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A Thermodynamic Model for Na-Mg-$B(OH)_3$-HCO_3-CO_3-Cl-SO_4 System to High Ionic Strengths[1]

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Outline of Presentation

- Introduction
- Objectives of This Work
- Results
- Summary

INTRODUCTION

- Borosilicate glasses in which boron is a major component, are strong candidate waste forms for immobilization of high level nuclear waste (HLW). Prediction of stability of borosilicate glasses in high ionic strength solutions at elevated temperatures requires accurate knowledge of solubility and speciation of borate.
- Borate could form a relatively strong complex with Am(III). Therefore, to accurately assess the contributions of borate complexation to solubility of Am(III), a comprehensive thermodynamic model for borate species is needed.
- Both GWB and ERDA-6 brines in the Waste Isolation Pilot Plant (WIPP) have high concentrations of sodium. The interactions between Na^+ and borate are important. GWB has high concentrations of magnesium.
- $Na_2B_4O_7 \bullet 10H_2O$ (Borax) is a geologically important mineral, occurring in evaporate deposits, salt lakes, playas, hot springs, and in soils in arid regions as efflorescences.

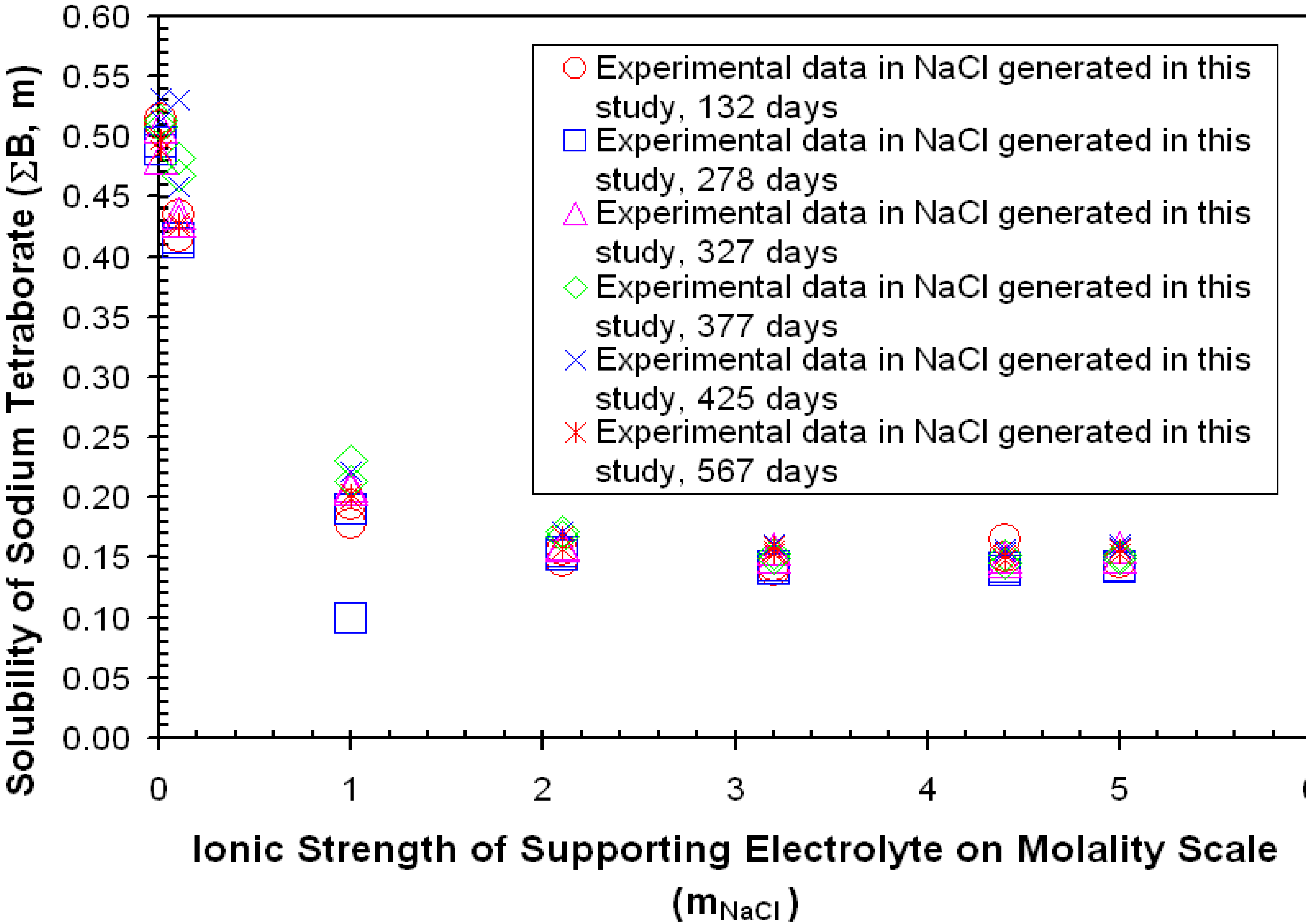
PURPOSE OF THIS STUDY

- To determine the solubility constant of sodium tetraborate ($Na_2B_4O_7 \bullet 10H_2O$), as it could be a solubility-controlling phase for borate in many environments.
- To obtain Pitzer parameters for Na^+ and borate interactions.
- To extend the borate model established at 25^oC to elevated temperatures, as the near-field environments in geological repositories for HLW and used nuclear fuel are expected to be at elevated temperatures, e.g., ~100^oC in shale, ~200^oC in salt formations.

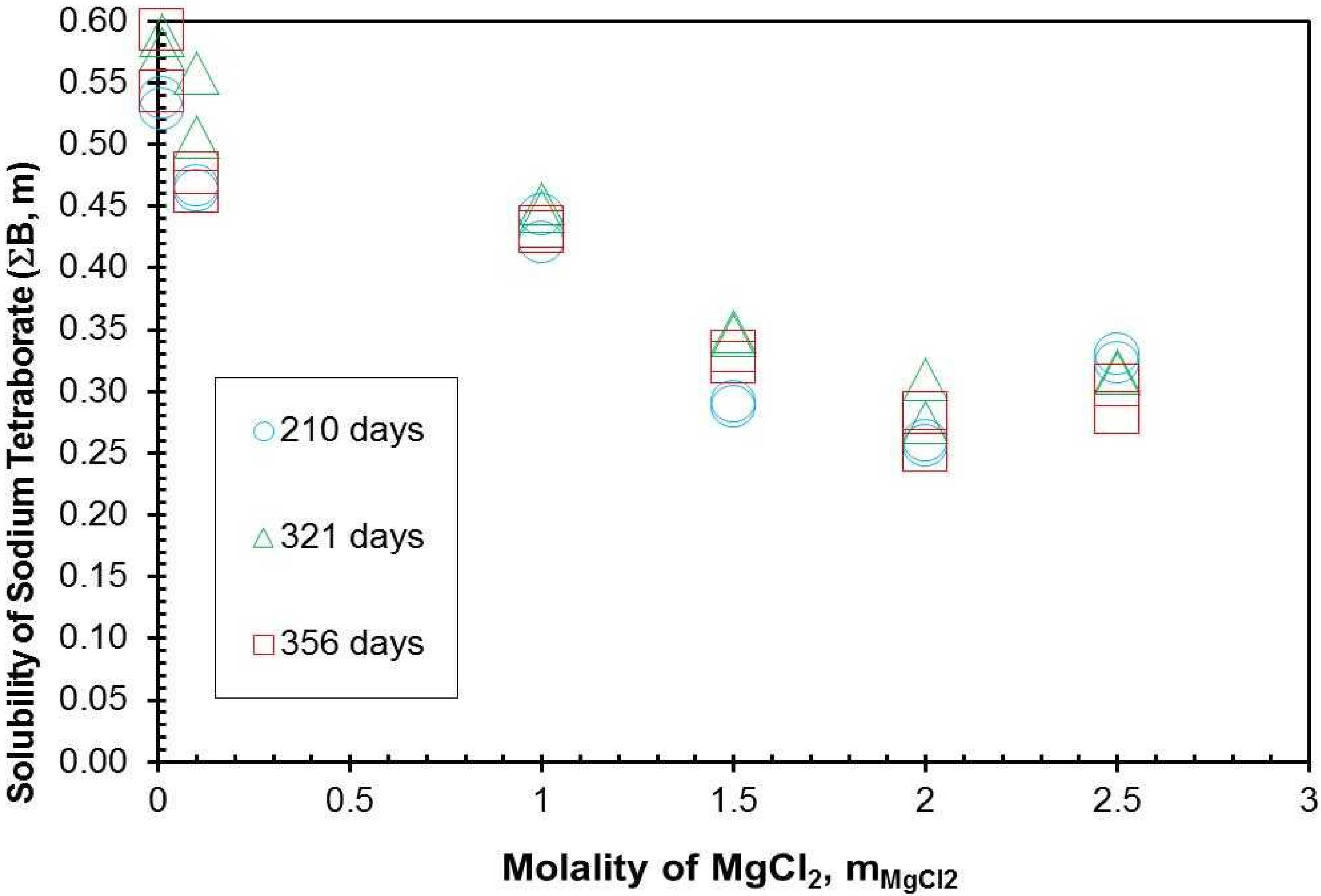
EXPERIMENTAL METHOD

- Experimental conditions: T = 22.5 ± 1.5 ^{o}C
- Starting material: sodium tetraborate from Fisher Scientific
- Undersaturation experiments
- Supporting solutions:
  - 0.010-5.0 m NaCl
  - 0.010-2.5 m $MgCl_2$
- Boron and sodium concentrations determined by using inductively coupled plasma atomic emission spectrometer (ICP-AES)
- pcH measured using pH electrode with correction factors

Experimental Results: NaCl Medium



Experimental Results: $MgCl_2$ Medium



Comparison of Results in NaCl and $MgCl_2$

- The total boron concentrations in equilibrium with $Na_2B_4O_7 \bullet 10H_2O$ in NaCl and $MgCl_2$ solutions with low ionic strengths are similar: ~0.5 m.
- The total boron concentrations in equilibrium with $Na_2B_4O_7 \bullet 10H_2O$ in NaCl and $MgCl_2$ solutions with high ionic strengths are different: ~0.15 m for NaCl; ~0.3 m for $MgCl_2$.

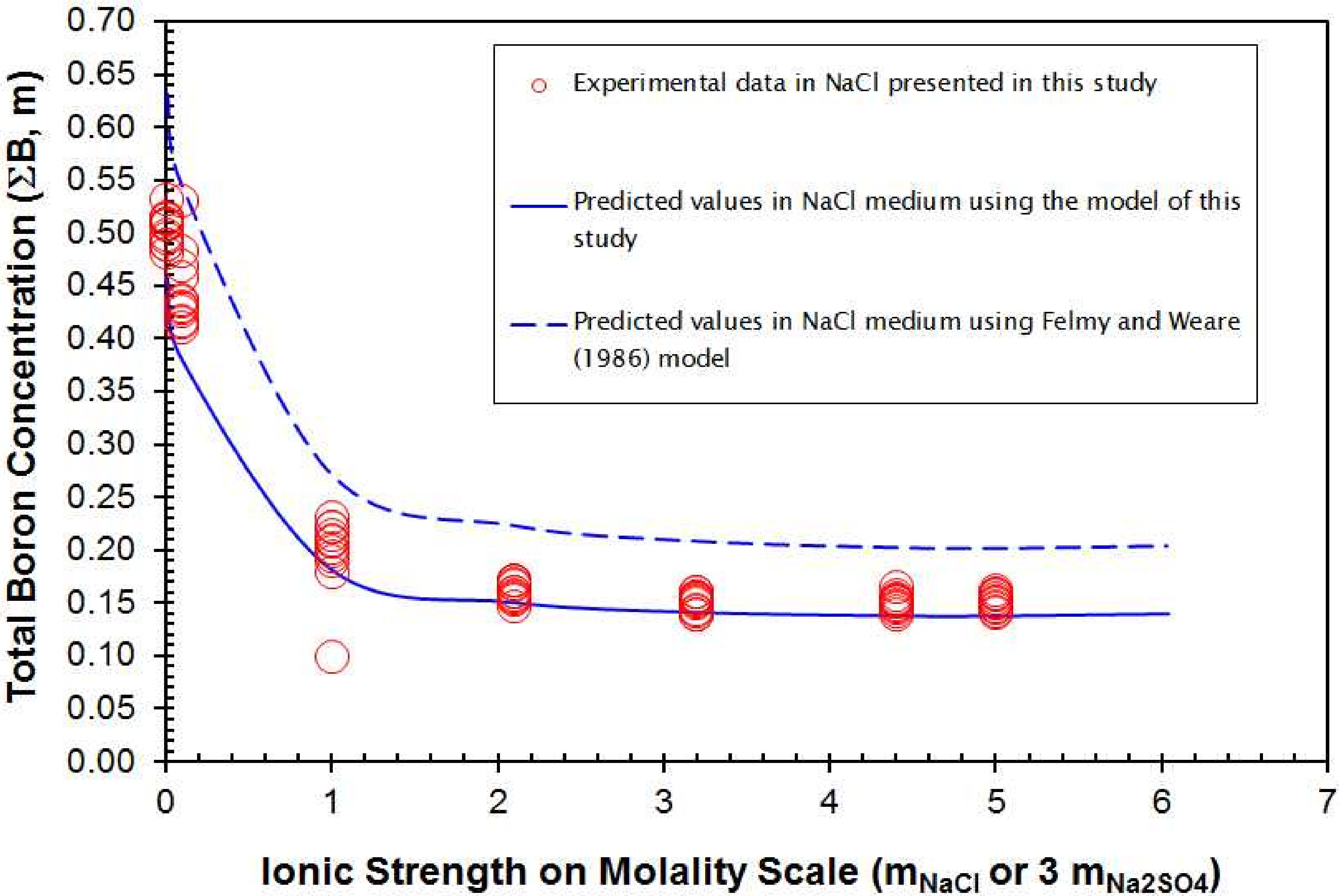
Pitzer Models

Values in red color or red boxes are revised values or additional parameters evaluated by this work

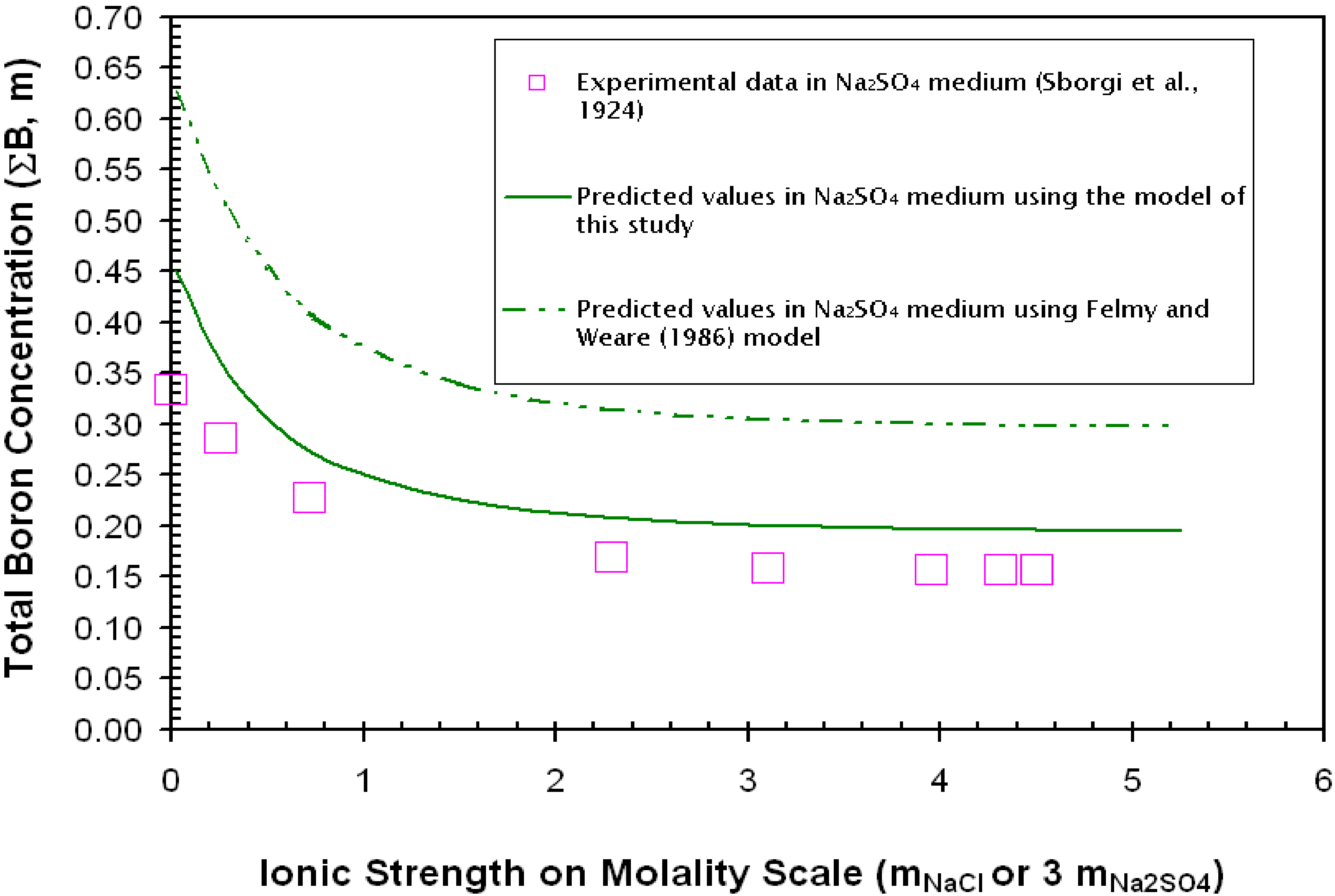
Table 1. Felmy and Weare (1986) model for the Na–$B(OH)_3$–Cl–SO_4 system

Pitzer Binary Interaction Cofficients				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Na^+	$B(OH)_4^-$	–0.0427	0.089	0.0114
Na^+	$B_3O_3(OH)_4^-$	–0.056	–0.910	
Na^+	$B_4O_5(OH)_4^{2-}$	–0.11	–0.40	
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Specis				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	Cl^-	Na^+	–0.065	–0.0073
$B(OH)_4^-$	SO_4^{-2}		–0.012 0.17 ± 0.03	
$B_3O_3(OH)_4^-$	Cl^-	Na^+	0.12	–0.024
$B_3O_3(OH)_4^-$	SO_4^{-2}		0.10	
$B_4O_5(OH)_4^{-2}$	Cl^-	Na^+	0.074	0.026
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}		0.12	0.1 ± 0.2
$B(OH)_3(aq)$	Cl^-		0.091	
$B(OH)_3(aq)$	SO_4^{-2}	Na^+	0.018	0.046
$B(OH)_3(aq)$	$B_3O_3(OH)_4^-$		–0.20	
$B(OH)_3(aq)$	Na^+		–0.097	
Equilibrium Constant for Solubility Reaction				
Reaction			log K	
$Na_2B_4O_7{\bullet}10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			–24.49 -24.80 ± 0.10	
$Na^+ + B(OH)_4^- = NaB(OH)_4(aq)$			0.25 ± 0.01 (25 °C)	
$NaB(OH)_4(aq)$	Na^+		0.093 ± 0.005	

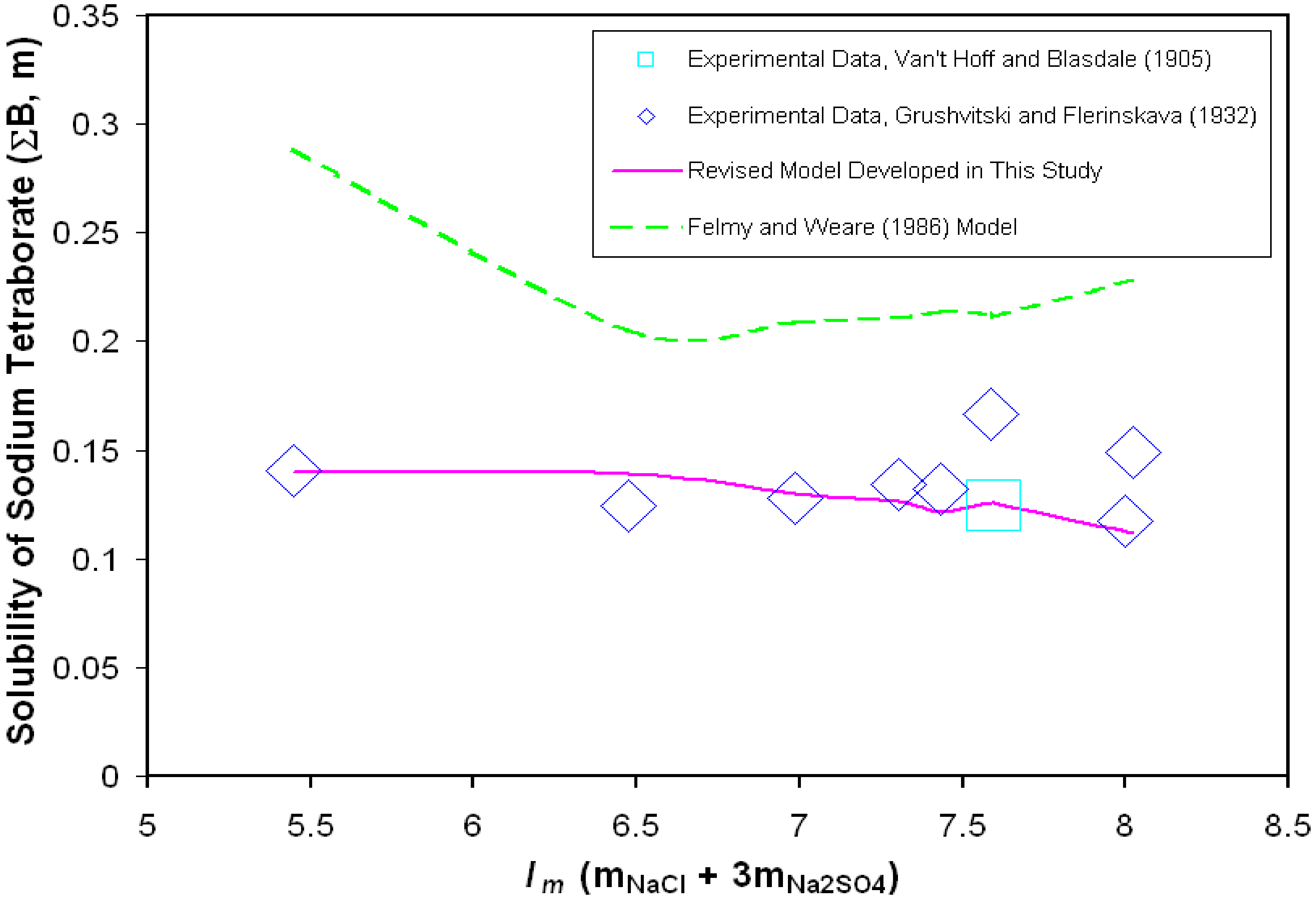
Modeling Results



Modeling Results



Validation Test



Model Extension to 100°C

- Strategy for model extension to 100°C
  - Borate species considered: $B_x(OH)^{y-}_{3x+y}$, x = 1, 2, 3, 4; y = 0, 1, 2; i.e., $B(OH)_3(aq)$, $B(OH)_4^-$, $B_2(OH)_7^-$, $B_3(OH)_{10}^-$, $B_4(OH)_{14}^{2-}$
  - Borate complex(es) considered in the Na-$B(OH)_3$-Cl-SO_4 system: $NaB(OH)_4(aq)$
- Equilibrium quotients at I_m = 1.0 m at elevated temperatures from Mesmer et al. (1972)
- Equilibrium constants at infinite dilution at elevated temperatures are obtained by this work according to the SIT model, based on log $Q_{x,y}$ from Mesmer et al. (1972).
- Assuming that the Pitzer parameters are constant over the temperature range from 25°C to 100°C

Model Extension to 100°C (cont.)

- log $K_{1,1}$ for the following reaction from Mesmer et al. (1972), $B(OH)_3 + OH^- = B(OH)_4^-$

T, °C	log $Q_{1,1}$, Mesmer et al., 1972	log $K_{1,1}$, Mesmer et al., 1972
25	4.89	4.76
50	4.32	4.19
75	3.83	3.71
100	3.42	3.31

log $Q_{1,1}$ at I_m = 1.0 m

Model Extension to 100°C (cont.)

- log $Q_{2,1}$ at I_m = 1.0 (KCl) for the following reaction from Mesmer et al. (1972),

  $$2B(OH)_3 + OH^- = B_2(OH)_7^-$$

  $$\log K_{2,1} = \log Q_{2,1} + \Delta\varepsilon \times I_m$$

  $$\Delta\varepsilon = \varepsilon(K^+, B_2(OH)_7^-) - \varepsilon(K^+, OH^-)$$

  Assuming $\varepsilon(K^+, B_2(OH)_7^-) \approx \varepsilon(Na^+, B(OH)_4^-)$

T, °C	log $Q_{2,1}$, Mesmer et al., 1972	log $K_{2,1}$, This Work
25	4.72	4.56
50	4.20	4.05
75	3.78	3.62
100	3.43	3.27

log $Q_{2,1}$ at I_m = 1.0 m

Model Extension to 100^{o}C (cont.)

- log $Q_{3,1}$ at I_m = 1.0 (KCl) for the following reaction from Mesmer et al. (1972),

  $3B(OH)_3 + OH^- = B_3(OH)_{10}^-$

  $\log K_{3,1} = \log Q_{3,1} + \Delta\varepsilon \times I_m$

  $\Delta\varepsilon = \varepsilon(K^+, B_3(OH)_{10}^-) - \varepsilon(K^+, OH^-)$

  Assuming $\varepsilon(K^+, B_3(OH)_{10}^-) \approx \varepsilon(Na^+, B(OH)_4^-)$

T, ^{o}C	log $Q_{3,1}$, Mesmer et al., 1972	log $K_{3,1}$, This Work
25	6.82	6.66
50	6.01	5.85
75	5.31	5.15
100	4.72	4.56

log $Q_{3,1}$ at I_m = 1.0 m

Model Extension to 100^{o}C (cont.)

- log $Q_{4,2}$ at I_m = 1.0 (KCl) for the following reaction from Mesmer et al. (1972),

  $4B(OH)_3 + 2OH^- = B_4(OH)_{14}^{2-}$

  $\log K_{4,2} = \log Q_{4,2} - 2D + \Delta\varepsilon \times I_m$

  $\Delta\varepsilon = \varepsilon(K^+, B_4(OH)_{14}^{2-}) - 2\times\varepsilon(K^+, OH^-)$

  Assuming $\varepsilon(K^+, B_4(OH)_{14}^{2-}) \approx \varepsilon(K^+, SO_4^{2-})$

  $D = A_\gamma * \sqrt{I_m}/(1+1.5\sqrt{I_m})$

T, ^{o}C	log $Q_{4,2}$, Mesmer et al., 1972	log $K_{4,2}$, This Work
25	12.62	11.98
50	10.77	10.10
75	9.28	8.59
100	8.09	7.37

log $Q_{4,2}$ at I_m = 1.0 m

Summary

In this study, an accurate thermodynamic model has been developed for the Na-$B(OH)_3$-Cl-SO_4 system

- The revised model incorporates a revised log K for sodium tetraborate, which is -24.80.
- The revised model contains the aqueous complex, $NaB(OH)_4(aq)$.
- The revised model includes the lambda parameter for Na^+—$NaB(OH)_4(aq)$ interaction, the psi parameter for $B_4O_5(OH)_4^{2-}$—SO_4^{2-}—Na^+ interaction, and the revised value for the $B(OH)_4^-$—SO_4^{2-} interaction.
- The revised model is validated by independent, experimental solubility data on sodium tetraborate in NaCl + Na_2SO_4 solutions up to ionic strength of 8 m.
- We are extending the borate model to elevated temperatures.