_DataPackage_Borate.zip". The optimization results indicate that the residual is minimized to be 0.26 when log K_{sp} is –24.80 and $\lambda_{Na^+-NaB(OH)_4(aq)}$ is between 0.093-0.098 (see Results_Na2B4O7_NaCl_Brute_PSD.txt, which is located in the folder named as "EQ3_NaCl"). An uncertainty of ±0.10 is assigned to log K_{sp}, and of 0.005 is assigned to $\lambda_{Na^+-NaB(OH)_4(aq)}$. The EQ3CodeModule optimization routine has been independently validated (Xiong, 2012b). The provisional database for the modeling is data0.psd, which is the precursor of data0.pd1 (see comment lines in data0.pd1 in Domski, 2012).

The experimental data of sodium tetraborate from Sborgi et al. (1924) (Table 3) are used to evaluate Ψ_{ijk} for the interaction of SO_4^{-2}—$B_4O_5(OH)_4^{-2}$—Na^+. In the evaluation, θ_{ij} for $B(OH)_4^-$—SO_4^{-2} was set to 0.17 ± 0.03, similar to the values for $B_3O_3(OH)_4^-$—SO_4^{-2} and $B_4O_5(OH)_4^{2-}$—SO_4^{-2} (Felmy and Weare, 1986). The Ψ_{ijk} for the interaction of SO_4^{-2}—$B_4O_5(OH)_4^{-2}$—Na^+ is evaluated as 0.1 ± 0.2 using the Python script (Na2B4O7_Na2SO4_BRUTE_OneParameter_data0psd.py) with EQ3NR input files SO4-1.3i through SO4-7.3i. These input files are located in the folder labeled as "EQ3_Na2SO4" in the zip file "Task10_DataPackage_Borate.zip". The value selected for the Ψ_{ijk} parameter is 0.1 ± 0.2 with a residual of 0.14-0.19 (see Results_Na2B4O7_Na2SO4_Brute_PSD.txt, which is located in the folder "EQ3_Na2SO4").

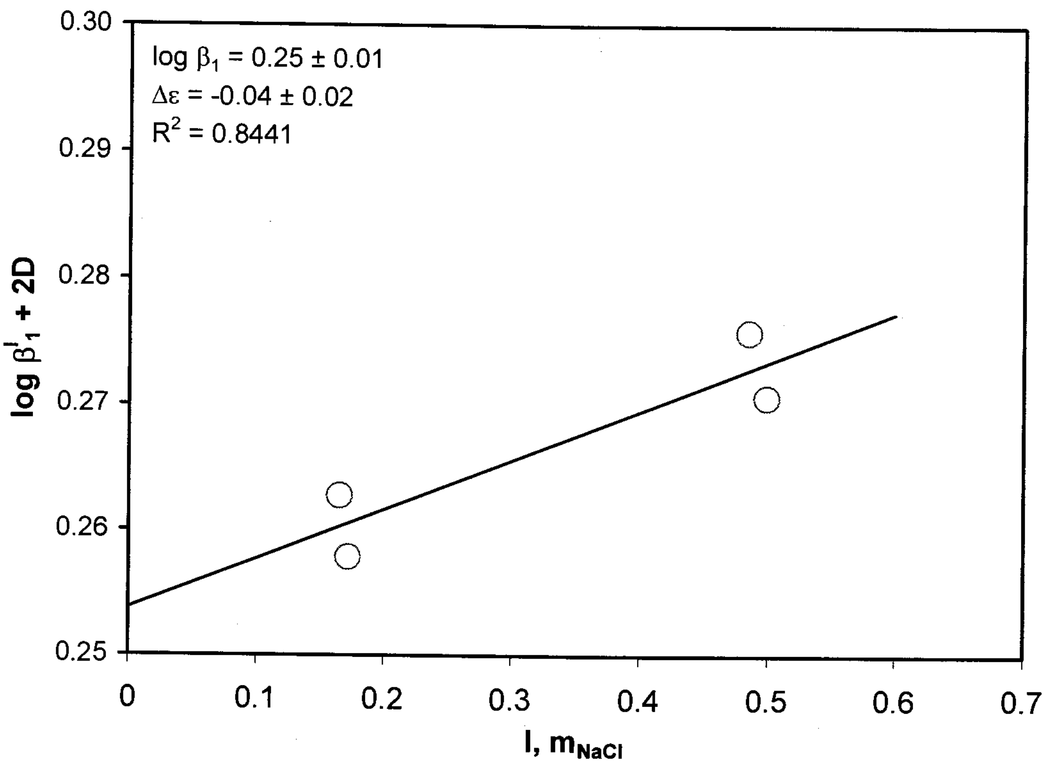

Figure 1. A plot showing [$\log \beta_1^I + 2D$] as a function of ionic strengths, where $\log \beta_1^I$ denotes conditional formation constants of $NaB(OH)_4(aq)$ at certain ionic strengths from Reardon (1976).

Table 2. Experimental results concerning solubility of sodium tetraborate in NaCl solutions produced at SNL at 22.5 ± 1.5 °C (from Xiong, 2012a)*.

Experimental Number	Supporting Medium, NaCl, molal	Experimental time, days	pmH**	Molal solubility of sodium tetraborate expressed as total boron concentrations, $m_{\Sigma B}$
$Na_2B_4O_7$-NaCl-0.01-1	0.010	132	9.10	0.515
$Na_2B_4O_7$-NaCl-0.01-2	0.010	132	9.03	0.509
$Na_2B_4O_7$-NaCl-0.1-1	0.10	132	8.97	0.435
$Na_2B_4O_7$-NaCl-0.1-2	0.10	132	8.95	0.417
$Na_2B_4O_7$-NaCl-1.0-1	1.0	132	8.70	0.179
$Na_2B_4O_7$-NaCl-1.0-2	1.0	132	8.72	0.194
$Na_2B_4O_7$-NaCl-2.0-1	2.1	132	8.66	0.157
$Na_2B_4O_7$-NaCl-2.0-2	2.1	132	8.81	0.147
$Na_2B_4O_7$-NaCl-3.0-1	3.2	132	8.81	0.139
$Na_2B_4O_7$-NaCl-3.0-2	3.2	132	8.77	0.143
$Na_2B_4O_7$-NaCl-4.0-1	4.4	132	8.88	0.165
$Na_2B_4O_7$-NaCl-4.0-2	4.4	132	8.89	0.151
$Na_2B_4O_7$-NaCl-5.0-1	5.0	132	8.80	0.145
$Na_2B_4O_7$-NaCl-5.0-2	5.0	132	8.79	0.146
$Na_2B_4O_7$-NaCl-0.01-1	0.010	278	9.28	0.488
$Na_2B_4O_7$-NaCl-0.01-2	0.010	278	9.28	0.495
$Na_2B_4O_7$-NaCl-0.1-1	0.10	278	9.26	0.411
$Na_2B_4O_7$-NaCl-0.1-2	0.10	278	9.24	0.415
$Na_2B_4O_7$-NaCl-1.0-1	1.0	278	9.04	0.190
$Na_2B_4O_7$-NaCl-1.0-2	1.0	278	9.03	0.099
$Na_2B_4O_7$-NaCl-2.0-1	2.1	278	9.00	0.155
$Na_2B_4O_7$-NaCl-2.0-2	2.1	278	8.98	0.152
$Na_2B_4O_7$-NaCl-3.0-1	3.2	278	8.96	0.143
$Na_2B_4O_7$-NaCl-3.0-2	3.2	278	8.93	0.140
$Na_2B_4O_7$-NaCl-4.0-1	4.4	278	9.06	0.139
$Na_2B_4O_7$-NaCl-4.0-2	4.4	278	9.05	0.142
$Na_2B_4O_7$-NaCl-5.0-1	5.0	278	8.96	0.141
$Na_2B_4O_7$-NaCl-5.0-2	5.0	278	8.96	0.142
$Na_2B_4O_7$-NaCl-0.01-1	0.010	327	9.33	0.482
$Na_2B_4O_7$-NaCl-0.01-2	0.010	327	9.28	0.508
$Na_2B_4O_7$-NaCl-0.1-1	0.10	327	9.26	0.436

$Na_2B_4O_7$-NaCl-0.1-2	0.10	327	9.22	0.430
$Na_2B_4O_7$-NaCl-1.0-1	1.0	327	9.09	0.207
$Na_2B_4O_7$-NaCl-1.0-2	1.0	327	9.10	0.210
$Na_2B_4O_7$-NaCl-2.0-1	2.1	327	8.99	0.160
$Na_2B_4O_7$-NaCl-2.0-2	2.1	327	9.00	0.161
$Na_2B_4O_7$-NaCl-3.0-1	3.2	327	9.00	0.151
$Na_2B_4O_7$-NaCl-3.0-2	3.2	327	8.95	0.157
$Na_2B_4O_7$-NaCl-4.0-1	4.4	327	9.10	0.151
$Na_2B_4O_7$-NaCl-4.0-2	4.4	327	9.11	0.147
$Na_2B_4O_7$-NaCl-5.0-1	5.0	327	8.97	0.151
$Na_2B_4O_7$-NaCl-5.0-2	5.0	327	9.01	0.158
$Na_2B_4O_7$-NaCl-0.01-1	0.010	377	9.39	0.513
$Na_2B_4O_7$-NaCl-0.01-2	0.010	377	9.38	0.509
$Na_2B_4O_7$-NaCl-0.1-1	0.10	377	9.32	0.468
$Na_2B_4O_7$-NaCl-0.1-2	0.10	377	9.33	0.482
$Na_2B_4O_7$-NaCl-1.0-1	1.0	377	9.09	0.214
$Na_2B_4O_7$-NaCl-1.0-2	1.0	377	9.09	0.231
$Na_2B_4O_7$-NaCl-2.0-1	2.1	377	9.03	0.168
$Na_2B_4O_7$-NaCl-2.0-2	2.1	377	9.03	0.171
$Na_2B_4O_7$-NaCl-3.0-1	3.2	377	9.01	0.153
$Na_2B_4O_7$-NaCl-3.0-2	3.2	377	9.00	0.149
$Na_2B_4O_7$-NaCl-4.0-1	4.4	377	9.08	0.152
$Na_2B_4O_7$-NaCl-4.0-2	4.4	377	9.09	0.146
$Na_2B_4O_7$-NaCl-5.0-1	5.0	377	9.00	0.152
$Na_2B_4O_7$-NaCl-5.0-2	5.0	377	9.02	0.149
$Na_2B_4O_7$-NaCl-0.01-1	0.010	425	9.35	0.514
$Na_2B_4O_7$-NaCl-0.01-2	0.010	425	9.31	0.532
$Na_2B_4O_7$-NaCl-0.1-1	0.10	425	9.26	0.531
$Na_2B_4O_7$-NaCl-0.1-2	0.10	425	9.25	0.458
$Na_2B_4O_7$-NaCl-1.0-1	1.0	425	9.04	0.221
$Na_2B_4O_7$-NaCl-1.0-2	1.0	425	9.03	0.222
$Na_2B_4O_7$-NaCl-2.0-1	2.1	425	8.96	0.171
$Na_2B_4O_7$-NaCl-2.0-2	2.1	425	8.97	0.171
$Na_2B_4O_7$-NaCl-3.0-1	3.2	425	8.95	0.161
$Na_2B_4O_7$-NaCl-3.0-2	3.2	425	8.93	0.156
$Na_2B_4O_7$-NaCl-4.0-1	4.4	425	9.02	0.158
$Na_2B_4O_7$-NaCl-4.0-2	4.4	425	9.04	0.154
$Na_2B_4O_7$-NaCl-5.0-1	5.0	425	8.96	0.159

$Na_2B_4O_7$-NaCl-5.0-2	5.0	425	8.97	0.162
$Na_2B_4O_7$-NaCl-0.01-1	0.010	567	9.28	0.489
$Na_2B_4O_7$-NaCl-0.01-2	0.010	567	9.28	0.497
$Na_2B_4O_7$-NaCl-0.1-1	0.10	567	9.24	0.429
$Na_2B_4O_7$-NaCl-0.1-2	0.10	567	9.23	0.426
$Na_2B_4O_7$-NaCl-1.0-1	1.0	567	9.00	0.199
$Na_2B_4O_7$-NaCl-1.0-2	1.0	567	9.00	0.203
$Na_2B_4O_7$-NaCl-2.0-1	2.1	567	8.94	0.157
$Na_2B_4O_7$-NaCl-2.0-2	2.1	567	8.94	0.167
$Na_2B_4O_7$-NaCl-3.0-1	3.2	567	8.93	0.160
$Na_2B_4O_7$-NaCl-3.0-1R	3.2	567	8.92	0.155
$Na_2B_4O_7$-NaCl-3.0-2	3.2	567	8.90	0.154
$Na_2B_4O_7$-NaCl-4.0-1	4.4	567	8.99	0.148
$Na_2B_4O_7$-NaCl-4.0-2	4.4	567	9.01	0.152
$Na_2B_4O_7$-NaCl-5.0-1	5.0	567	8.93	0.158
$Na_2B_4O_7$-NaCl-5.0-2	5.0	567	8.93	0.154

*Experimental data at 567 days were not reported in Xiong (2012a). They were generated after that report (see Pages 10–11 of WIPP–Borate–5).
**In Xiong (2012a), pH reading were reported. Values of pmH reported in this analysis report are calculated by using the correction factors (A_M) for pH readings, and conversion factors (Θ) from molarity to molality, $pmH = pH_{ob} + A_M - \log \Theta$ (Xiong et al., 2010). The correction factors are from Rai et al. (1995). The conversion factors are calculated from densities for NaCl solutions, which are from Sőhnel and Novotný (1985). Please see the spreadsheet “XIONG_Na2B4O7_NaCl_Paper.xls”.

Table 3. Solubility data of sodium tetraborate in Na_2SO_4 solutions at 25 °C (Sborgi et al., 1924).

Molal solubility of sodium tetraborate expressed as total boron concentrations, $m_{\Sigma B}$	Molality of SO_4^{2-}	Molality of Na^+
0.3344*	0.0000*	0.1672*
0.2868	0.08711	0.3176
0.2281	0.2393	0.5927
0.1699	0.7633	1.6115
0.1585	1.036	2.151
0.1576	1.318	2.715
0.1573	1.439	2.956
0.1572	1.503	3.085

*These data were not used for calculation, because there was no SO_4^{2-} in solution.

Table 4. Equilibrium Constants for Complex Formation Reaction

Reaction	log β_1 at 25 °C unless otherwise noted
$Na^+ + B(OH)_4^- = NaB(OH)_4(aq)$	0.29 ± 0.01 (10 °C) 0.25 ± 0.01 (25 °C) with Δε = -0.04 ± 0.02 0.24 ± 0.01 (40 °C) 0.26 ± 0.02 (50 °C)

Table 5. Locations of the Excel Spreadsheets, EQ3/6 I/O Files Associated with Calculations for This Analysis.

Description or Title of File(s)	Location of File(s)
Spreadsheet XIONG_NaB(OH)4(aq)_SIT.xls	In zip file Task10_DataPackage_Borate.zip, library LIBAP155
Spreadsheet XIONG_Na2B4O7_NaCl_Paper.xls	In zip file Task10_DataPackage_Borate.zip, library LIBAP155
EQ3/6 DB DATA0.PSD EQ3/6 DB DATA0.PD1	In zip file Task10_DataPackage_Borate.zip, library LIBAP155
EQ3/6 I/O files: NaTC-1.3i/o through NaTC-85.3i/o SO4-1.3i/o through SO4-7.3i/o ClSO4-1.3i/o through ClSO4-8.3i/o ClSO4-1.6i/o through ClSO4-8.6i/o	In zip file Task10_DataPackage_Borate.zip, library LIBAP155
Python scripts: Na2B4O7_NaCl_BRUTE_PSD.py Na2B4O7_Na2SO4_BRUTE_OneParameter_data0psd.py	In zip file Task10_DataPackage_Borate.zip, library LIBAP155

The EQ3/6 thermodynamic databases (DB) DATA0.FM1 and DATA0.PSD were used for this analysis. The DATA0.FM1 (Xiong, 2001a) has the Felmy and Weare (1986) model on borate species. The DATA0.PSD database contains the revised parameters for the borate species generated in this analysis. The DATA0.PSD database is in Task10_DataPackage_Borate.zip, LIBAP155, in the CMS. All supporting EQ3/6 input and output (I/O) files are also located in the above zip file.

3 RESULTS

Table 6 provides the Pitzer parameters and log K_{sp} derived in this study.

Table 7 provides the comparison between the FW86 model and the revised model developed in this study. These two models are benchmarked versus the independent experimental data. The comparison demonstrates that the model developed in this study is superior in prediction of solubilities of sodium tetraborate in concentrated brines to ionic strengths of ~8 m. The EQ3/6 input and output files for the model comparison are ClSO4-1.3i/o through ClSO4-8.3i/o, and ClSO4-1.6i/o through ClSO4-8.6i/o. respectively. In the folder labeled as "Felmy" in the zip file "Task10_DataPackage_Borate.zip", output files were generated by using the officially released database, data0.fm1 (Xiong, 2011a). In the folder labeled as "Xiong_Yongliang" in the zip file "Task10_DataPackage_Borate.zip", output files were generated by using the provisional database, DATA0.PD1 (Domski, 2012), in which the data0.fm1 has been modified by incorporating the respective parameters described in this report. As data0.fm1 has been officially released, it is not included in the zip file.

Table 6. The revised thermodynamic model for the Na–$B(OH)_3$–Cl–SO_4 system developed in this study*.

Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	SO_4^{-2}		0.17 ± 0.03	
$NaB(OH)_4(aq)$	Na^+		0.093 ± 0.005	
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}	Na^+		0.1 ± 0.2
Equilibrium Constants for Solubility and Complex Formation Reactions				
Reaction			log *K* or log β_1 at 25 °C unless otherwise noted	
$Na_2B_4O_7 \cdot 10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			–24.80 ± 0.10 (2σ)	
$Na^+ + B(OH)_4^- = NaB(OH)_4(aq)$			0.25 ± 0.01 (25 °C)	

*Unless otherwise noted, other parameters, which are not listed, are the same as those in Felmy and Weare (1986) model.

Table 7. Comparison of independent, experimental equilibrium compositions for multiple equilibrium assemblages containing sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) (borax) with predicted compositions in mixtures of NaCl and Na_2SO_4 at 25 °C*

Experimental data for equilibrium compositions					
m_{Na}	m_{Cl}	m_{SO4}	$m_{\Sigma B}$	Equilibrium Assemblage**	References
6.967	5.516	0.694	0.125	BRX+HLT+THNDT	Van't Hoff and Blasdale (1905)
6.355	5.925	0.183	0.128	BRX+HLT	Grushvitski and Flerinskava (1932)
6.527	5.408	0.526	0.134	BRX+HLT	*ibid.*
6.716	5.286	0.673	0.167	BRX+HLT	*ibid.*
6.939	5.441	0.716	0.132	BRX+HLT+THNDT	*ibid.*
6.603	4.723	0.903	0.149	BRX	*ibid.*
6.477	3.168	1.619	0.141	BRX+MRBLT+THNDT	*ibid.*
3.774	0.248	1.734	0.117	BRX+MRBLT	*ibid.*
Equilibrium compositions predicted by the Felmy and Weare (1986) model, produced by using data0.fm1					
m_{Na}	m_{Cl}	m_{SO4}	$m_{\Sigma B}$	Equilibrium Assemblage**	
6.971	5.484	0.691	0.212	BRX+HLT+THNDT	
6.364	5.896	0.182	0.206	BRX+HLT	
6.532	5.381	0.523	0.209	BRX+HLT	
6.704	5.260	0.670	0.211	BRX+HLT	
6.943	5.413	0.712	0.212	BRX+HLT+THNDT	
6.602	4.699	0.898	0.214	BRX	
6.367	3.229	1.512	0.229	BRX+MRBLT+THNDT	
3.833	0.246	1.721	0.289	BRX+MRBLT	
Equilibrium compositions predicted by the model developed in this study, produced by using data0.pd1					
m_{Na}	m_{Cl}	m_{SO4}	$m_{\Sigma B}$	Equilibrium Assemblage**	
6.946	5.494	0.692	0.135	BRX+HLT+THNDT	
6.347	5.906	0.183	0.150	BRX+HLT	
6.511	5.393	0.524	0.140	BRX+HLT	
6.682	5.272	0.671	0.136	BRX+HLT	
6.921	5.426	0.714	0.134	BRX+HLT+THNDT	
6.577	4.711	0.900	0.130	BRX	
6.283	3.274	1.475	0.119	BRX+MRBLT+THNDT	

3.779	0.247	1.728	0.150	BRX+MRBLT
Difference in %** between experimental values and those predicted by the FW86 model				
ΔNa in %	ΔCl in %	ΔSO_4 in %	ΔΣB in %	Equilibrium Assemblage**
0.060	-0.586	-0.507	69.788	BRX+HLT+THNDT
0.133	-0.483	-0.482	60.851	BRX+HLT
0.084	-0.496	-0.497	55.925	BRX+HLT
-0.170	-0.504	-0.503	26.362	BRX+HLT
0.072	-0.508	-0.507	60.305	BRX+HLT+THNDT
-0.016	-0.514	-0.515	43.776	BRX
-1.701	1.941	-6.656	62.343	BRX+MRBLT+THNDT
1.555	-0.725	-0.725	145.848	BRX+MRBLT
Difference in %*** between experimental values and those predicted by the model developed in this study				
ΔNa in %	ΔCl in %	ΔSO_4 in %	ΔΣB in %	Equilibrium Assemblage**
-0.298	-0.402	-0.273	8.326	BRX+HLT+THNDT
-0.128	-0.308	-0.308	17.643	BRX+HLT
-0.234	-0.283	-0.284	4.448	BRX+HLT
-0.502	-0.274	-0.273	-18.668	BRX+HLT
-0.252	-0.272	-0.271	1.726	BRX+HLT+THNDT
-0.399	-0.258	-0.259	-12.713	BRX
-2.991	3.341	-8.915	-15.424	BRX+MRBLT+THNDT
0.134	-0.306	-0.306	28.001	BRX+MRBLT

*Comparison was performed by running EQ3/6 calculations. In EQ3NR calculations, input compositions for total Na^+, total Cl^-, and total SO_4^{2-} are the same as the experimental values, and for total $B(OH)_4^-$ is at trace level (1×10^{-20} m). In EQ6 calculations, the above compositions are in equilibrium with sodium tetraborate (borax), and a new set of compositions for total Na^+, total Cl^-,total SO_4^{2-}, and total $B(OH)_4^-$ is obtained.
**Abbreviations for minerals: BRX, borax ($Na_2B_4O_7$•$10H_2O$); HLT, halite (NaCl); MRBLT, mirabilite (Na_2SO_4•$10H_2O$); THNDT, thenardite (Na_2SO_4).
***Difference in % is defined as, using concentrations of sodium on molal scale as an example,

$$\Delta\text{Na in \%} = 100\times\frac{m_{Na,Model} - m_{Na,Experimental}}{m_{Na,Experimental}}$$

4 CONCLUSIONS

In this analysis report, a thermodynamic model with high precision is developed for the Na^+–$B(OH)_3$–Cl^-–SO_4^{2-} system, based on new experimental data. This model is validated by independent experimental data in ternary mixtures of NaCl and Na_2SO_4. With this model, solubilities of borax in concentrated NaCl, Na_2SO_4, and NaCl+Na_2SO_4 solutions can be accurately modeled.

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