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Interactions with INE regarding Updates for Am(III) Model for the WIPP Thermodynamic Model

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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 Florida State University (FSU) (e.g., Thakur, Xiong, Borkowski, and Choppin, 2014; Thakur, Xiong, and Borkowski, 2015).

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.

Thakur, P., Xiong, Y.-L., and Borkowski, M., 2015, Improved thermodynamic model for the complexation of trivalent actinides and lanthanide with oxalic acid to high ionic strength. Chemical Geology, 413:7-17.

Am(III)-EDTA 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), and Thakur, Xiong, and Borkowski (2015), which are the collaborative work between Carlsbad Environment Monitoring and Research Center (CEMRC) and Sandia National Laboratories (SNL). Dr. Thakur is a research scientist at CEMRC.
- The experimental work was performed by Dr. Thakur at FSU.
- The Pitzer calculations were performed at SNL by Dr. Xiong.

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)

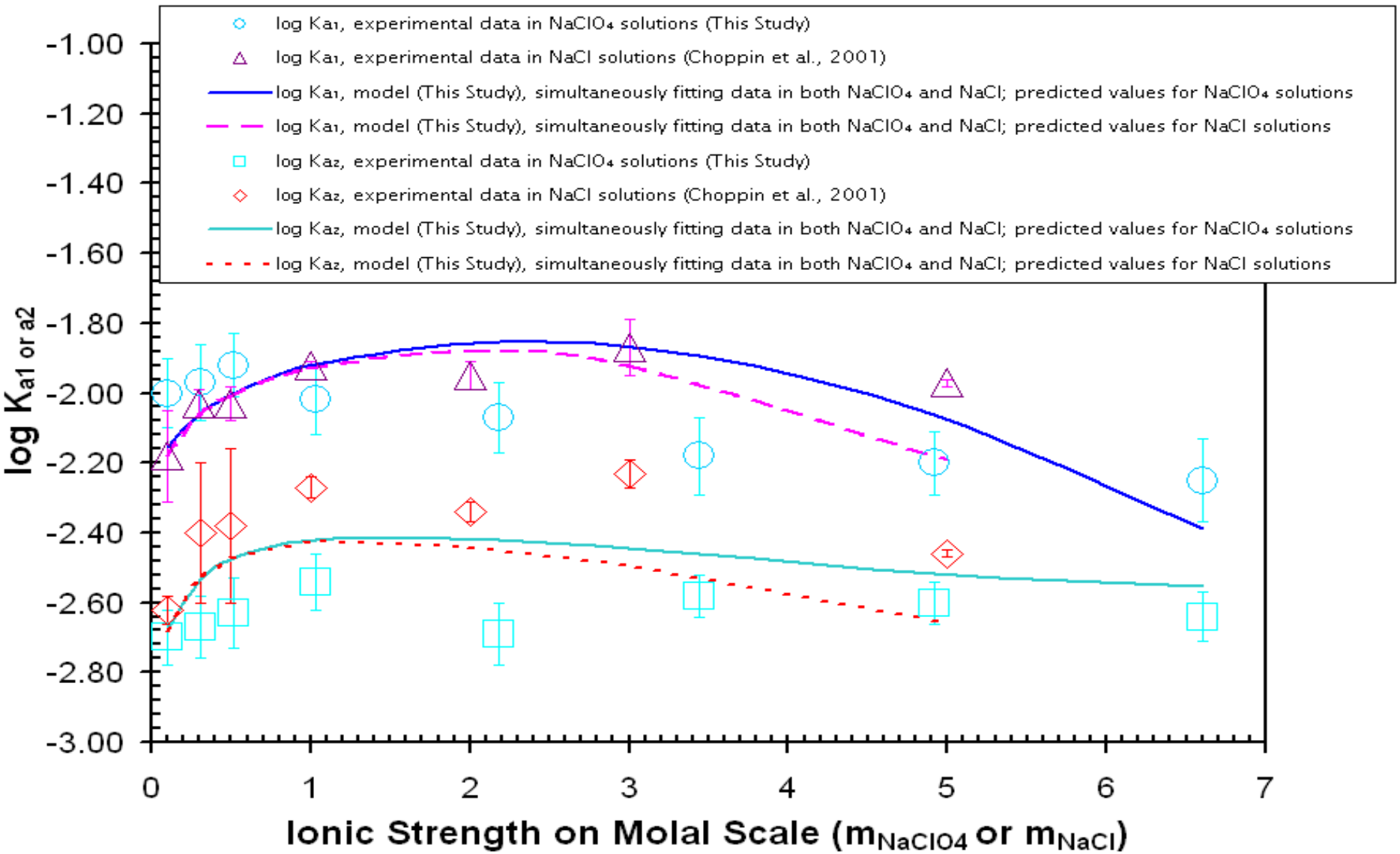
*Analogs for the interaction parameters for Am^{3+}-Cl^-.

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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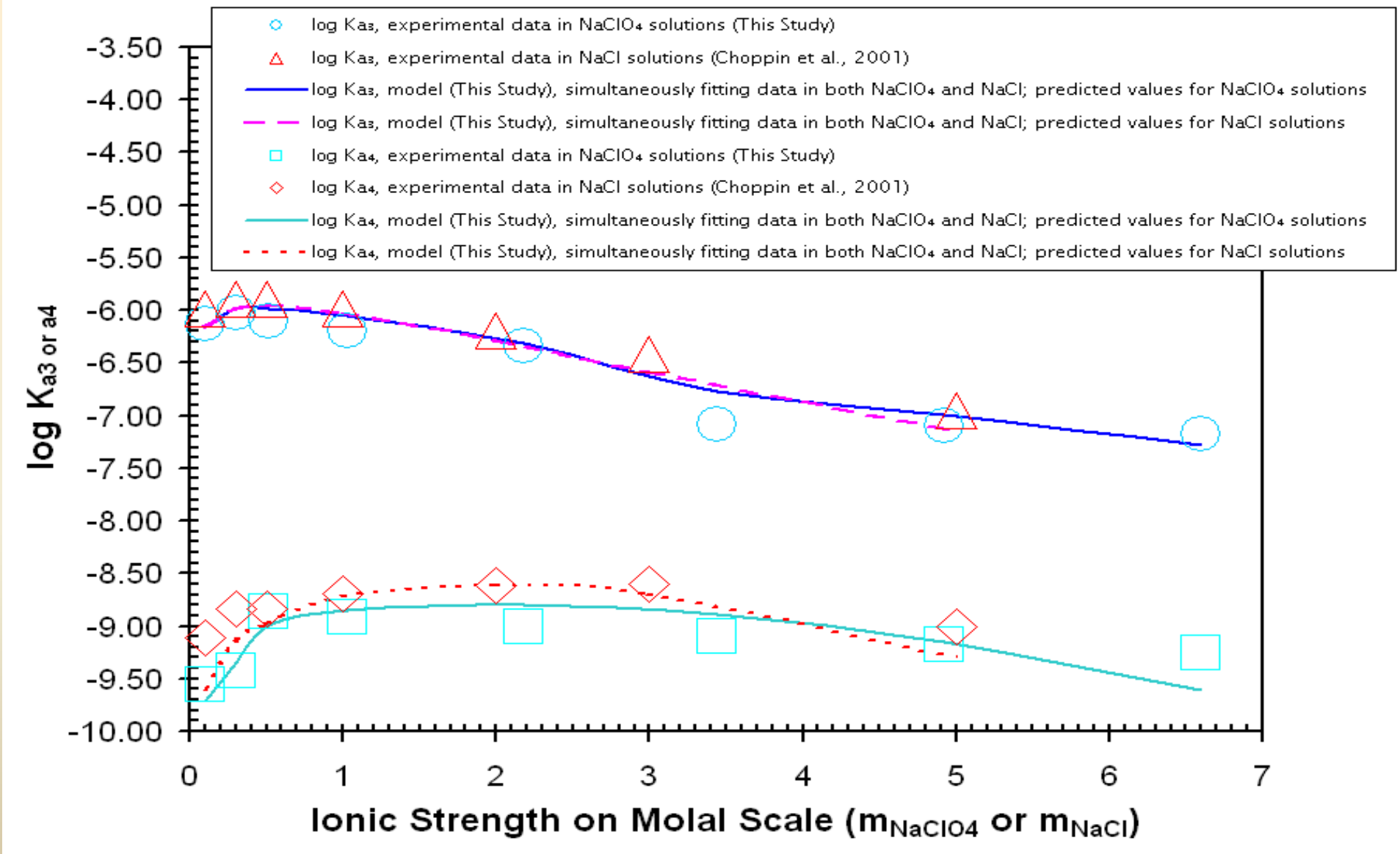

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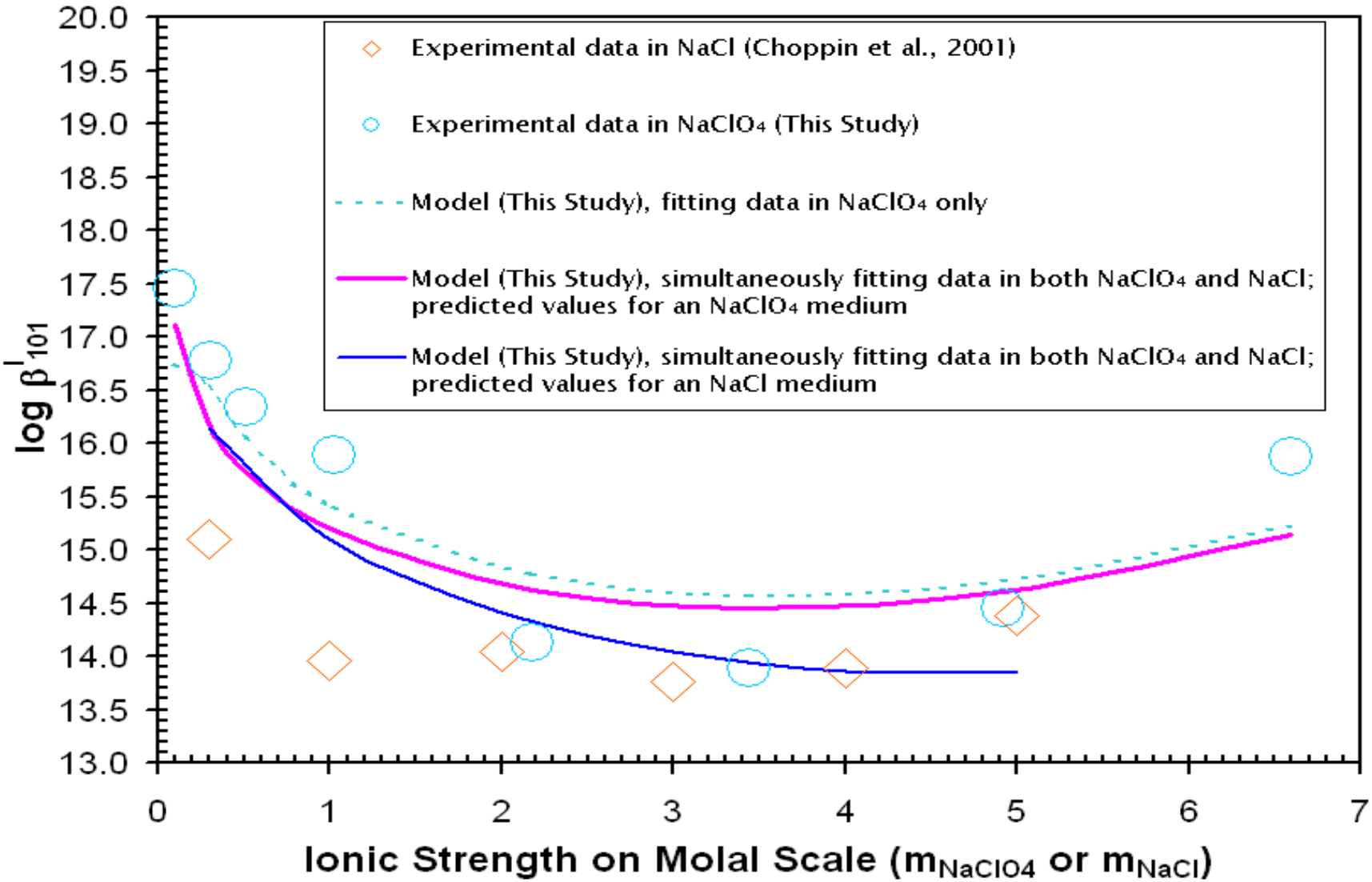

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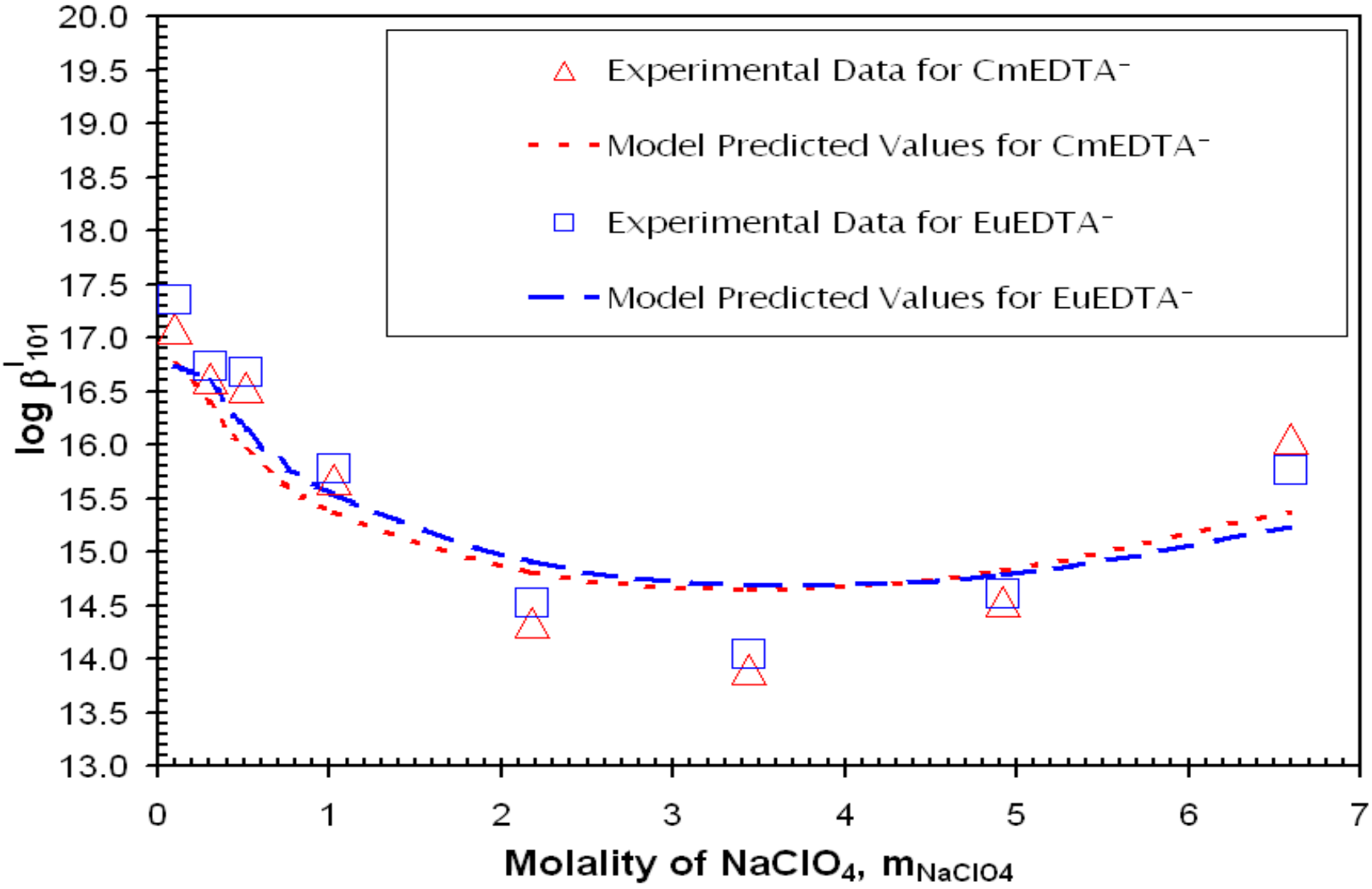

Am(III)-Oxalate Model

- Na-H-Am(III)-Cm(III)-Eu(III)-Cl-ClO_4-Oxalate System
- The current WIPP model contains only $Am(Oxalate)^+$. The updated model will have $Am(Oxalate)_2^-$, in addition to $Am(Oxalate)^+$.

Table 5 Interaction parameters involving oxalate system

Binary Interaction Parameters					
Species *i*	**Species *j***	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	**References and Remarks**
Na^+	HOx^-	–0.2448	0.29	0.068	Choppin et al. (2001)
Na^+	HOx^-	–0.2886	0.29	0.068	This study, by simultaneously fitting data in both NaCl and $NaClO_4$ for μ^o/RT of HOx^- and $\beta^{(0)}$ of Na^+–HOx^-
Na^+	Ox^{2-}	–0.2176	1.74	0.122	Choppin et al. (2001)
Na^+	Ox^{2-}	–0.2770	1.74	0.122	This study, simultaneously fitting data in both NaCl and $NaClO_4$ for μ^o/RT of Ox^{2-} and $\beta^{(0)}$ of Na^+– Ox^{2-}
Na^+	ClO_4^-	0.0554	0.2755	–0.00118	Pitzer (1991)
$AmOx^+$	Cl^-	–0.9374	0.29	0.248	Choppin et al. (2001), fitting data in NaCl
$AmOx^+$	ClO_4^-	–0.7655	0.29	0.2424	This study, by simultaneously fitting data in both NaCl and $NaClO_4$ for μ^o/RT of $AmOx^+$, $\beta^{(0)}$ and C^{ϕ} of $AmOx^+$–ClO_4^-
$CmOx^+$	ClO_4^-	–0.5326	0.29	0.1809	This Study
$EuOx^+$	ClO_4^-	–0.6063	0.29	0.2173	This Study
Na^+	$Am(Ox)_2^-$	–1.4349	0.29	0.3718	This Study, by simultaneously fitting data in both NaCl and $NaClO_4$ for μ^o/RT of $Am(Ox)_2^-$, $\beta^{(0)}$ and C^{ϕ} of Na^+–$Am(Ox)_2^-$
Na^+	$Cm(Ox)_2^-$	–1.3302	0.29	0.3665	This Study
Na^+	$Eu(Ox)_2^-$	–1.3053	0.29	0.3665	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)

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)

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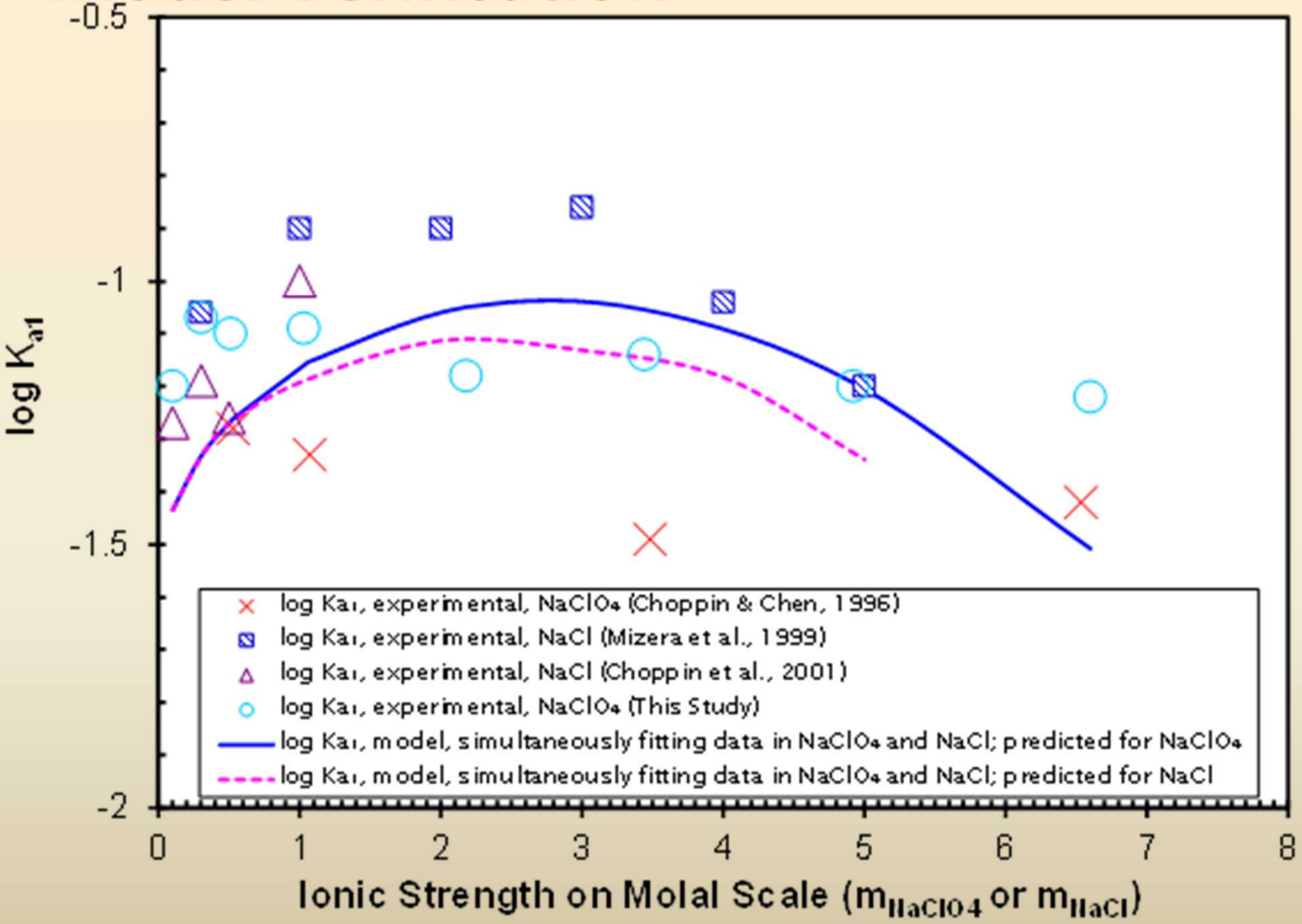
Table 6

Thermodynamic formation constants (infinite dilution reference state) at 298.15 K and 1 bar obtained in this study.

Acid dissociation or formation reaction	log Ka or log $\beta_{101/102}$	μ^o/RT for aqueous complexes[a]	References
$H_2Ox = H^+ + HOx^-$	−1.39	3.21	Choppin et al. (2001) in NaCl solutions; uncertainties not evaluated
$H_2Ox = H^+ + HOx^-$	−1.71 ± 0.15 (2σ)	3.93 ± 0.30 (2σ)	This study, simultaneously fitting data both in NaCl media from Mizera et al. (1999) and Choppin et al. (2001) and in $NaClO_4$ media from Choppin and Chen (1996) and those presented in the present work.
$HOx^- = H^+ + Ox^{2-}$	−4.26	13.02	Choppin et al. (2001) in NaCl solutions; uncertainties not evaluated
$HOx^- = H^+ + Ox^{2-}$	−4.36 ± 0.04 (2σ)	13.96 ± 0.08 (2σ)	This study, simultaneously fitting data both in NaCl media from Mizera et al. (1999) and Choppin et al. (2001) and in $NaClO_4$ media from Choppin and Chen (1996) and those presented in the present work.
$Am^{3+} + Ox^{2-} = AmOx^+$	6.16	−242.85	Choppin et al. (2001) in NaCl solutions; uncertainties not evaluated.
$Am^{3+} + Ox^{2-} = AmOx^+$	6.30 ± 0.06 (2σ)	−242.23 ± 0.14 (2σ)	This study, by simultaneously fitting data both in NaCl medium from Choppin et al. (2001) and in $NaClO_4$ medium from Choppin and Chen (1996) and from this study, using auxiliary parameters for oxalic acid from this work.
$Am^{3+} + 2Ox^{2-} = Am(Ox)_2^-$	10.84 ± 0.06 (2σ)	−238.73 ± 0.15 (2σ)	This study, by simultaneously fitting data both in NaCl medium from Choppin et al. (2001) and in $NaClO_4$ medium from Choppin and Chen (1996) and from this study, using auxiliary parameters for oxalic acid from this work.
$Cm^{3+} + Ox^{2-} = CmOx^+$	6.72 ± 0.08 (2σ)	−241.86 ± 0.18 (2σ)	This study, by fitting data in $NaClO_4$ medium, using auxiliary parameters for oxalic acid from this work.
$Cm^{3+} + 2Ox^{2-} = Cm(Ox)_2^-$	11.05 ± 0.09 (2σ)	−237.89 ± 0.20 (2σ)	This study, by fitting data in $NaClO_4$ medium, using auxiliary parameters for oxalic acid from this work.
$Eu^{3+} + Ox^{2-} = EuOx^+$	6.67 ± 0.08 (2σ)	−233.01 ± 0.17 (2σ)	This study, by fitting data in $NaClO_4$ medium, using auxiliary parameters for oxalic acid from this work.
$Eu^{3+} + 2Ox^{2-} = Eu(Ox)_2^-$	11.15 ± 0.09 (2σ)	−229.36 ± 0.20 (2σ)	This study, by fitting data in $NaClO_4$ medium, using auxiliary parameters for oxalic acid from this work.

[a] The standard dimensionless chemical potentials are consistent with the auxiliary μ^o/RT of −241.694 for Am^{3+} from Fuger and Oetting (1976); μ^o/RT of −240.357 for Cm^{3+} from Fuger and Oetting (1976); and μ^o/RT of −231.602 for Eu^{3+} from Haynes and Lide (2011).

Model Verification



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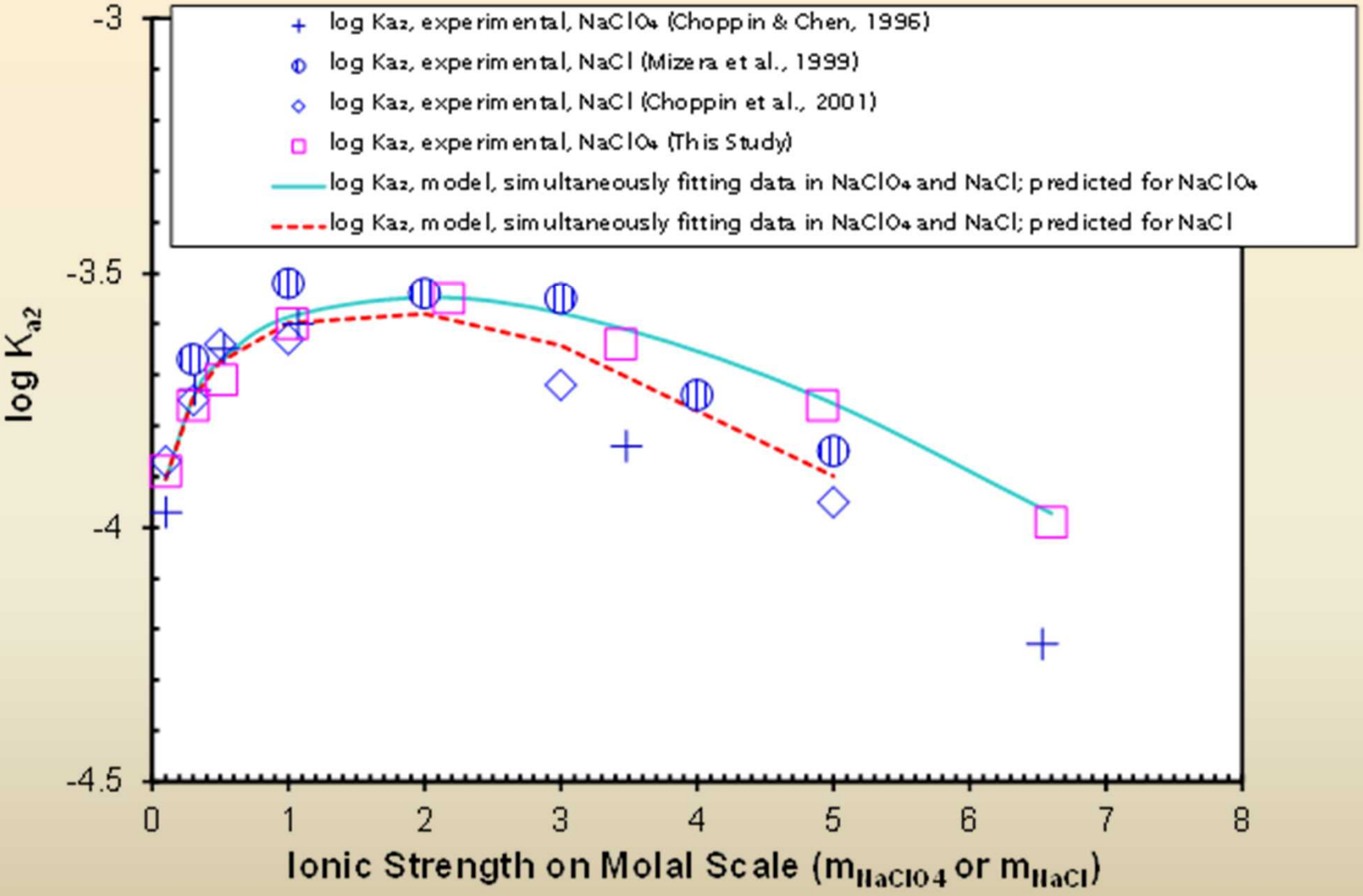

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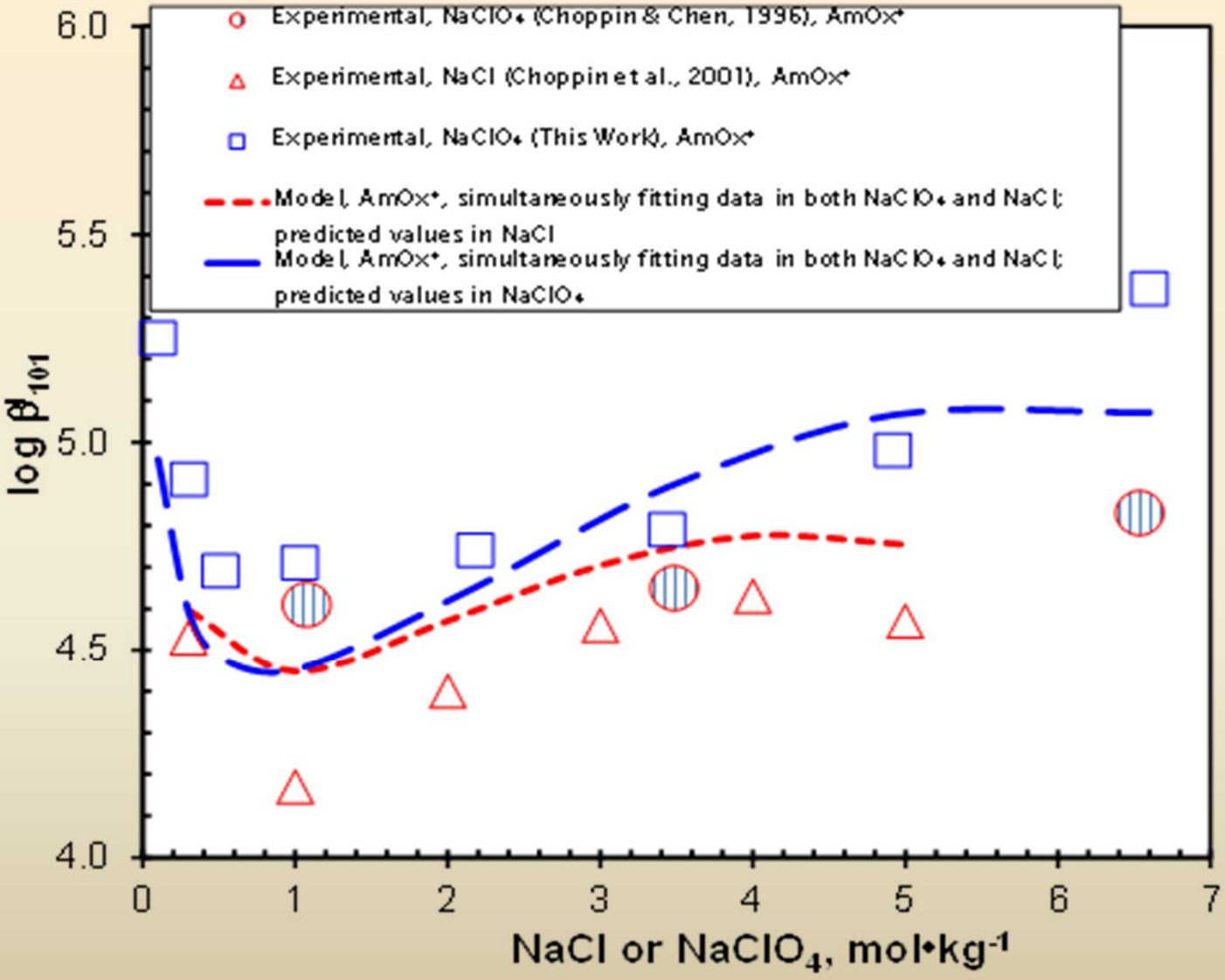

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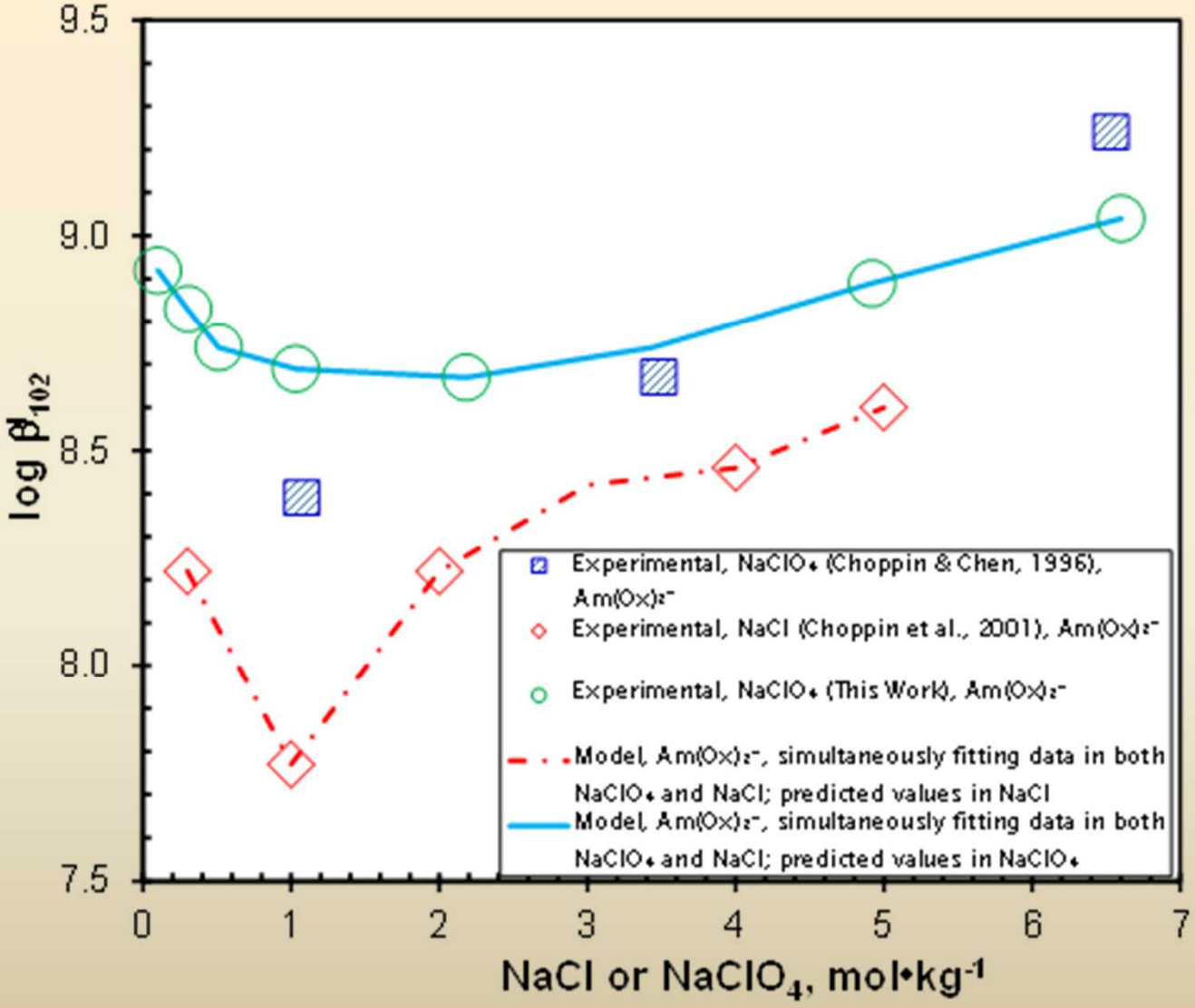

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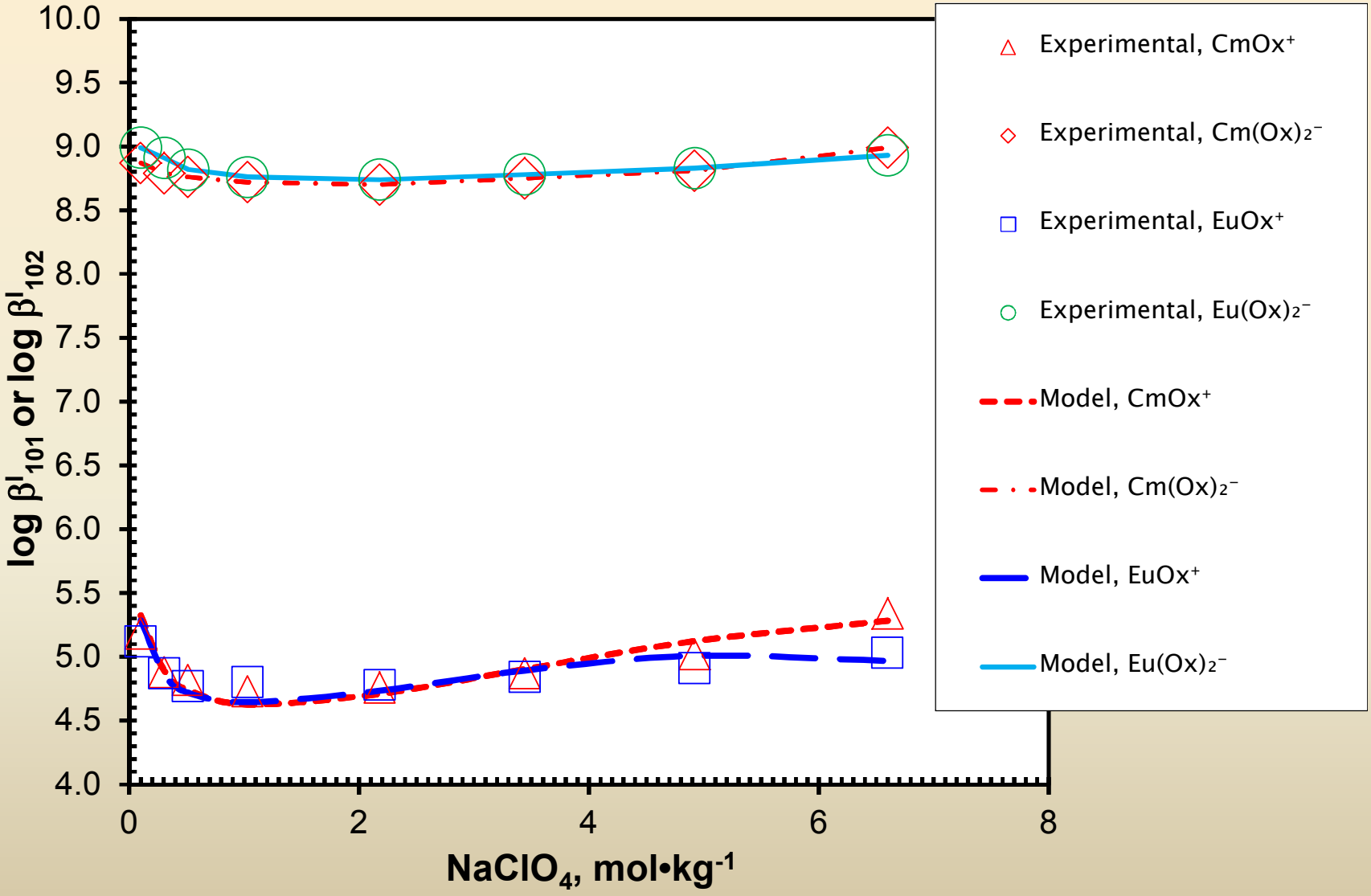

Conclusions

- The Am(III) sub-model in the WIPP Thermodynamic Model will be updated to include the most recent, relevant publications from the collaborative work between CEMRC and SNL.