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**A Thermodynamic Model for Acetate and Lactate Complexation
with Am(III), Th(IV), Np(V), and U(VI) Valid to High Ionic
Strength**

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ABSTRACT

The organic ligands acetate, lactate, oxalate and EDTA have been identified as components of wastes targeted for disposal in the Waste Isolation Pilot Plant (WIPP) located in Southeastern New Mexico. The presence of these ligands is of concern because complexation of the actinides with the ligands may increase dissolved actinide concentrations and impact chemical retardation during transport. The current work considers the complexation of Am(III), Th(IV), Np(V), and U(VI) with two of the organic ligands, acetate and lactate, in NaCl media from dilute through high concentration. A thermodynamic model for actinide complexation with the organic ligands has been developed based on the Pitzer activity coefficient formalism and the Harvie-Moller-Weare, Felmy-Weare database for describing brine evaporite systems. The model was parameterized using first apparent stability constant data from the literature. Because of complexation of other metal ions (Fe, Mg, Ni, Pb, etc.) present in the WIPP disposal room with the organic ligands, preliminary results from model calculations indicate the organic ligands do not significantly increase dissolved actinide concentrations.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) located in southeastern New Mexico is a U.S. Department of Energy facility designed for the disposal of defense-generated transuranic wastes. The facility is located in an evaporite salt bed at a depth of approximately 655 m. The waste is a mixture of materials including machining equipment, protective clothing, glove box parts, and process waste streams such as pyrochemical salts and solidified sludges.⁽¹⁾ Presently the waste is stored in steel drums and waste boxes and the WIPP design involves emplacement of these containers directly into the disposal rooms without reprocessing. A magnesium oxide backfill will be used to control the disposal room chemistry. Creep closure of the bedded salt is expected to seal off the waste, inhibiting the ability of the actinides to move away from the disposal

room. Associated with the bedded salt are inter- and intragranular brines with ionic strengths as much as 10 times greater than that of sea water. The brines are composed predominantly of $\text{Na}^+ - \text{Cl}^-$ or $\text{Na}^+ - \text{Mg}^{2+} - \text{Cl}^-$ with smaller amounts of K^+ , Ca^{2+} , SO_4^{2-} , and CO_3^{2-} .⁽²⁾

Because the waste will remain untreated before emplacement, it will still contain organic acids that were used as decontamination or process agents, including: acetic, oxalic, citric and ethylenediaminetetraacetic (EDTA) acids. Also, microbial degradation of certain components of the waste may lead to the formation of lactic acid. In the event brine contacts the waste, complexation between the organic ligands and dissolved actinides may increase dissolved actinide concentrations, thus impacting repository performance. This work quantitatively evaluates the effect of acetate and lactate on dissolved actinide concentrations by constructing a thermodynamic model to describe complexation of the organic ligands with the actinides. The variation in brine compositions necessitated development of a model for actinide-ligand complexation as a function of ionic strength. Because NaCl is the dominant electrolyte affecting acetate complexation in all of the brines, the model was constructed to calculate actinide-ligand complexation as a function of NaCl concentration.

The model constructed in this work is an extension of the Harvie and coworkers⁽³⁻⁵⁾ parameterization of the Pitzer activity coefficient model⁽⁶⁾ which was later modified to include borate speciation by Felmy and Weare.⁽⁷⁾ The Harvie and coworker database has been augmented to include Pitzer parameters and standard chemical potentials for calculating acetic acid and lactic acid complexation with the actinides Am(III), Th(IV), Np(V) and U(VI). The model is based on complexation data in NaCl media up to 5 m.

ACTIVITY COEFFICIENT MODEL

The Pitzer ion-interaction model^(6,8) is a semi-empirical model for calculating activity coefficients to high ionic strength, and has been proven accurate for calculating solubility in multicomponent electrolyte solutions.⁽⁴⁾ In the Pitzer model, the excess free energy is represented by combining a modified Debye-Hückel equation for the dilute solution region with a virial expansion for higher ionic concentrations. The model is reliably extended to multicomponent systems using parameters derived from binary and ternary systems.^(3,4,9)

For mixed electrolytes, the Pitzer equations representing the activity coefficients for cation, M, and anion, X, are given by:

$$\ln \gamma_M = z_M^2 F + \sum m_a (2B_{Ma} + Z C_{Ma}) + \sum m_c (2 \Phi_{Mc} + \sum m_a \psi_{Mca}) + \sum \sum m_a m_a \psi_{Maa'} + |z_M| \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nM} + \dots \quad [1]$$

$$\ln \gamma_X = z_X^2 F + \sum m_c (2B_{cX} + Z C_{cX}) + \sum m_a (2\Phi_{Xa} + \sum m_c \psi_{Xac}) \\ + \sum \sum m_c m_c' \psi_{cc'X} + |z_X| \left[\sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nX} + \dots \right] \quad [2]$$

where Σ represents the summation over all species and F is a modified Debye-Hückel expression given by

$$F = -A^\phi (I^{-3/2} / (1+1.2I) + 2/1.2 \ln(1+1.2I)) + \sum \sum m_c m_a B'_{ca} + \sum \sum m_a m_c \phi'_{aa} \quad [3]$$

$$C_{MX} = C_{MX}^\phi / 2 |z_M z_X|^{1/2} \quad [4]$$

$$Z = \sum |z_i| m_i \quad [5]$$

Pitzer gives phenomenological expressions defining the ionic strength dependence of the second virial coefficient B as

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 \sqrt{I}) + \beta_{MX}^{(2)} g(\alpha_2 \sqrt{I}) \quad [6]$$

$$B'_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g'(\alpha_1 \sqrt{I}) + \beta_{MX}^{(2)} g'(\alpha_2 \sqrt{I}) \quad [7]$$

where $g(x) = 2 [1 - (1+x)e^{-x}] / x^2$ [8]

$$g'(x) = -2 [1 - (1+x + x^2/2)e^{-x}] / x^2 \quad [9]$$

The second virial coefficients Φ , are given by

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij}(I) + I {}^E\theta'_{ij}(I) \quad [10]$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad [11]$$

$$\Phi'_{ij} = {}^E\theta'_{ij}(I) \quad [12]$$

The complete set of parameters in the Pitzer equation are $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^ϕ for representing interactions between binary cation-anion pairs, θ_{ij} for representing like ion interactions, ψ_{ijk} for ternary ion interactions, λ_{ij} and for neutral-ion interactions. A complete description of the Pitzer formalism and compilation of model parameters for many ionic species are given by Pitzer.⁽⁸⁾

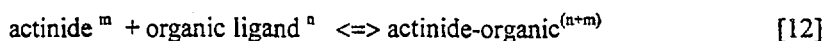
The Pitzer model has been successfully applied to marine evaporite systems,^(4,10,11) mineral precipitation in lakes,^(7,12) and actinide and lanthanide solubility in high ionic strength brines.⁽¹³⁻²³⁾ Additionally, a model based on the Pitzer formalism for NpO₂-acetate complexation has been reported Novak et al.⁽²⁴⁾

THERMODYNAMIC DATABASE FOR WIPP

Numerous models exist for accurately calculating equilibrium concentrations in low ionic strength aqueous solutions. Very few methods can adequately describe solution behavior in concentrated electrolytes. The activity coefficient formalism of Pitzer⁽⁸⁾ has been parameterized for concentrated aqueous electrolyte systems by Harvie et al.⁽⁴⁾, who have demonstrated the reliability of this formalism and data base for predicting mineral solubility using chemical equilibrium in electrolyte solutions from zero to high ionic strength. The Harvie et al.⁽⁴⁾ data base includes all parameters necessary to predict equilibrium in the Na^+ - K^+ - H^+ - Ca^{2+} - Mg^{2+} - OH^- - SO_4^{2-} - HSO_4^- - Cl^- - HCO_3^- - CO_3^{2-} - CO_2 - H_2O system, and serves as the reference data base for the parameterization described in this work. A complete description of the Pitzer parameters used to describe actinide speciation is given by Novak et al.⁽²⁵⁾

MODEL PARAMETERIZATION

The general expression describing complexation reactions between an actinide and organic ligand is:



$$\beta_{101} = [\text{actinide-organic complex}] / [\text{actinide}]_{\text{free}}[\text{organic ligand}]_{\text{free}} \quad [13]$$

where β_{101} is the first apparent stability constant for the complexation reaction, and the square brackets signify molality. Apparent stability constant data used in this work for actinide complexation with acetate and lactate were taken from results reported by Choppin et al.⁽²⁶⁾ Values were determined in NaCl media with concentrations of 0.3, 1, 2, 3, 4 and 5 m NaCl. All data were measured using a solvent extraction technique.

Pitzer parameters for the actinides in chloride media have been reported by Felmy et al.,⁽²⁷⁾ Neck et al.,⁽²⁸⁻³⁰⁾ Pitzer,⁽⁸⁾ and Roy et al.⁽²¹⁾ Data and Pitzer parameters for lactic acid deprotonation are reported by Mizera et al.⁽³¹⁾ Parameters for the deprotonation of acetic acid have been reported by Mesmer et al.,⁽³²⁾ Pitzer,⁽⁸⁾ and Novak et al.⁽²⁴⁾ A complete model for acetic acid complexation with Np(V) is reported by Novak et al.⁽²⁴⁾ Pokrovsky et al.⁽³³⁾ has reported stability constants and Pitzer parameters representing the data for NpO_2^- and UO_2^{2-} complexation with EDTA species in high ionic strength NaCl media. In this work model parameters were determined using the NONLIN (version 2.0M) computer code developed by A. Felmy and run on a Power Macintosh. NONLIN uses the MINPACK nonlinear least-squares program combined with a chemical equilibrium program based on the Gibbs free energy minimization procedure of Harvie and coworkers.⁽⁵⁾ All data points were given equal weight in the modeling calculations.

Table 1 lists all standard chemical potentials used in this work and values located in the literature for actinide-organic complexation including the EDTA values of

Table 1. Standard chemical potentials for actinide-organic complexation. Values determined in the present work were calculated using the data of Choppin et al.⁽²⁶⁾ using a Gibbs energy minimization calculation.

species	standard chemical potential, μ^0/RT (dimensionless)	reference
Brine system (Na ⁺ - K ⁺ - Mg ²⁺ - Ca ²⁺ - H ⁺ - Cl ⁻ - SO ₄ ²⁻ - OH ⁻ - HCO ₃ ⁻ - CO ₃ ²⁻ - CO ₂ - H ₂ O - B)		Harvie et al. ⁽⁴⁾ Felmy and Weare ⁽⁷⁾
Am ³⁺	-241.694	Felmy et al. ⁽²⁷⁾
NpO ₂ ⁺	-369.1	Fanghanel et al. ⁽³⁵⁾
UO ₂ ²⁺	-384.259	Pitzer ⁽⁶⁾
Th ⁴⁺	-284.23	Felmy et al. ⁽²⁰⁾
C ₂ O ₂ H ₄ (acetic acid)	-158.3	Novak et al. ⁽²⁴⁾
C ₂ O ₂ H ₃ ⁻ (acetate ion)	-147.347	Novak et al. ⁽²⁴⁾
C ₃ O ₃ H ₆ (lactic acid)	0*	Mizera et al. ⁽³¹⁾
C ₃ O ₃ H ₅ ⁻ (lactate ion)	8.798	Mizera et al. ⁽³¹⁾
UO ₂ - EDTA ²⁻	-361.555	Pokrovsky et al. ⁽³³⁾
UO ₂ - HEDTA ⁻	-374.787	Pokrovsky et al. ⁽³³⁾
NpO ₂ - EDTA ³⁻	-335.708	Pokrovsky et al. ⁽³³⁾
NpO ₂ - HEDTA ²⁻	-351.852	Pokrovsky et al. ⁽³³⁾
NpO ₂ - H ₂ EDTA ⁻	-364.098	Pokrovsky et al. ⁽³³⁾
Am - acetate ²⁺	-395.239	present work
Am - lactate ²⁺	-241.436	present work
Th - acetate ³⁺	-448.525	present work
Th - lactate ³⁺	-291.152	present work
NpO ₂ - acetate ²⁺	-526.061	present work
NpO ₂ - lactate ²⁺	-364.837	present work
UO ₂ - acetate ⁺	-538.585	present work
UO ₂ - lactate ⁺	-382.596	present work

* set to 0

Pokrovsky et al. ⁽³³⁾ Values for acetate are from Novak et al. ⁽²⁴⁾ The standard chemical potential for lactic acid was set to 0 because of a lack of data for this species in NaCl media. ⁽³¹⁾ All other standard chemical potentials for lactate and actinide-lactate complexes were calculated based on this zero reference value. For use in WIPP calculations, this simplification is of no consequence since organic acid solubilities do not need to be determined. Concentrations in WIPP brines are based on inventory limits and are well below solubilities reported in the literature. ^(1, 34) Data on organic acid solubility as a function of NaCl concentration are needed to add additional parameters for organic acid solubility.

Table 2 lists binary, neutral-ion, and like-ion, and ternary Pitzer parameters for actinide-ligand complexation developed in this work and located in the literature. As previously discussed, in this work, the values for lactic acid were set to 0. Parameters for Pitzer equations are not unique and different sets of parameters may be used to provide an identical description of the same data. ⁽²⁵⁾ For the systems in this work, no accurate measurements of data could be located below an ionic strength of 0.3 in NaCl media. Therefore, values for $\beta^{(1)}$ had to be estimated. It has been recommended to fix $\beta^{(1)}$ to a certain value. ⁽³⁵⁾ For 1:1 and 2:1 interactions values of 0.29 and 1.74 were calculated based on the data compilation of Pitzer. ^(8, p.102, 106) Values for $\beta^{(0)}$ and C^ϕ were calculated based on the average $\beta^{(1)}$ values.

The literature data along with the Pitzer model for acetate and lactate are plotted in figures 1 and 2, respectively. For all of the data modeled in this work the Pitzer equation gave an excellent representation of the data using only binary parameters. The parameters $\beta^{(2)}$ as well as mixing parameters of cationic, anionic (Θ_{ij}) and ternary (ψ_{ijk}) interactions were set equal to 0, since no experimental information was available to separate these effects from the binary interactions. For Am-Ac²⁺, Am-Lac²⁺, and Th-Lac³⁺ it was necessary to use large values for C^ϕ to represent the data. All other parameters are reasonable for the type of interactions they represent.

EFFECT OF ACETATE AND LACTATE AT WIPP

Because organic ligands may complex with actinides, resulting in increased dissolved actinide concentrations, the potential effect of organic liquids is important in assessing the performance of nuclear waste repositories. While this effect may be significant, organic ligands also complex strongly with other multivalent metal cations, possibly mitigating the ability of the organic ligands to impact repository performance with respect to actinide solubility. In support of the compliance application for the WIPP, an assessment of the ability of multivalent metal cations to effectively sequester the organic ligands was performed. The analysis, summarized below, demonstrates that organic ligands will not generally be available to complex the actinides and thus will not significantly impact dissolved actinide concentrations and transport in the WIPP.

Table 2. Pitzer parameters used in this work and reported in the literature. Values determined in this study were calculated using a Gibbs energy minimization routine.

Binary Pitzer Parameters

Species i	Species j	$\beta 0_{ij}$	$\beta 1_{ij}$	$\beta 2_{ij}$	c_{ij}^0	reference
brine system: $\text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} - \text{Ca}^{2+} - \text{H}^+ - \text{Cl}^- - \text{SO}_4^{2-} - \text{OH}^- - \text{HCO}_3^- - \text{CO}_3^{2-} - \text{CO}_2 - \text{H}_2\text{O} - \text{B}$						Harvie et al. ⁽⁶⁾ Felmy and Weare ⁽⁷⁾
Am^{3+}	Cl^-	1.537	4.185	0	-0.286	Felmy et al. ⁽²⁷⁾
NpO_2^+	Cl^-	0.1415	0.281	0	0	Neck et al. ⁽³⁰⁾
UO_2^{2+}	Cl^-	0.4274	1.644	0	-0.0184	Pitzer ⁽⁸⁾
Th^{4+}	Cl^-	1.092	13.7	-160	-0.122	Roy et al. ⁽²¹⁾
Na^+	HAc	0	0	0	0	Novak et al. ⁽²⁴⁾
Na^+	Ac^-	0.1426	0.22	0	-0.00629	Pitzer ⁽⁸⁾ , Mesmer et al. ⁽³²⁾
Na^+	$\text{NpO}_2\text{-EDTA}^{3-}$	0.683	5.911	0	0	Pokrovsky et al. ⁽³³⁾
Na^+	$\text{NpO}_2\text{-HEDTA}^{2-}$	0.04733	-1.504	0	0	Pokrovsky et al. ⁽³³⁾
Na^+	$\text{NpO}_2\text{-H}_2\text{EDTA}^-$	-0.8285	0.2575	0	0.256	Pokrovsky et al. ⁽³³⁾
Na^+	$\text{UO}_2\text{-EDTA}^{2-}$	-0.1516	1.74	0	0.095	Pokrovsky et al. ⁽³³⁾
Na^+	$\text{UO}_2\text{-HEDTA}^-$	0.382	0.2575	0	0.172	Pokrovsky et al. ⁽³³⁾
Na^+	HLac	0	0	0	0	present work ⁽¹⁾
Na^+	Lac^-	-0.0563	0.29	0	0.047	present work
$\text{Am} - \text{Ac}^{2+}$	Cl^-	1.014	1.74	0	-0.265	present work
$\text{Am} - \text{Lac}^{2+}$	Cl^-	1.584	1.74	0	-0.486	present work
$\text{Th} - \text{Ac}^{3+}$	Cl^-	1.061	5.22	0	0.109	present work
$\text{Th} - \text{Lac}^{3+}$	Cl^-	0.6677	5.22	0	0.341	present work
$\text{UO}_2 - \text{Ac}^+$	Cl^-	0.0124	0.29	0	0.007	present work
$\text{UO}_2 - \text{Lac}^+$	Cl^-	-0.042	0.29	0	0.091	present work

⁽¹⁾ values set to 0

Neutral-ion, like-ion and ternary Pitzer Parameters

Species i	Species j	$\theta_{ij} ; \lambda_{ij}$	ψ_{ij, Na^+}	reference
Ac^-	Cl^-	-0.09	0.01029	Novak et al. ⁽²⁴⁾
$\text{NpO}_2 - \text{Ac}^{2+}$	Cl^-	0	0	Novak et al. ⁽²⁴⁾
$\text{NpO}_2\text{-Lac}^0$	Cl^-	0.015	-	present work

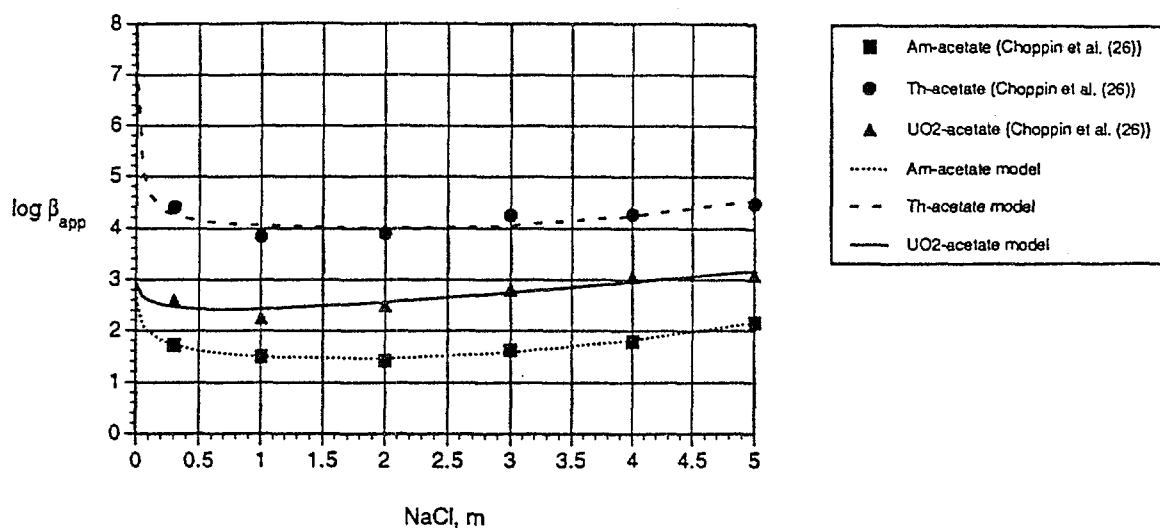


Fig. 1. First apparent stability constants for actinide complexation with acetate as a function of NaCl molality. Lines through data represent Pitzer model fit to literature data.

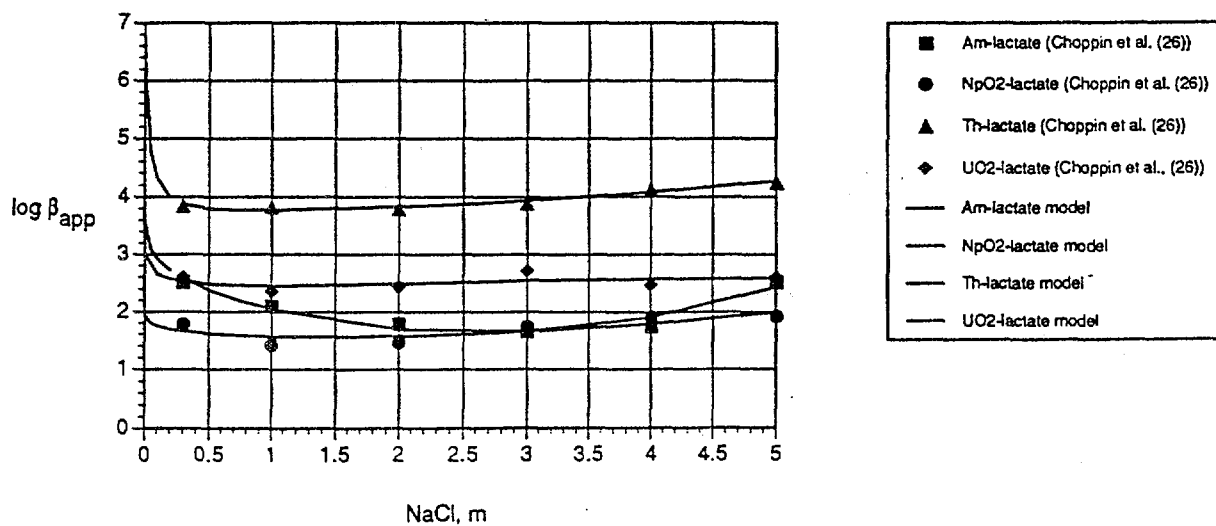


Fig. 2. First apparent stability constants for actinide complexation with lactate as a function of NaCl molality. Lines through data represent Pitzer model fit to literature data.

To assess the ability of competing metals present in the waste disposal area to complex with the organic ligands, simplified competition calculations were performed. These calculations involved the simultaneous solution of equations representing the complexation of the organic ligands of interest (acetate and lactate) with each of the actinides of interest to WIPP (i.e. Am, Pu, Th, and U) and the competing metals which are known to be in the disposal area (e.g. Fe, Ca, Mg, Ni, Cr, Pb, Ga) along with an equation representing mass balance. Complexation constants for the non-actinide metals at low ionic strength are reported in Smith and Martell. ⁽³⁶⁾ These calculations utilized low ionic strength complexation constants and solubilities for the competing metals due to the lack of data at high ionic strength. While no significant change to the complexation constants are anticipated with an increase in ionic strength, the solubilities of the competing metals may increase in high ionic strength solutions, particularly when chloride complexation is considered. The solution of these equations demonstrated that the presence of the organic ligands acetate and lactate do not have a significant impact on actinide solubility. Complexation and solubility data for the competing metals (Mg, Fe, Ni, Pb, etc.) are being collected to support the quantification of this effect, if any.

CONCLUSIONS

A thermodynamic model for describing acetate and lactate complexation with Am(III), Th(IV), Np(V), and U(VI) in NaCl media has been developed. The model accurately represents the data to high ionic strength using the Pitzer activity coefficient formalism, and the Harvie et al. database describing brine evaporite systems. The model can be used to calculate acetate-actinide complexation in high ionic strength NaCl brines such as those encountered at the WIPP. In order to fully evaluate the effect of organic ligands on dissolved actinide concentrations, data must be available for other metals (Fe, Ni, Pb, Mg, etc.) that can "compete" for binding sites on the organic ligands for complexation. We are currently developing Pitzer parameters to describe complexation of actinides and other "competing metals" with oxalate, citrate, and EDTA,

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