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Updating Thermodynamic Model for the Waste Isolation Pilot Plant (WIPP)

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U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

Outline of Presentation

- The WIPP Thermodynamic Model
  - Major Ion Chemistry
  - Borate Chemistry
  - Actinide Chemistry
- Updates for the WIPP Thermodynamic Model
  - Updates on Borate Chemistry
  - Updates on Lead and Iron Chemistry
  - Updates on Actinide Chemistry

WIPP Thermodynamic Database

- The WIPP thermodynamic database at 25°C uses the Pitzer model for calculation of activity coefficients of aqueous species.
- Major Ion Chemistry
  - Harvie-Moller-Weare Model (Harvie et al., 1984): Na-K-H-Ca-Mg-Cl-SO_4-CO_2-H_2O
- Borate Chemistry
  - Felmy-Weare Model (Felmy & Weare, 1986): Na-K-H-Ca-Mg-Cl-SO_4-CO_2-$B(OH)_3$-H_2O
- Actinide Chemistry
  - Oxidation State Analogs
    - ✓ Am(III) Model: Am(III), Pu(III)
    - ✓ Th(IV) Model: Np(IV), Pu(IV), Th(IV)
    - ✓ Np(V) Model: Np(V)
    - ✓ U(VI) Model: U(VI)
  - Sources
    - ✓ Am(III) Model: Pacific Northwest National Laboratory (PNNL), funded by Sandia National Laboratories (SNL)
    - ✓ Th(IV) Model: PNNL, funded by SNL
    - ✓ Np(V) Model: Lawrence Berkeley National Laboratory (LBNL), funded by SNL
    - ✓ Organic Species: Florida State University (FSU), funded by SNL
    - ✓ U(VI) Model: Set to 10^{-3} M by EPA
- FMT database FMT_050405.CHEMDAT migrated to EQ3/6 data0.fmt.
- For details about oxidation state analog models and organic species, please attend HiTAC for my presentation "Extension Of The WIPP Actinide Oxidation State Analog Models To Elevated Temperatures Under Reducing Conditions"

Updating Borate Model

- The need to update borate model:
  - Recent experimental work indicates that borate could form a relatively strong complex with Nd(III) (log $\beta_1 = 4.99 \pm 0.30$) at 25°C (Borkowski et al., 2010), an analog to Am(III).
  - 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 in the WIPP have boron concentrations on an order of ~0.1-0.2 m.
  - The objective is to revise the Felmy & Weare model to accurately describe the interactions between borate and major ions in the WIPP brines.

Borkowski, M., Richmann, M., Reed, D.T., and Xiong, Y.-L., 2010. Complexation of Nd(III) with tetraborate ion and its effect on actinide(III) solubility in WIPP brine. Radiochimica Acta 98, 577-582.

An Example of Updating Borate Model

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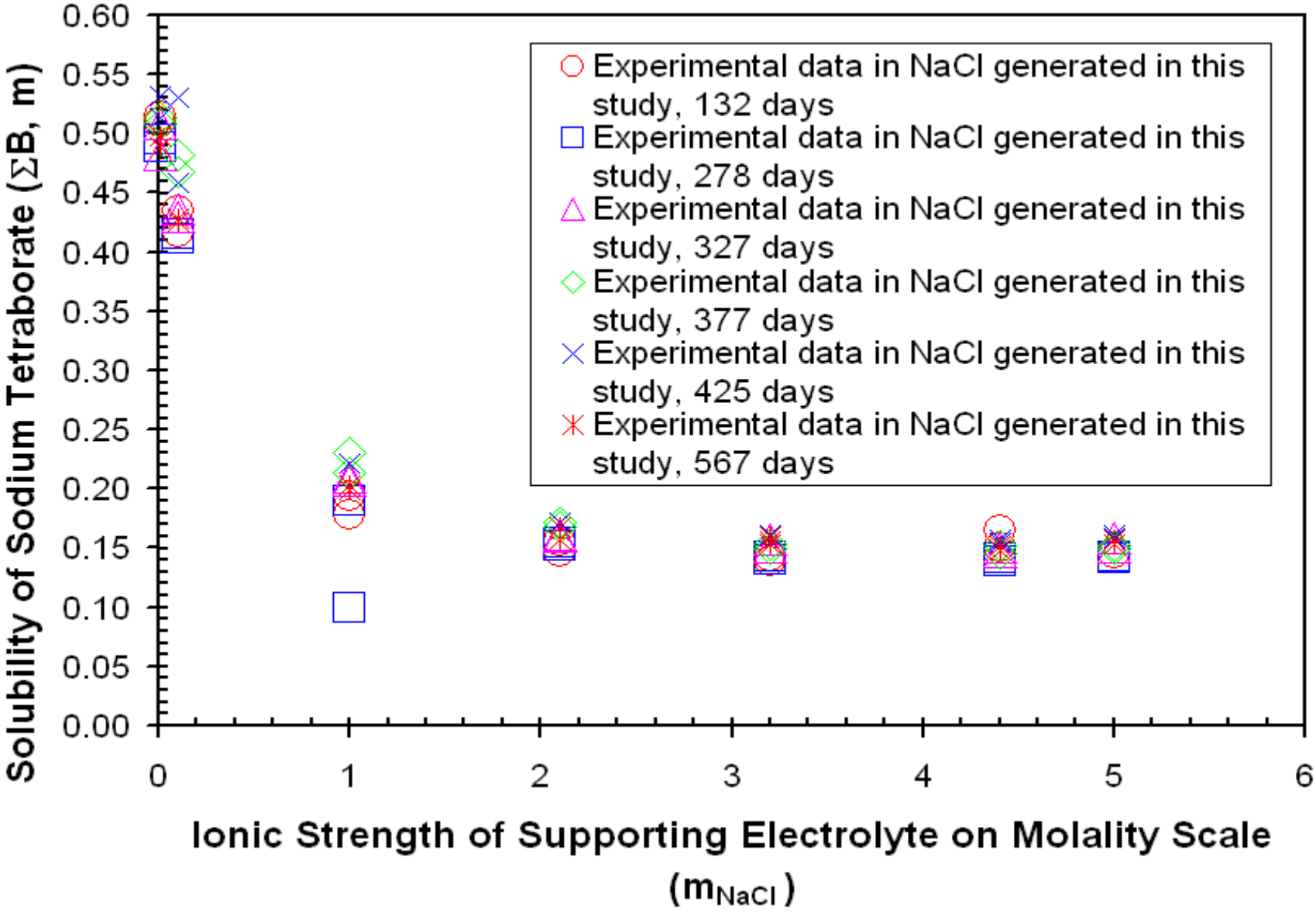
- $Na–B(OH)_3–Cl–SO_4$ system
- Experimental data used to update this system
  - Experimental solubility data of sodium tetraborate in NaCl solutions produced at Carlsbad Facility of SNL
  - Literature solubility data of sodium tetraborate in Na_2SO_4 solutions

Experimental Section

- Experimental conditions: T = 22.5 ± 0.5 °C
- Starting material: sodium tetraborate ($Na_2B_4O_7 \bullet 10H_2O$) from Fisher Scientific
- Undersaturation experiments
- Supporting solutions:
  - 0.010-5.0 m NaCl
- 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



Pitzer Model

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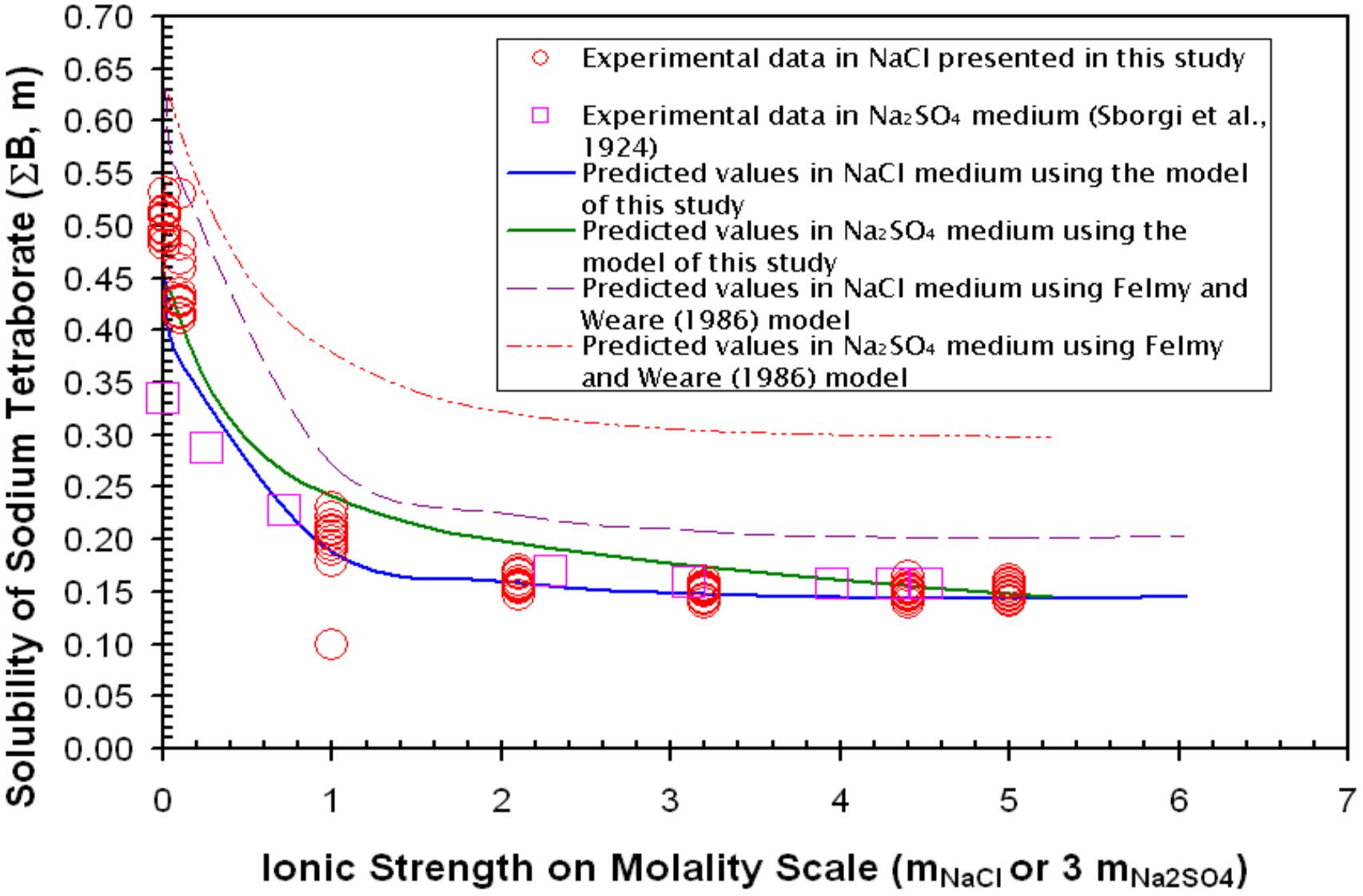
Table 2. The revised thermodynamic model for the Na–$B(OH)_3$–Cl–SO_4 system developed in this study*.

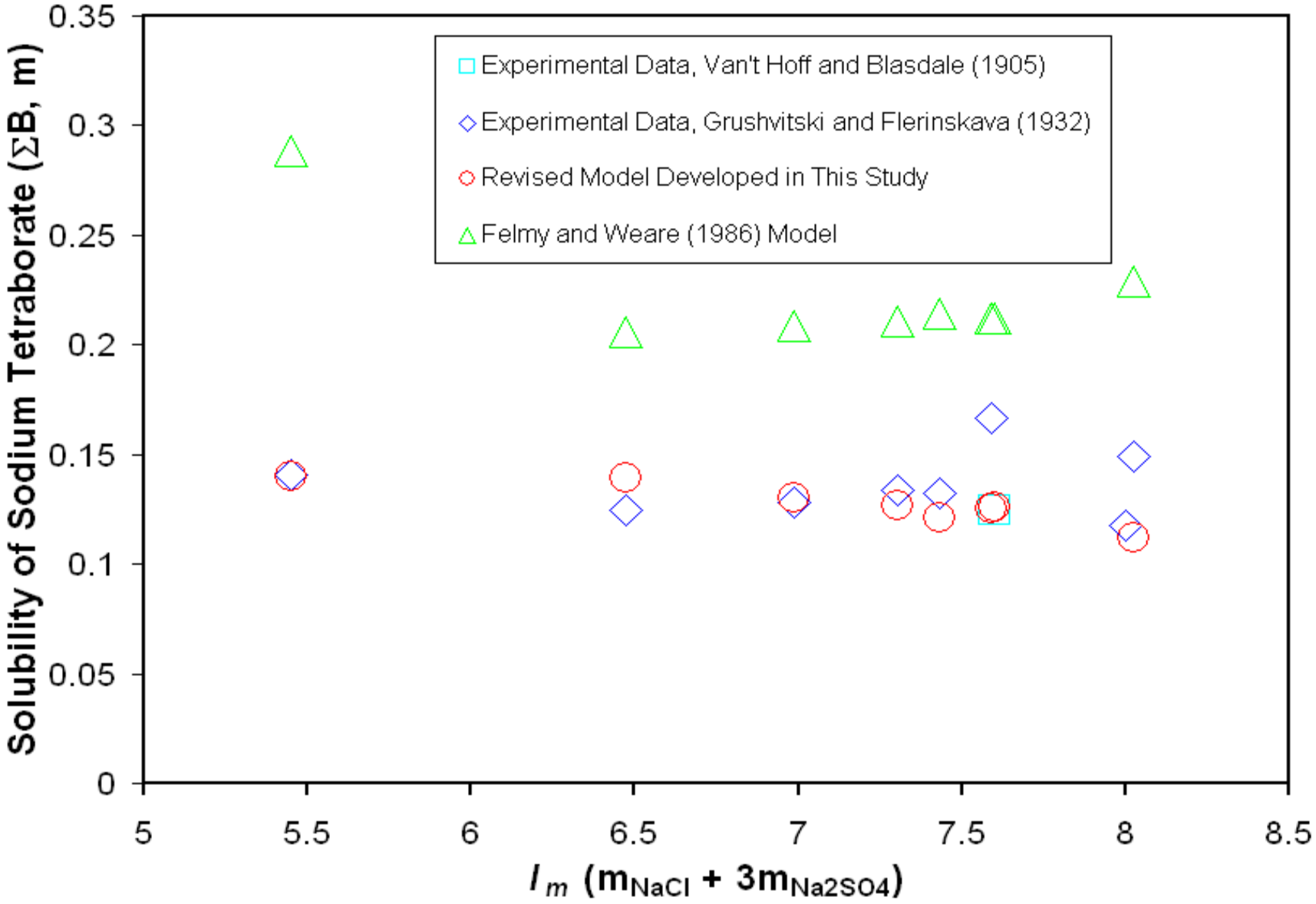
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	SO_4^{-2}		0.1697	
$NaB(OH)_4(aq)$	Na^+		0.09192	
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}	Na^+		0.096
Equilibrium Constants for Solubility and Complex Formation Reactions				
Reaction			log *K* or log β_1 at 25 °C unless otherwise noted	
$Na_2B_4O_7 \cdot 10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			-24.88 ± 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.

Modeling Results



Validation Test



Updating Lead Chemical Model

- In the current WIPP thermodynamic database, there are no lead species.
- As lead is already present in the waste stream, and significant inventories of lead are to be present as shielded containers in the WIPP, lead chemistry will be important.
- For instance, Pb^{2+} will compete for soluble citrate, EDTA, and oxalate, lowering concentrations of chelating agents available for complexation with actinides.
- The objective is to develop an accurate model to describe the interactions between lead species and important species including organic ligands in the WIPP brines.

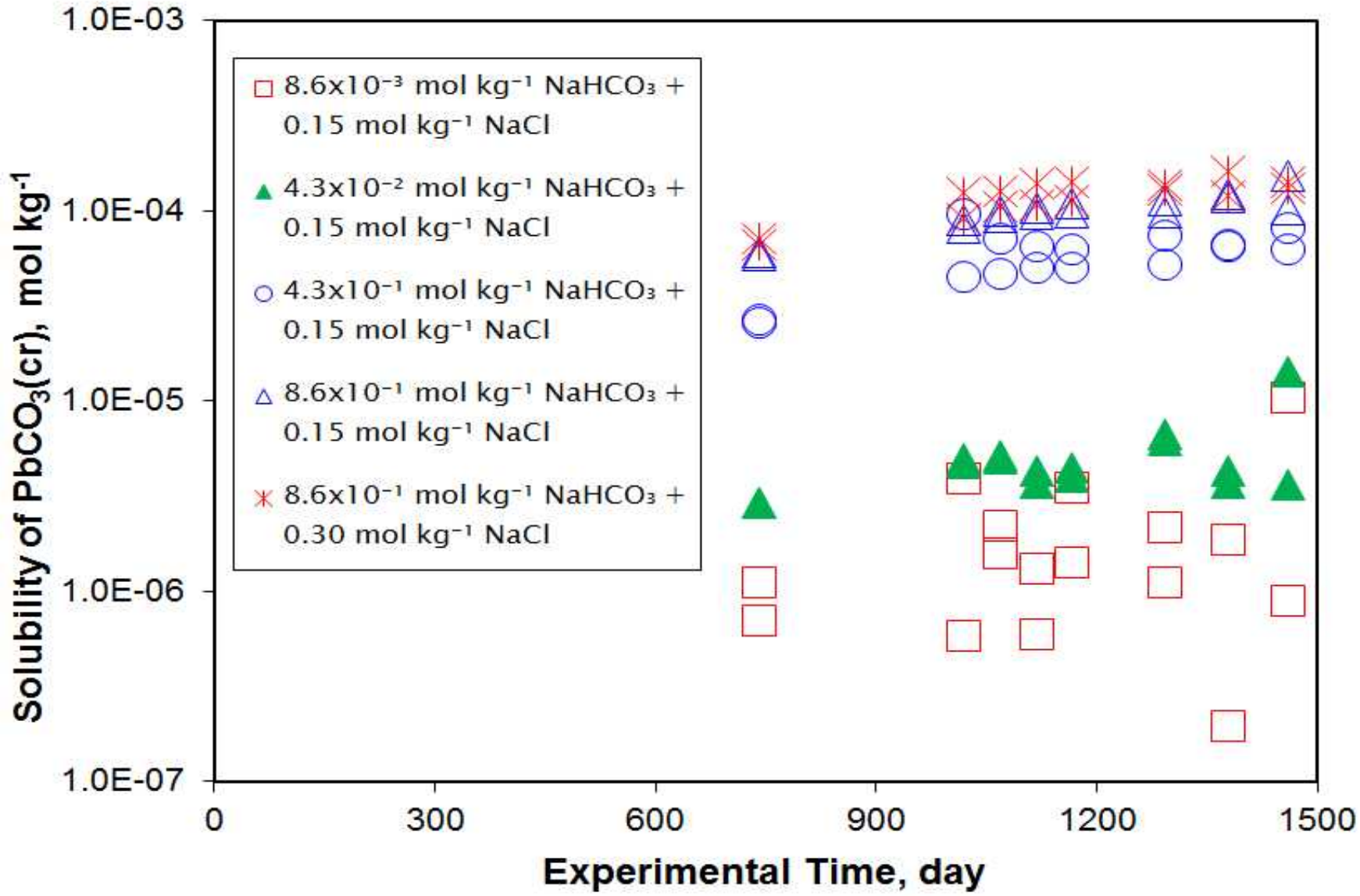
An Example of Updating Lead Model

- Na^{+}–Pb^{2+}–Cl^{-}–HCO_3^{-}–CO_3^{2-} system
- Experimental data used to update this system
  - Experimental solubility data of lead carbonate, $PbCO_3$(cr), cerussite, in mixtures of NaCl+$NaHCO_3$ and $NaHCO_3$+Na_2CO_3, produced at Carlsbad Facility of SNL
  - Literature solubility data of lead carbonate for validation tests

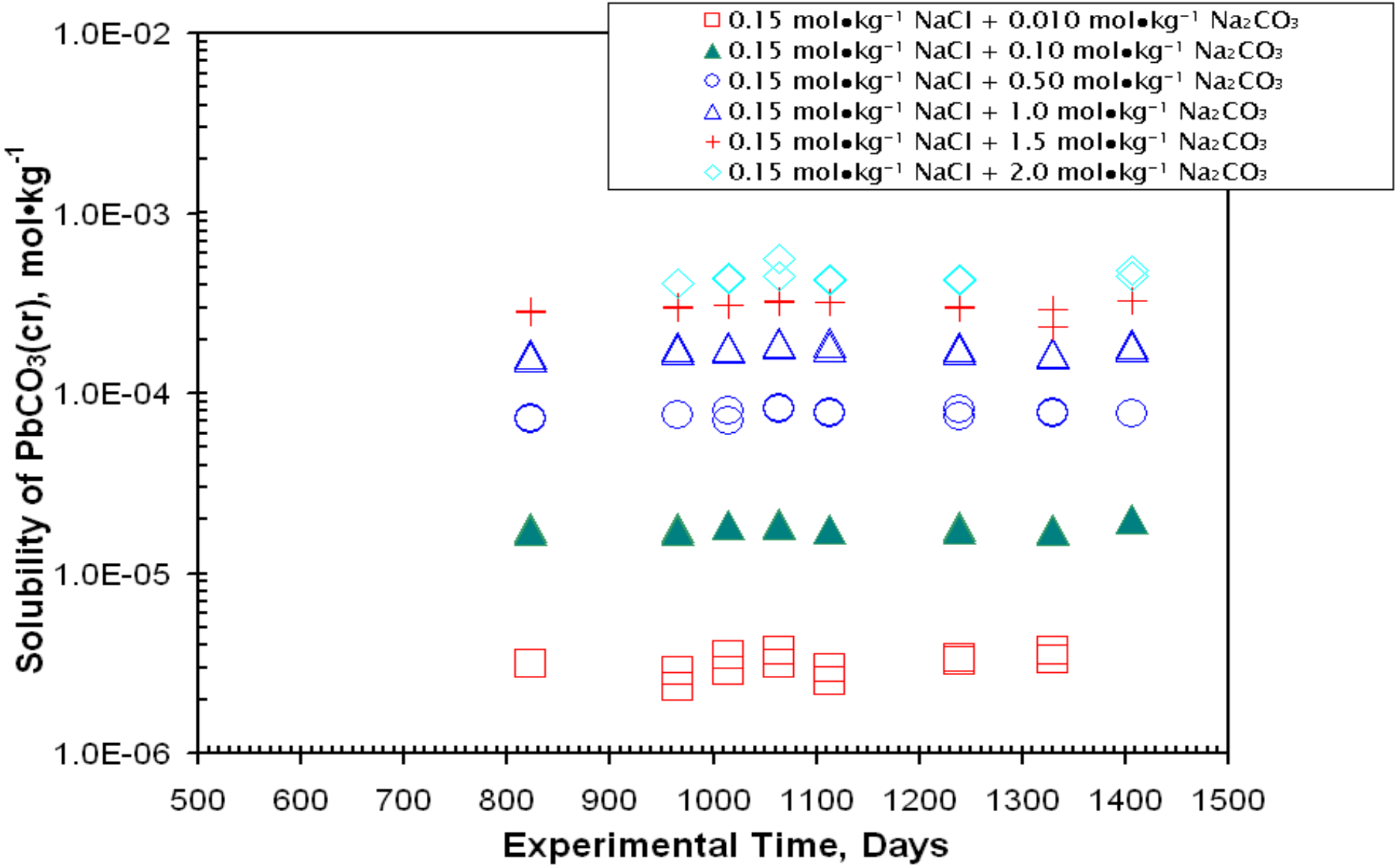
Experimental Section

- Experimental conditions: T = 22.5 ± 0.5 °C
- Starting material: Starting material: lead carbonate ($PbCO_3$) from Alfa Aesar, 99.999% purity
- Undersaturation experiments
- Supporting solutions:
  - $NaCl+NaHCO_3$ with total ionic strengths ranging from 0.159 to 1.16 $mol \cdot kg^{-1}$
  - $NaHCO_3 + Na_2CO_3$ with total ionic strengths ranging from 0.208 to 5.16 $mol \cdot kg^{-1}$
- Lead concentrations determined by using inductively coupled plasma atomic emission spectrometer (ICP-AES)
- pcH measured using pH electrode with correction factors

Experimental Results



Experimental Results



Pitzer Model

Table 1. Equilibrium constants at infinite dilution at 25°C and 1 bar for the Na^+—Pb^{2+}—Cl^-—HCO_3^-—CO_3^{2-} system

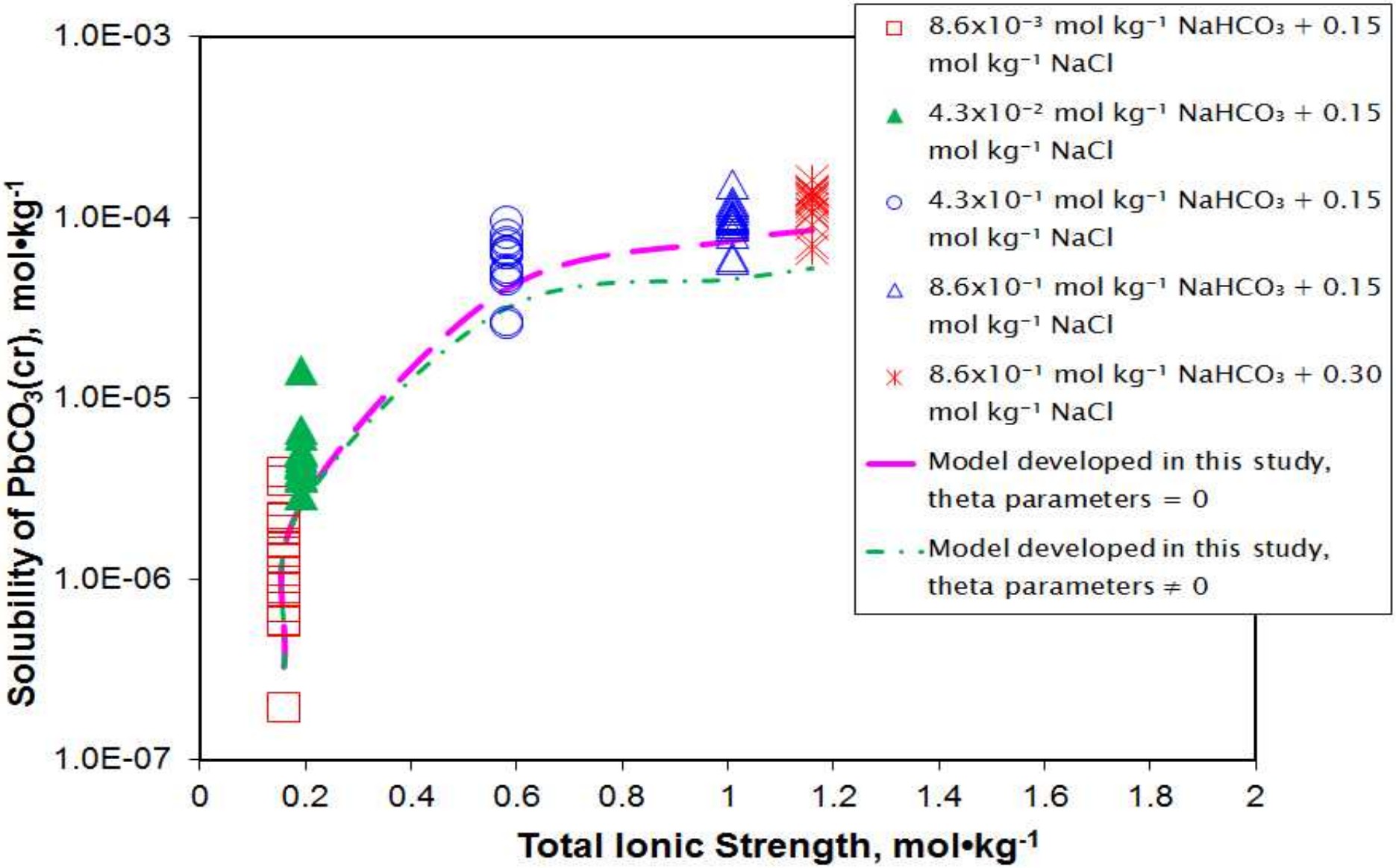
Reactions	log K_s^o, log β_1^o, log β_2^o or log β_{11}^o	Reference and Remarks
$PbCO_3(cr) = Pb^{2+} + CO_3^{2-}$	-13.75 ± 0.15 (2σ) [A]	This study, based on solubility of $PbCO_3$(cr) in the mixtures of $NaHCO_3$ and NaCl and in the mixtures of $NaHCO_3$ and Na_2CO_3
$Pb^{2+} + CO_3^{2-} = PbCO_3(aq)$	6.87 ± 0.09 (2σ)	Woosley and Millero (2013)
$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$	10.41 ± 0.18 (2σ)	Easley and Byrne (2011)
$Pb^{2+} + CO_3^{2-} + Cl^- = Pb(CO_3)Cl^-$	7.23 ± 0.74 (2σ)	Woosley and Millero (2013)

Pitzer Model (continued)

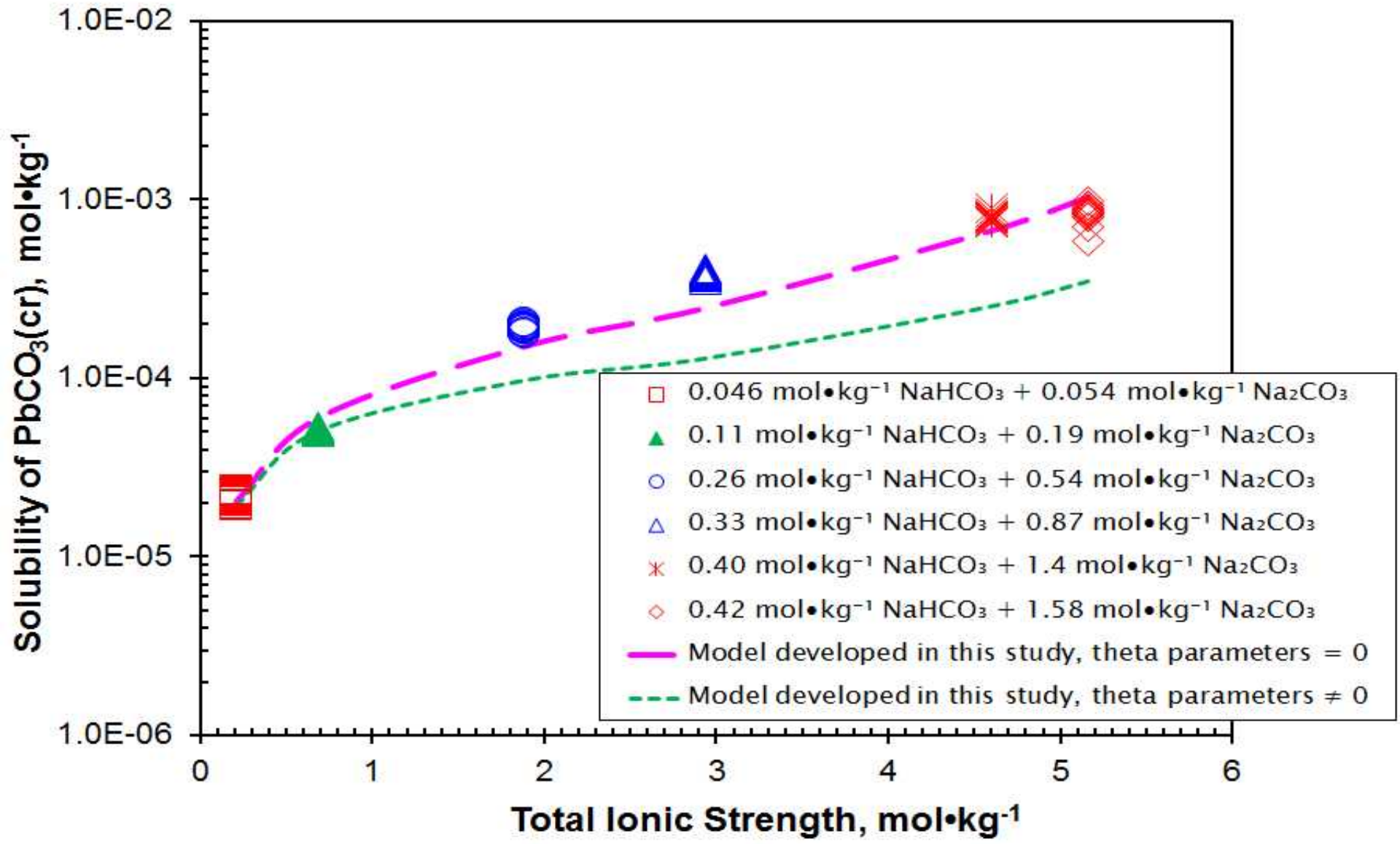
Table 2. Pitzer interaction parameters at 25°C and 1 bar for the Na^+—Pb^{2+}—Cl^-—HCO_3^-—CO_3^{2-} system

Pitzer Binary Interaction Parameters					
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Reference
Na^+	$Pb(CO_3)_2^{2-}$	0.4168	1.74	–0.3161	This study
Na^+	$Pb(CO_3)Cl^-$	0.2419	0.29	–0.1802	This study
Pitzer Mixing Interaction Parameters and Interaction Parameters Involving Neutral Species					
Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	ζ_{ijk}	Reference
HCO_3^-	$Pb(CO_3)_2^{2-}$		0.2956		This study, Model I
CO_3^{2-}	$Pb(CO_3)_2^{2-}$		0.2707		This study, Model I
HCO_3^-	$Pb(CO_3)_2^{2-}$		0		This study, Model II
CO_3^{2-}	$Pb(CO_3)_2^{2-}$		0		This study, Model II
Cl^-	$PbCO_3(aq)$		–0.02		Woosley and Millero (2013)
Na^+	$PbCO_3(aq)$	Cl^-	0	–0.145	Woosley and Millero (2013)

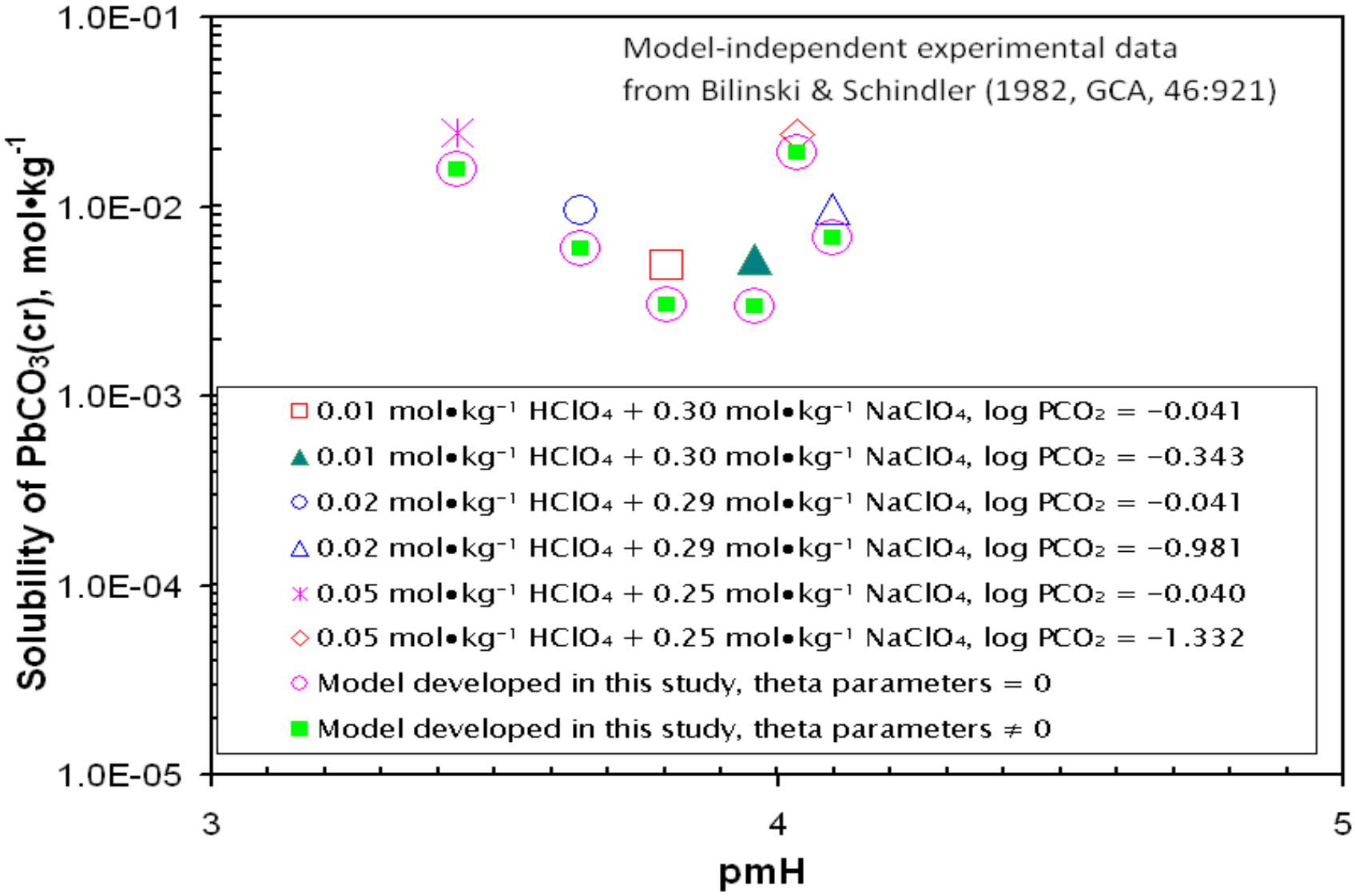
Model Verification



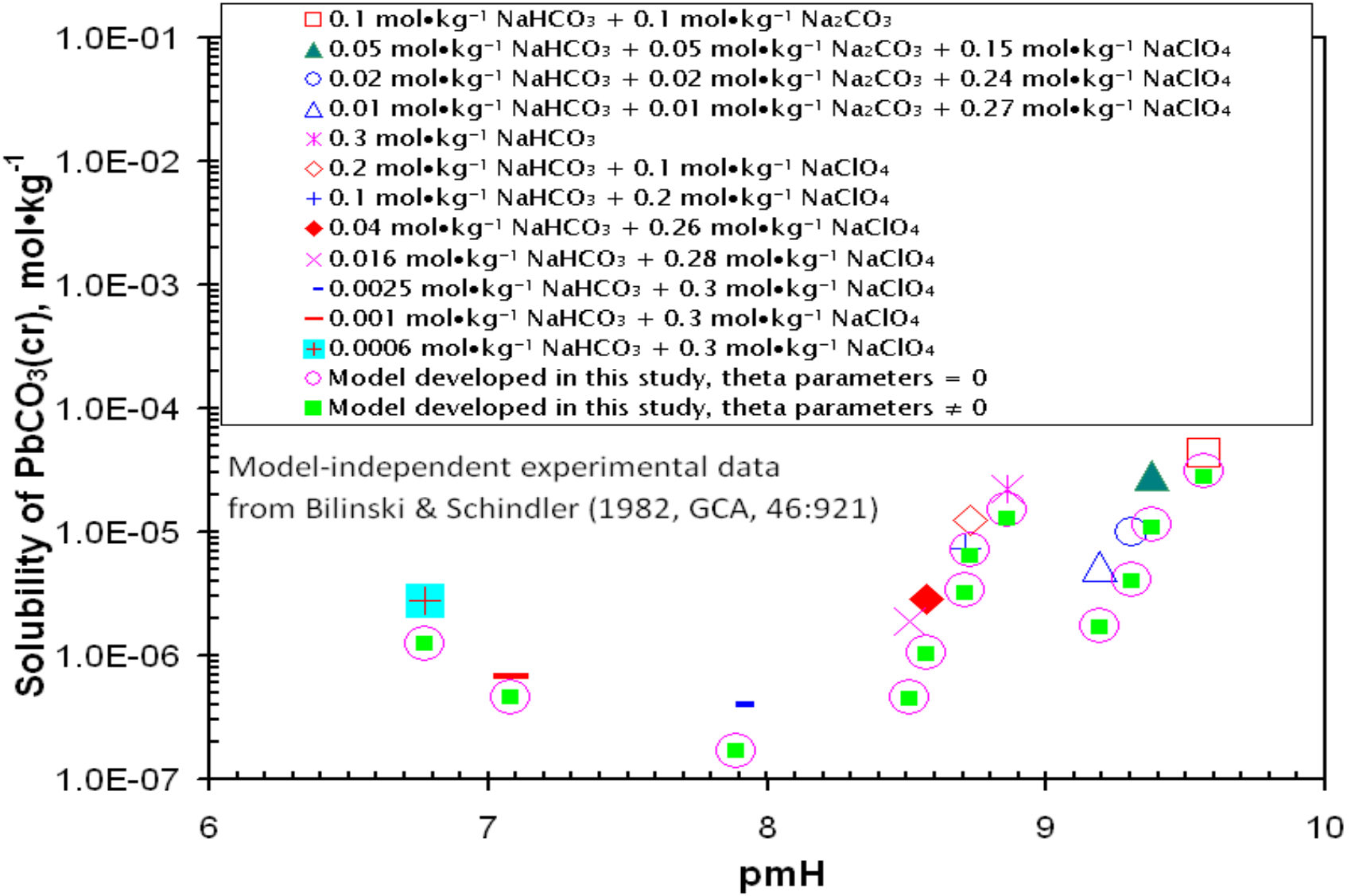
Model Verification (continued)



Model Validation



Model Validation (continued)



Updating Iron Chemical Model

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- In the current WIPP thermodynamic database, there are no iron species.
- As iron is already present in the waste stream, and significant inventories of iron are to be present as waste containers in the WIPP, iron chemistry will be important.
- For instance, Fe^{2+} will compete for soluble citrate, EDTA, and oxalate, lowering concentrations of chelating agents available for complexation with actinides.
- The objective is to develop an accurate model to describe the interactions between iron species and important species including organic ligands in the WIPP brines.

An Example of Updating Iron Model

- Please attend the talk given by my colleague from Sandia National Laboratories.

Updating Am(III) Model

- Previous model was developed in the ionic strength range from 0.3 m to 5.0 m in NaCl solutions.
- Since the Recertification of the WIPP in 2009 (CRA-2009), new experimental data in the ionic strength range from 0.10 m to 6.60 m in $NaClO_4$ solutions have been produced at the Choppin Group at Florida State University (e.g., Thakur, Xiong, Borkowski, and Choppin, 2014).

Thakur, P., Xiong, Y.-L., Borkowski, M., and Choppin, G.R., 2014, Improved thermodynamic model for interaction of EDTA with trivalent actinides and lanthanide to ionic strength of 6.60 m. Geochimica et Cosmochimica Acta, 133:299-312.

An Example of Updating Am(III) Model

- Na-H-Am(III)-Cm(III)-Eu(III)-Cl-ClO_4-EDTA System
- The materials for the following presentation are from Thakur, Xiong, Borkowski and Choppin (2014), which is the collaborative work between Carlsbad Environment Monitoring and Research Center (CEMRC) and Sandia National Laboratories.
  Dr. Thakur is a research scientist at CEMRC.

Table 4. Binary and Ternary Pitzer parameters for Am^{3+}, Cm^{3+} and Eu^{3+} complexation with EDTA used and calculated in the present work.

Binary Interaction Parameters					
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{Φ}	Remarks
Na^+	H_3EDTA^-	−0.2345	0.29	0.059	Choppin et al. (2001)
Na^+	H_3EDTA^-	−0.2262	0.29	0.059	This study, simultaneously fitting of experimental data in both $NaClO_4$ and NaCl.
Na^+	H_2EDTA^{2-}	−0.1262	1.74	0.054	Choppin et al. (2001)
Na^+	H_2EDTA^{2-}	−0.1176	1.74	0.054	This study, simultaneously fitting of experimental data in both $NaClO_4$ and NaCl.
Na^+	$HEDTA^{3-}$	0.5458	5.22	−0.048	Choppin et al. (2001)
Na^+	$HEDTA^{3-}$	0.5908	5.22	−0.048	This study, simultaneously fitting of experimental data in both $NaClO_4$ and NaCl.
Na^+	$EDTA^{4-}$	1.016	11.6	0.001	Choppin et al. (2001).
Na^+	$EDTA^{4-}$	1.087	11.6	0.001	This study, simultaneously fitting of experimental data in both $NaClO_4$ and NaCl.
Na^+	ClO_4^-	0.0554	0.2755	−0.00118	Pitzer (1991).
Na^+	$Am(EDTA)^-$	−0.2239	0.29	0.002	Choppin et al. (2001), fitting data in NaCl.
Na^+	$Am(EDTA)^-$	0.4372	0.29	−0.01303	This study, fitting data in $NaClO_4$ for μ^o/RT of $Am(EDTA)^-$ and $\beta^{(0)}$ of Na^+-$Am(EDTA)^-$
Na^+	$Am(EDTA)^-$	0.4372	−0.6794	−0.01303	This study, simultaneously fitting data in both NaCl and $NaClO_4$ for μ^o/RT of $Am(EDTA)^-$ and $\beta^{(1)}$ of Na^+-$Am(EDTA)$
Na^+	$Cm(EDTA)^-$	0.3791	0.29	−0.01303	This study
Na^+	$Eu(EDTA)^-$	0.4423	0.29	−0.01303	This study
H^+	ClO_4^-	0.1747	0.2931	0.00819	Pitzer (1991)
Am^{3+}	ClO_4^-	0.800	5.35	−0.0048	Felmy et al., (1990)
Am^{3+}	Cl^-	0.5856*	5.6*	−0.0166*	Konnecke et al., (1997)
Ternary Interaction Parameters					
Species *i*	Species *j*	Species *k*	θ_{ij}	ψ_{ijk}	
Na^+	H^+	ClO_4^-	0.036	−0.016	Neck et al., (1995)
Na^+	Am^{3+}		0.100		Fanghänel and Kim (1998)

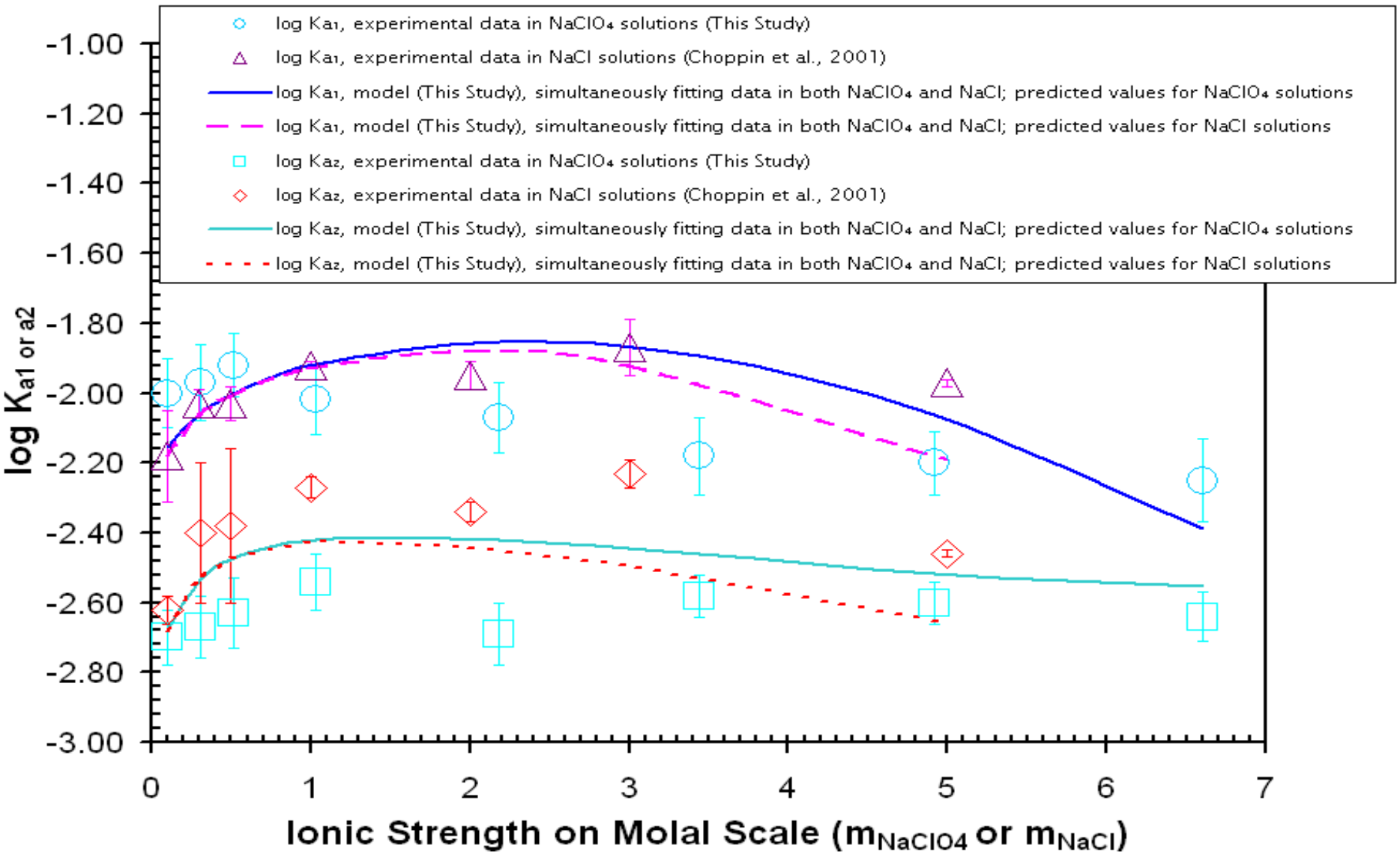
*Analogs for the interaction parameters for Am^{3+}-Cl^-.

Table 5
Thermodynamic dissociation or formation constants (infinite dilution reference state) at 25 °C and 1 bar.

Dissociation or formation reaction	$\log K_a$ or $\log \beta_{101}$	μ°/RT for aqueous complexes [A]	References and remarks
$H_4EDTA \leftrightarrows H^+ + H_3EDTA^-$	-2.40 ± 0.17	5.53 ± 0.39 (2σ) for H_3EDTA^-	This study, simultaneously fitting data both in an NaCl medium from Choppin et al. (2001) and in an $NaClO_4$ medium from this work
$H_3EDTA^- \leftrightarrows H^+ + H_2EDTA^{2-}$	-3.13 ± 0.19	12.74 ± 0.44 (2σ) for H_2EDTA^{2-}	This study, simultaneously fitting data both in an NaCl medium from Choppin et al. (2001) and in an $NaClO_4$ medium from this work
$H_2EDTA^{2-} \leftrightarrows H^+ + HEDTA^{3-}$	-6.85 ± 0.07	28.52 ± 0.17 (2σ) for $HEDTA^{3-}$	This study, simultaneously fitting data both in an NaCl medium from Choppin et al. (2001) and in an $NaClO_4$ medium from this work
$HEDTA^{3-} \leftrightarrows H^+ + EDTA^{4-}$	-10.86 ± 0.08	53.53 ± 0.18 (2σ) for $EDTA^{4-}$	This study, simultaneously fitting data both in an NaCl medium from Choppin et al. (2001) and in an $NaClO_4$ medium from this work
$Am^{3+} + EDTA^{4-} \leftrightarrows Am(EDTA)^-$	18.97	−232.324	Choppin et al. (2001); uncertainties not evaluated
$Am^{3+} + EDTA^{4-} \leftrightarrows Am(EDTA)^-$	20.55 ± 0.18 (2σ)	-235.48 ± 0.43 (2σ)	This study, fitting data in $NaClO_4$ medium from this work, using auxiliary parameters for EDTA acid from this work
$Am^{3+} + EDTA^{4-} \leftrightarrows Am(EDTA)^-$	20.05 ± 0.40 (2σ)	-234.33 ± 0.90 (2σ)	This study, simultaneously fitting data both in NaCl medium from Choppin et al. (2001) and in $NaClO_4$ medium from this work using auxiliary parameters for EDTA acid from this work
$Cm^{3+} + EDTA^{4-} \leftrightarrows Cm(EDTA)^-$	20.43 ± 0.20 (2σ)	-233.86 ± 0.46 (2σ)	This study, fitting data in $NaClO_4$ medium using auxiliary parameters for EDTA acid from this work
$Eu^{3+} + EDTA^{4-} \leftrightarrows Eu(EDTA)^-$	20.65 ± 0.19 (2σ)	-225.61 ± 0.44 (2σ)	This study, fitting data in $NaClO_4$ medium using auxiliary parameters for EDTA acid from this work

[A] The standard dimensionless chemical potentials are consistent with the auxiliary μ°/RT of 0 for H_4EDTA and H^+ from Choppin et al. (2001); μ°/RT of −241.694 for Am^{3+} from Fuger and Oetting (1976); μ°/RT of −240.357 for Cm^{3+} from Fuger and Oetting (1976); and μ°/RT of −231.602 for Eu^{3+} from Haynes and Lide (2011).

Model Verification



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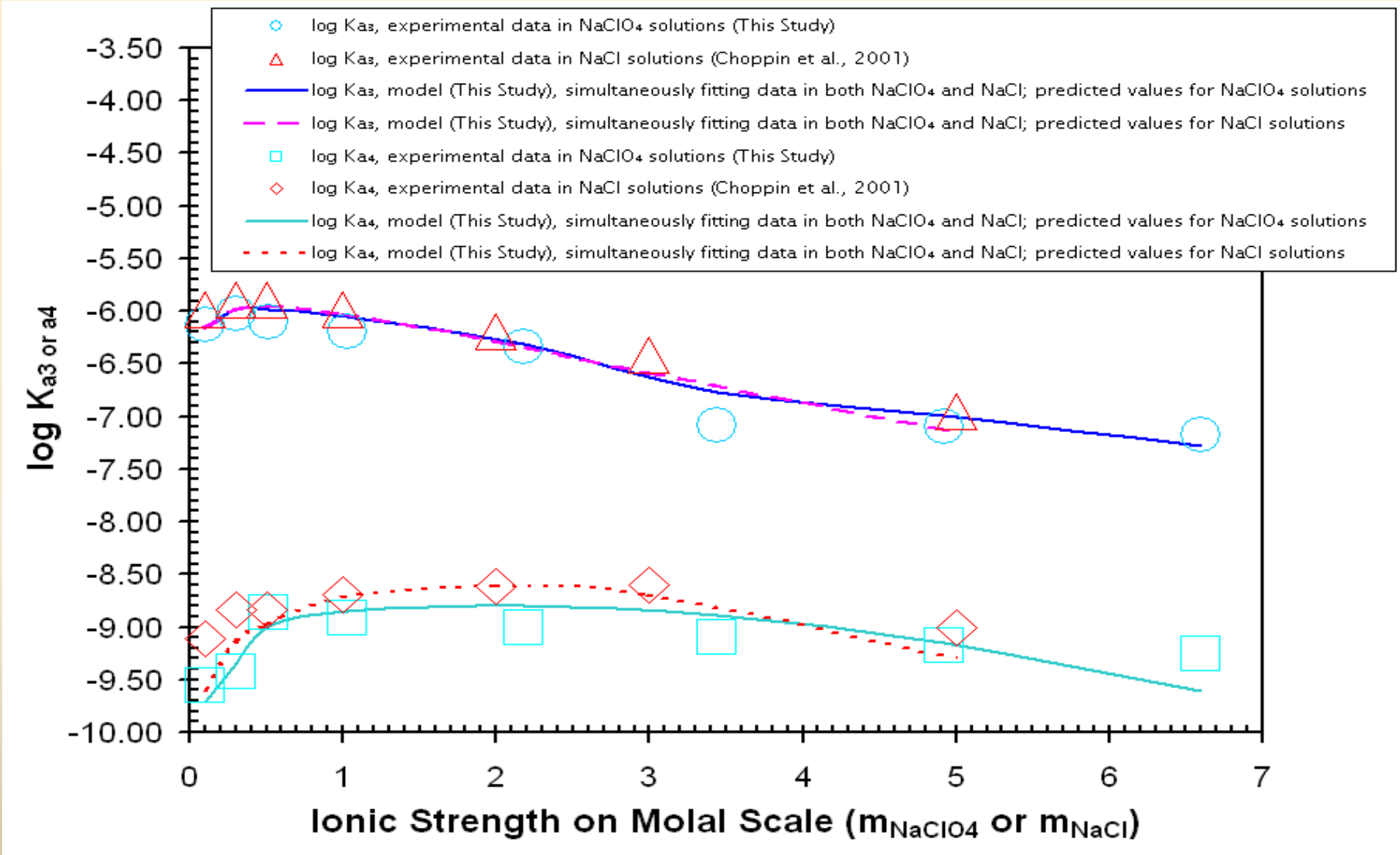

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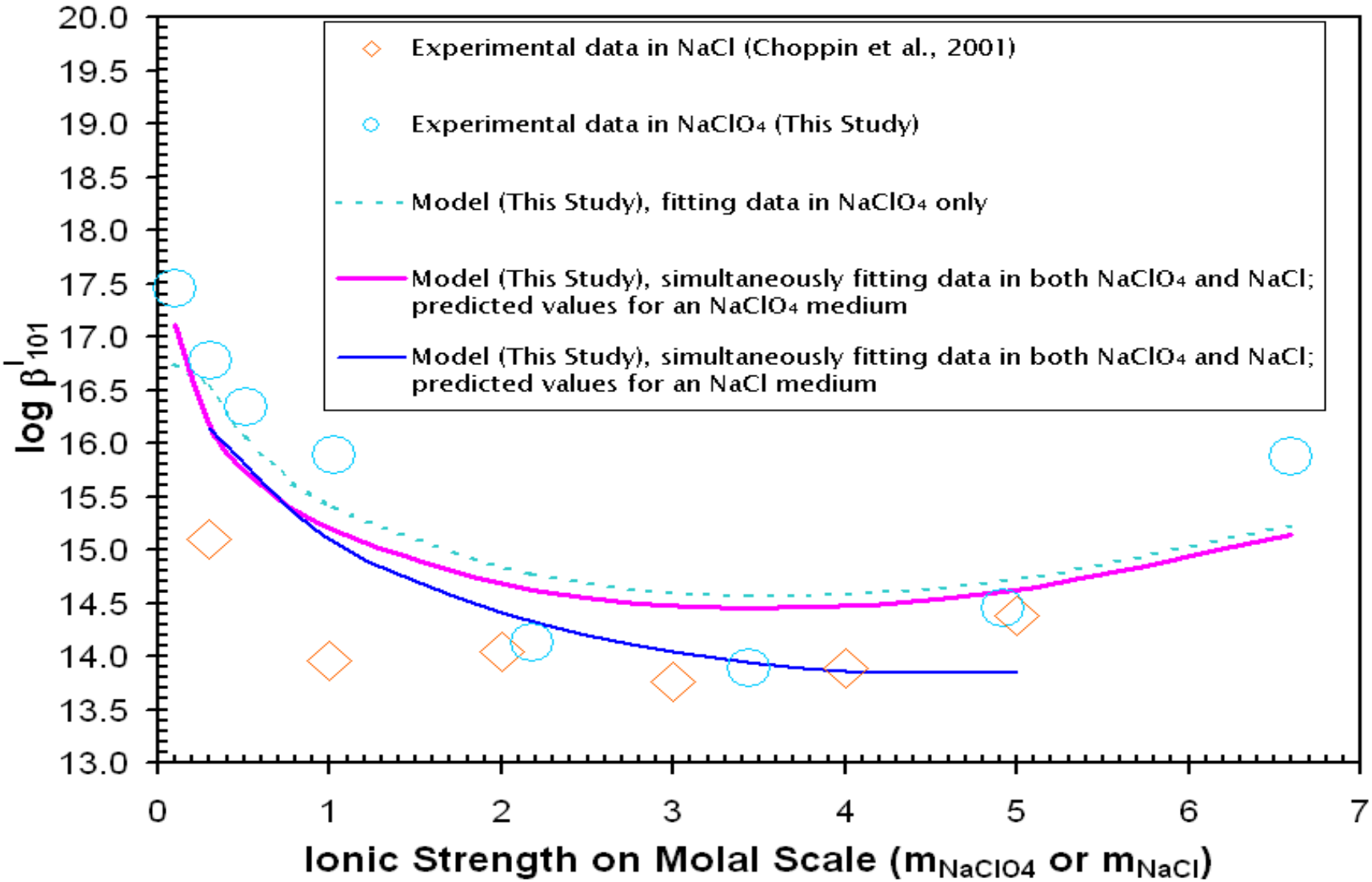

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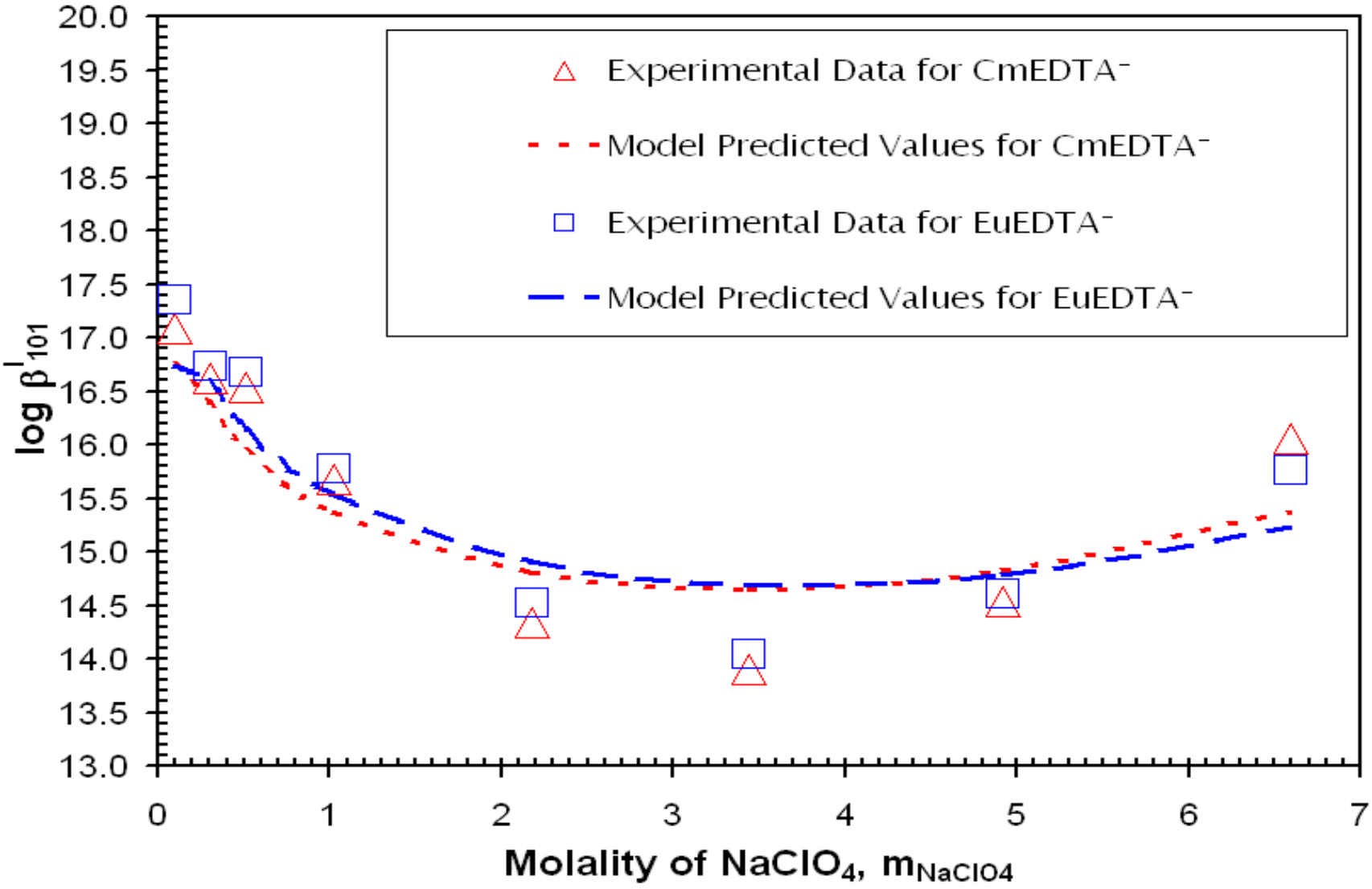

Conclusions

- The updated WIPP Thermodynamic Model will include parameters evaluated from high quality experimental data, which make it a powerful modeling tool.
- High precision models developed from high quality experimental data can provide reliable predictions that are important to numerous applications beyond nuclear waste management.
  - For instance, revised borate model would provide valuable guidance for extraction of boron from concentrated brines, including seawater.
  - Eu-EDTA model for extraction of rare earth elements (REE) using EDTA
- In general, high precision models predict what would happen in the future with confidence.