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An improved thermodynamic model for the complexation of trivalent actinides and lanthanide with oxalic acid valid to high ionic strength

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ABSTRACT

The dissociation constants of oxalic acid (Ox), and the stability constants of Am^{3+}, Cm^{3+} and Eu^{3+} with Ox^{2-} have been determined at 25 °C, over a range of concentration varying from 0.1 to 6.60 m $NaClO_4$ using potentiometric titration and extraction techniques, respectively. The experimental data support the formation of complexes, $M(Ox)_n^{3-2n}$, where (M = Am^{3+}, Cm^{3+} and Eu^{3+} and n = 1 and 2). The dissociation constant and the stability constant values measured as a function of $NaClO_4$ concentration were used to estimate the Pitzer parameters for the respective interactions of Am^{3+}, Cm^{3+} and Eu^{3+} with Ox. Furthermore, the stability constants data of Am^{3+}–Ox measured in $NaClO_4$ and in NaCl solutions from the literature were simultaneously fitted in order to refine the existing actinide–oxalate complexation model that can be used universally in the safety assessment of radioactive waste disposal. The thermodynamic stability constant: log $\beta^0_{101} = 6.30 \pm 0.06$ and log $\beta^0_{102} = 10.84 \pm 0.06$ for Am^{3+} was obtained by simultaneously fitting data in NaCl and $NaClO_4$ media. Additionally, log $\beta^0_{101} = 6.72 \pm 0.08$ and log $\beta^0_{102} = 11.05 \pm 0.09$ for the Cm^{3+} and log $\beta^0_{101} = 6.67 \pm 0.08$ and log $\beta^0_{102} = 11.15 \pm 0.09$ for the Eu^{3+} were calculated by extrapolation of data to zero ionic strength in $NaClO_4$ medium only. For all stability constants, the Pitzer model gives an excellent representation of the data using interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} determined in this work. The thermodynamic model developed in this work will be useful in accurately modeling the potential solubility of trivalent actinides and early lanthanides to ionic strength of 6.60 m in low temperature environments in the presence of Ox. The work is also applicable to the accurate modeling transport of rare earth elements in various environments under the surface conditions.
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1. Introduction

The Waste Isolation Pilot Plant, abbreviated as WIPP, is a transuranic (TRU) waste repository operated by the U.S. Department of Energy (DOE). The repository is emplacing defense-related TRU wastes in the Salado Formation, a bedded salt formation approximately 655 m (2150 ft.) below the surface of the Earth. Located 42 km east of Carlsbad, New Mexico in a sparsely populated area, the WIPP facility is the world's first deep geologic disposal facility licensed to accept TRU waste. The TRU waste is defined as the radioactive waste with activity concentrations of alpha-emitting isotopes >3700 Bq/g (>100 nCi/g). Since its operation in March 1999, more than 81,000 m^3 of legacy TRU waste have been removed from temporary locations around the nation and shipped to WIPP for permanent disposal. In accordance with the current permit the repository will contain ca. 176,000 m^3 of TRU waste. The WIPP is about half full in terms of its legally defined capacity.

The composition of US defense waste is extremely diverse. Because the wastes buried in the WIPP site are not treated prior to disposal, organic ligands used in actinide processing and decontamination are present in the waste. In the event brine contacts the waste in the repository, these organic ligands might increase the solubility of actinides by complexation, thus impacting repository performance. Among the organic ligands known to be present in the WIPP waste, acetic acid (Ac), oxalic acid (Ox), citric acid (Cit), and ethylenediamine tetraacetic acid (EDTA) are of significance because they have the most potential to increase concentrations of dissolved actinides in the WIPP (40 CFR Part 1). The estimated concentrations of these organic ligands in the WIPP brine are: EDTA = 6.5×10^{-5} M, Ac = 1.9×10^{-2} M, Ox = 1.7×10^{-2} M, and Cit = 2.4×10^{-3} M (Brush and Xiong, 2009). These concentrations were estimated using the projected inventory amount of the organic ligand divided by the minimum brine volume needed for the direct brine release. In addition, oxalate is also present in relatively high concentrations in several natural environments such as soil solutions, oil field sedimentary basin brines, and deposits from thermal degradation of complex organic matter (Gammons and Wood, 2000). As a result, complexation of actinides with Ox could play an important role in determining the migration of actinides in the

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repository. In this context, study of coordination chemistry of actinides especially interactions with organic ligands expected in the repository is important to repository performance assessment (PA). High ionic strength groundwater may be encountered at repository depth in several types of geologic host rock formations. If the selected host rock is salt, as in the case of WIPP, the only water present will be saturated brines. This means that there is a need to understand and quantify the complexation of actinides with organic ligands at high ionic strength.

Studies on complexation of actinides in high ionic strengths solutions with ligands of interest to the WIPP are rare. It is often possible to find a constant obtained for similar experimental conditions at low ionic strengths and 25 °C. However, there is a shortage of reported literature constants above 1–2 m ionic strength. Significant part of the currently available data on complexation between trivalent actinides and Ox were measured at I < 2.0 m. Most of the available data measured under high ionic strength, relevant to the WIPP conditions, were studied by Choppin and coworkers. They have measured the stability constants of Am^{3+}, Th^{4+}, NpO_2^+ and UO_2^{2+} with Ac, lactate, Ox, Cit, and EDTA by solvent extraction as a function of NaCl/$NaClO_4$ concentration up to 5 m and the data were modeled using ion-interaction model of Pitzer. For instance, Choppin and Chen (1996) reported the complexation of Ox with Am^{3+} in $NaClO_4$ media up to 9.0 M $NaClO_4$. Erten et al. (1994) measured the stability constants of Th(IV) and U(VI) with Ox in 0.1 to 9.0 M $NaClO_4$. The same group has also reported the thermodynamic modeling of actinide complexation (Am^{3+}, Th^{4+}, NpO_2^+ and UO_2^{2+}) with oxalate in NaCl media (Borkowski et al., 2001). Furthermore, the complexation of NpO_2^+ with acetate, oxalate, citrate, and EDTA over a range of ionic strength (I = 0.1–9.0 m $NaClO_4$) were reported by several researchers (Bronikowski et al., 1999; Choppin et al., 1996; Novak et al., 1996; Pokrovsky et al., 1998; Pokrovsky and Choppin, 1997), while Moore et al. (1999) reported the stability constants of NpO_2^+, UO_2^{2+}, Am^{3+} and Th^{4+} with acetate and lactate in 0.3–5.0 m NaCl. The complexation of Am^{3+} by EDTA was also studied over a wide range of NaCl concentration (Chen et al., 1999). The stability constants of the complex, $Am(EDTA)^-$ were measured, and an aqueous thermodynamic model with ion interaction parameters were calculated. The Sandia report (SAND99-0943) (Choppin et al., 2001) lists raw experimental data provided by Choppin and co-workers on thermodynamic parameters required in the performance assessment calculations for WIPP. This report contains protonation constant values for several ligands including Ox, Cit, and EDTA as well as their stability constants with Am^{3+}, Th^{4+}, NpO_2^+ and UO_2^{2+}.

In this context, it is important to note that the previous experimental work and the model constructed by Choppin and co-workers were based on the complexation data of oxalate obtained as a function of NaCl concentration up to 5.0 m. It is necessary to extend the existing experimental results and associated model to higher ionic strengths because the two important brines in the WIPP repository (GWB and ERDA-6), which are important for the repository PA have ionic strengths of 8.26 m and 5.82 m, respectively (Xiong and Lord, 2008). In addition, the Q-brine in the Asse repository, Germany, has even higher ionic strength (~13 m) (Schuessler et al., 2001).

For all of the above reasons, in this study, the complexation of Am^{3+}, Cm^{3+} and Eu^{3+} with Ox as well as dissociation constants of Ox over a range of ionic strength varying from 0.1–6.60 m $NaClO_4$ were measured using solvent extraction and potentiometric titration techniques, respectively. Stability constant data collected in 0.1 m to 6.60 m $NaClO_4$ were used for the Pitzer interaction parameter calculations. The thermodynamic data obtained from this study, measured in non-complexing $NaClO_4$ medium, were then compared to similar data published in NaCl to assess the role of Cl^- complexation. The Pitzer ion interaction parameters for Am^{3+}–Ox in $NaClO_4$ and NaCl have been previously separately calculated by Choppin and Chen (1996), Borkowski et al. (2001) and Choppin et al. (2001). Since the WIPP repository contains two important brines i.e., GWB (a Na–Mg–Cl dominated brine — US DOE, 2004) and ERDA-6 (a Na–Cl dominated brine — Popielak et al., 1983), it is always best to develop a model that is consistent with all of the available data. Therefore in this study, a "combined fitting model approach" was undertaken in which stability constants data of Am^{3+}–Ox measured in $NaClO_4$ (from this study) and NaCl data (from Choppin et al., 2001) were fitted simultaneously. In contrast to the earlier model, the model developed is this study was intended to provide an excellent interpretation of the experimental data over the entire ionic strength range of up to 6.6 m. The standard chemical potentials and ion interaction parameters calculated using this approach has been shown to be superior to those that currently exist in the WIPP database.

2. Experimental

2.1. Materials

All of the reagents were ACS certified grade. $NaClO_4$ (99%, Sigma-Aldrich, ACS certified) stock solution was prepared in deionized water and filtered through a 0.45 μm membranes filter. Deionized water (Barnstead Nanopure, >17 MΩ-cm), purged with N_2, was used to prepare the solutions. The stock solution of oxalic acid (>99.5%, Fisher Scientific) was prepared by dissolving the required amounts of the acid in $NaClO_4$ solutions of the desired ionic strength. All aqueous solutions were filtered through a 0.45 μm filter to minimize the possible sorption of the radioactive tracers by suspended particles. Di(2-ethylhexyl) phosphoric acid, HDEHP (Sigma Aldrich, 95%) was used without purification. Stock solution of 2×10^{-4} to 5×10^{-4} M HDEHP in heptane (Fisher Scientific, ACS) were prepared and used as the organic phase for extraction of Eu^{3+}, Am^{3+} and Cm^{3+}, respectively. The organic phase was pre-equilibrated with aqueous phase of desire ionic strength to at pcH = 3.60 prior to extraction.

The ^{241}Am, ^{244}Cm and $^{152,\ 154}Eu$ radionuclides were obtained from Oak Ridge National Laboratory and their purity checked by α- and/or γ-spectrometry. The ^{244}Cm was purified from its daughter nuclide ^{240}Pu by anion exchange (Dowex 1 × 4) in 7.5 M HNO_3. The working stock of the tracer was prepared in a solution of pcH = 3.0 ($HClO_4$) with radioactive concentration of ca. 50,000 ± 1000 counts per minutes (cpm) per 10.0 μL (~1×10^{-7}–1×10^{-6} M). The activities of ^{241}Am, ^{244}Cm and $^{152,\ 154}Eu$ were counted with a Beckman Liquid Scintillation Counter (LSC) using Ecolite liquid scintillation cocktail (ICN, Research Product Division) suitable for high ionic strength solution.

2.2. Calculation of stability constant

The partitioning of Am, Cm and Eu into the aqueous (e.g., 6.60 m $NaClO_4$) and the organic phase (HDEHP, represented as H_2A_2, in the dimeric form) can be expressed as:

$$M^{3+}{}_{(a)} + 3H_2A_{2(o)} \leftrightarrows DM(HA_2)_{3(o)} + 3H^+{}_{(a)} \quad (1)$$

where (a) and (o) represent respectively, the aqueous and organic phases. In the presence of Ox in the aqueous phase the complexation of the metal ions can be written as:

$$M^{3+} + n\ Ox^{3-} \leftrightarrows M(Ox)_n{}^{3-2n} \quad (2)$$

where n = 1 and 2. The concentration range of Ox was so chosen to form only 1:1 and 1:2 complexes. The distribution coefficient of the actinide ions between the organic and aqueous phases in the presence of the Ox can be described by:

$$D_0/D-1 = \beta_{101}\left[Ox^{2-}\right] + \beta_{102}\left[Ox^{2-}\right]^2 \quad (3)$$

where D_0 is the distribution ratio in the absence of Ox. $[Ox^{2-}]$ is free ligand concentration calculated from the measured pcH after reaching the extraction equilibrium, the total ligand concentrations, and the

relevant protonation constants. All experiments were performed at least twice and six to eight data points were obtained in each measurement.

In the extraction experiments, the pH/pcH values measured after extraction sometimes varied slightly. The minor corrections to the D values for this pcH fluctuation were made by the following relationship:

$$\log D_{corr.} = \log D - n(pcH - pcH_{av}) \quad (4)$$

where n is the experimental slope of the log D_{exp} dependence on pcH in the absence of the ligand for the certain $NaClO_4$ ionic strength solution (6.6 m) at required temperature. The pcH_{avg} is an average value of pcH measured for each sample.

2.3. Potentiometric titration

Potentiometric titrations were conducted to determine the dissociation constants of the Ox using an automated titration system. A 665 Dosimat (Metrohm) burette was used to conduct the potentiometric titrations in a 50 mL jacketed cell thermally controlled to 25.0 ± 0.1 °C by water flow from Isotemp bath. Nitrogen gas was bubbled through the titration solution to remove the dissolved carbon dioxide. NaOH titrant solutions at different ionic strengths were prepared by adding measured volumes of 50% NaOH to a N_2-saturated $NaClO_4$ solution. The NaOH solutions were standardized by titration with potassium hydrogen phthalate. The $HClO_4$ solutions at desired ionic strengths were prepared and standardized with the standard NaOH. 15 mL of 0.005 to 0.01 M Ox in $NaClO_4$ of desired ionic strengths were titrated with 0.100 M NaOH at the same ionic strength from the burette over a pcH range from 2 to 11, collecting 120 data points per titration. The titrations were performed with stirring on a Corning model PC420 stirrer/hot plate. The system was interfaced to a computer that operated software prepared in the laboratory to control burette additions and to record the mV reading of the electrode. The delay between the readings was ≥30 s to assure equilibrium. After the addition was made, the system waited a mixing time, typically 30 s, before restarting the measurement cycle. Prior to each titration, the electrode was calibrated by an acid–base titration using the standardized perchloric acid and sodium hydroxide solutions at the desired ionic strength so that hydrogen ion concentrations could be calculated from the emf readings in the subsequent titrations. The titration data were fitted by PSEQUAD to calculate the acid dissociation constants (Zekany and Nagypal, 1985).

2.4. pcH measurement

An Accumet 950 (Fisher Scientific) pH meter was used with glass combination electrode (Corning semi-micro) to measure pcH. The electrode was calibrated with 4.00 ± 0.01 and 7.00 ± 0.01 standard pH buffer (Fisher Scientific). The pH meter readings, pHr, were converted to negative logarithm of hydrogen ion concentrations, pcH, using calibration curves obtained by a series of measurements of various concentrations of $HClO_4$ and NaOH solutions of known H^+ concentrations for I = 0.1 to 6.6 m ($NaClO_4$) at room temperature similar to those described in several publications (Bates et al., 1970; Knauss et al., 1993; Rai et al., 1995; Xiong, 2008; Xiong et al., 2010). The pcH was calculated from the pH meter readings using the relation:

$$pcH = pHr + 0.259(\pm 0.025) \times C_{NaClO_4} \quad (5)$$

where C = molal concentration of $NaClO_4$.

As hydrogen ion concentration determined above is on molar scale (M), it is necessary to convert this concentration to molal scale (m). The hydrogen ion concentration (M_{H^+}) measured in ionic strength multicomponent system is converted to value in (m) according to the following equation:

$$m_{H^+} = \frac{M_{H^+}}{d - \sum \frac{M_i F_i}{1000}} \quad (6)$$

where m_{H^+} = hydrogen ion concentration in molal units, M_{H+} = hydrogen ion concentration in molar units, d = density of the solution in g/cm^3, M_i = molar concentration of component *i*, and F_i = formula weight of component *i* in g/mol.

3. Results

The dissociation constants of the Ox measured at 25 °C in the range 0.1–6.60 m $NaClO_4$ are listed in Table 1. The errors reported in Table 1 represent estimated standard deviations of duplicate pKa determinations. The reproducibility of the titration experiments corresponds to the precision typically obtained by potentiometry with a hydrogen ion glass electrode. The potentiometric titration data of Ox obtained at different ionic strength are listed in the Supporting Information (Table S1). The PSEQUAD program (Zekany and Nagypal, 1985) was used to evaluate the dissociation values from the titration curve. For all calculations, including construction of the pcH vs pHr calibration curves, pK_w (ionization constant of water) values determined at the appropriate ionic strengths of $NaClO_4$ were used. The dissociation of the positively charged species H_3Ox^+ was not taken into account in this study. Although, in one study (Likachina, 1970), formation of H_3Ox^+ in strong acids has been postulated based on electro-migration in concentrated perchloric acid solutions. However, the existence of the species H_3Ox^+ has not been confirmed by any other method. In the NEA review by Hummel et al. (2005), no consideration was given to the formation of this cationic species.

A large number of references can be found in the literature on the dissociation constants of Ox. For example, Kettler et al. (1998) carefully measured the first and second molal dissociation constants of Ox by potentiometric titrations in a concentrated cell fitted with hydrogen electrodes. Measurements were made at six temperatures ranging from 5 °C to 125 °C at four ionic strength ranging from 0.1 to 1.0 m NaCl and $NaCF_3SO_3$. The second molal dissociation constant was measured in $NaCF_3SO_3$ media only. McAuley and Nancollas (1960) used Harned cells (i.e., cells that contained a hydrogen electrode and a silver–silver chloride electrode without a liquid junction) to measure Ka_1 values in very dilute oxalic acid and HCl solutions at temperatures from 0 to 45 °C. Pinching and Bates (1948) determined the second dissociation constant of Ox at intervals of 5° from 0° to 50 °C by measurement of the electromotive force of cells without liquid junction. Hydrogen and silver–silver chloride electrodes were employed. The solutions were composed of KHOx, Na_2Ox and NaCl with an ionic strength ranging from 0.05 to 0.75 mol/kg. The data collection comprises 617 measurements made at 11 temperatures and 4 different ionic media with

Table 1
Dissociation constants of Ox determined for different $NaClO_4$ concentrations at 25 °C ($H_{n-i+1}L \leftrightarrows H_{n-i}L + H$, where Ka_i is a constant and n = 2).

Method	Ionic medium	−log Ka_1	−log Ka_2	Reference
Pot	0.1 m $NaClO_4$	1.20 ± 0.08	3.89 ± 0.05	This work
	0.30 m $NaClO_4$	1.07 ± 0.09	3.76 ± 0.04	This work
	0.51 m $NaClO_4$	1.10 ± 0.10	3.71 ± 0.04	This work
	1.03 m $NaClO_4$	1.09 ± 0.11	3.60 ± 0.04	This work
	2.18 m $NaClO_4$	1.18 ± 0.10	3.55 ± 0.05	This work
	3.44 m $NaClO_4$	1.14 ± 0.09	3.64 ± 0.03	This work
	4 .92 m $NaClO_4$	1.20 ± 0.10	3.76 ± 0.05	This work
	6.60 m $NaClO_4$	1.22 ± 0.09	3.99 ± 0.03	This work

Pot = potentiometer.

respect to the ratio of KHOx (potassium hydrogen oxalate), Na_2Ox and NaCl. Their experimental emf data were later refitted together with new measurements by Kettler et al. (1998). Partanen et al. (2009) re-evaluate the first and second molal dissociation constants of Ox at temperatures ranging from 0 °C to 60 °C in aqueous buffer solutions containing oxalic acid, KHOx, and KCl and an ionic strength of up to 1.0 mol/kg. The required Hückel parameters for oxalate and Ka_1 and Ka_2 values for oxalic acid at various temperatures were estimated experientially using Harned cell or taken directly from Pinching and Bates (1948) and Juusola et al. (2007). The selected literature data on the dissociation constants of the Ox are summarized in Table 2.

Solvent extraction technique was used for the measurement of the distribution ratio, D ($=[M]_{total,\ org}/[M]_{total,\ aq}$) of Am^{3+}, Cm^{3+} and Eu^{3+} between an aqueous phase and the organic phase The extraction experiments were conducted in 20 mL liquid scintillation vials at pcH = 3.60 ± 0.05. The HDEHP solution in heptane was pre-equilibrated with an aqueous phase identical to that used in the extraction to ensure that the pcH of the solution was constant during the extraction experiments. Volumes, 3.0 mL, of the pre-equilibrated organic phase (2.0×10^{-4} for Eu^{3+} and 5.0×10^{-4} M for Am^{3+} and Cm^{3+}) and of the aqueous phase containing one of the radiotracer and Ox in desired ionic strength were shaken in a water bath (Cole-Parmer Inst. Co, Polystat Model 1200-00 circulator) at 180 rpm for 1 h at 25.0 ± 0.1 °C. Kinetics studies confirmed that the extraction equilibrium was attained in 1 h. The concentration of Ox was varied from 1.0×10^{-4} to 1.0×10^{-3} M for the determination of the stability constant. After the equilibrium was reached, the vials were centrifuged for 3–5 min, 0.50 mL of duplicate samples were taken from both phases to measure the α-activity in a LSC by mixing aliquots of the samples with approximately 10 mL ecolite. A separate set of experiments were conducted to determine the quenching effect of the aqueous and organic phases. No quenching effect was observed either by the aqueous or organic phase under the experimental conditions. The remaining aqueous phase was used for measurement of the equilibrium pcH.

The distribution coefficients of Am^{3+}, Cm^{3+}, and Eu^{3+} measured in the presence of different concentrations of oxalate at the different ionic strengths, were used to calculate the stability constants for the complex. The stability constants of Am^{3+}, Cm^{3+}, and Eu^{3+} with Ox calculated from the solvent extraction experiments are listed in Table 3. Typical plots of $(D_0/D - 1)$ as a function of $[Ox]^{2-}$ for Am^{3+} at different ionic strength are shown in Fig. 1. Non-linear curve indicates the formation of more than one complex species. The measured Am^{3+}–Ox stability constants in 5.0 m $NaClO_4$ were used for the speciation calculation. The speciation diagram illustrated in Fig. 2 indicates percentage of 1:1 Am^{3+}–Ox complexation increases to a maximum at 0.00012 M Ox and then, decreases as the higher oxalate concentrations favor formation of the 1:2 complex. The protonated Am^{3+}–Ox complex was not observed under the conditions employed in this study.

Data from Tables 1 and 2 were used to calculate parameters for the Pitzer model. All data were given equal weight in the calculations. Tables 5 and 6 list Pitzer parameters and standard state dimensionless chemical potential, respectively calculated in this work. To test the reliability of the combine fitting model, the stability constant data obtained by Choppin et al. (2001) are reproduced. A comparison of these values with the model is shown in (Table 6 and Fig. 4).

4. Discussion

The dissociation constants of Ox measured at 25 °C in the range 0.1–6.60 m $NaClO_4$ are listed in Table 1. Many literature data are available for Ox in a number of ionic media and temperature. Some of them are listed in Table 2 for comparison. The large errors for pKa_1 of Ox reflect the difficulty in calculating this constant when less than 5% of the deprotonated species is present at the beginning of the forward

Table 2
Literature data on the dissociation constants of Ox. Uncertainties are included as reported in the references.

Method	Ionic medium	$-\log Ka_1$	$-\log Ka_2$	Reference
Pot	dil NaCl	–	4.266	Pinching and Bates (1948)
Pot	0.1 M $NaClO_4$	1.37 ± 0.02	3.81 ± 0.02	McAuley and Nancollas (1960)
Pot	0.5 M $NaClO_4$	1.32 ± 0.01	3.63 ± 0.01	Bhat et al. (1965)
Pot	1.0 M $NaClO_4$	1.07 ± 0.05	3.57 ± 0.02	Bottari and Ciavatta (1965)
Pot	1.0 M $NaClO_4$	1.08 ± 0.01	3.55 ± 0.01	Moorhead and Sutin (1966)
Pot	3.0 M $NaClO_4$	1.26 ± 0.03	3.80 ± 0.01	Moorhead and Sutin (1966)
Pot	3.0 M $NaClO_4$	1.27 ± 0.01	3.82 ± 0.01	Cruywagen and Heyns (1983)
Sp	3.0 M $NaClO_4$	1.26 ± 0.01	3.84 ± 0.01	Cruywagen and Heyns (1983)
Pot	0.1 M KNO_3	1.26 ± 0.05	3.82 ± 0.01	Condike and Martell (1969)
Pot	1.0 M KNO_3	1.1	3.62 ± 0.01	Rajan and Martell (1967)
Pot	0.52 M $LiClO_4$	1.00 ± 0.05	3.50 ± 0.03	Deneux et al. (1968)
Pot	1 M $LiClO_4$	0.84 ± 0.05	3.35 ± 0.01	Ciavatta et al. (1970)
Pot	0.5 M NaCl	1.16 ± 0.03	3.60 ± 0.010	Fuentes et al. (1989)
Pot	1 M NaCl	0.89 ± 0.02	3.52 ± 0.02	Cruywagen et al. (1986)
Pot	0.1 M $NaClO_4$	–	3.97 ± 0.01	Choppin and Chen (1996)
	0.3 M $NaClO_4$	–	3.73 ± 0.01	Choppin and Chen (1996)
	0.5 M $NaClO_4$	1.28 ± 0.03	3.65 ± 0.01	Choppin and Chen (1996)
	1 M $NaClO_4$	1.33 ± 0.04	3.60 ± 0.01	Choppin and Chen (1996)
	3 M $NaClO_4$	1.49 ± 0.02	3.84 ± 0.01	Choppin and Chen (1996)
	5 M $NaClO_4$	1.42 ± 0.04	4.23 ± 0.01	Choppin and Chen (1996)
	7 M $NaClO_4$	1.75 ± 0.01	4.71 ± 0.01	Choppin and Chen (1996)
	9 M $NaClO_4$	2.13 ± 0.05	5.11 ± 0.04	Choppin and Chen (1996)
Pot	0.3 m NaCl	1.06 ± 0.03	3.67 ± 0.02	Mizera et al. (1999)
	1 m NaCl	0.9 ± 0.20	3.52 ± 0.02	Mizera et al. (1999)
	2 m NaCl	0.9 ± 0.10	3.54 ± 0.02	Mizera et al. (1999)
	3 m NaCl	0.86 ± 0.07	3.55 ± 0.02	Mizera et al. (1999)
	4 m NaCl	1.04 ± 0.05	3.74 ± 0.02	Mizera et al. (1999)
	5 m NaCl	1.2 ± 0.2	3.85 ± 0.02	Mizera et al. (1999)
Pot	0.1 M NaCl	–	3.80 ± 0.01	Kettler et al. (1998)
	2.0 M NaCl	–	3.47 ± 0.01	Kettler et al. (1998)
	3.15 M NaCl	–	3.52 ± 0.01	Kettler et al. (1998)
	5 M NaCl	–	3.73 ± 0.01	Kettler et al. (1998)

Pot = potentiometer; Sp = spectrophotometer, m = molal, M = molar.

Table 3
The stability constants (log β_{101} and log β_{102}) for the formation of $M(Ox)^{+}$ and $M(Ox)_2^{-}$ complexes at 25 °C for the reactions: $M^{3+}+Ox^{2-} \leftrightarrows M(Ox)^{+}$; $M^{3+}+2Ox^{2-} \leftrightarrows M(Ox)_2^{-}$, (where M^{3+} = Am, Cm and Eu; temp. 25 °C).

Cation	Ionic medium	log β_{101}	log β_{102}
Am^{3+}	0.1 m $NaClO_4$	5.25 ± 0.08	8.92 ± 0.07
	0.30 m $NaClO_4$	4.91 ± 0.09	8.83 ± 0.06
	0.51 m $NaClO_4$	4.69 ± 0.07	8.74 ± 0.05
	1.03 m $NaClO_4$	4.71 ± 0.08	8.69 ± 0.06
	2.18 m $NaClO_4$	4.74 ± 0.07	8.67 ± 0.07
	3.44 m $NaClO_4$	4.79 ± 0.08	8.74 ± 0.08
	4 .92 m $NaClO_4$	4.98 ± 0.08	8.89 ± 0.09
	6.60 m $NaClO_4$	5.37 ± 0.08	9.04 ± 0.09
Cm^{3+}	0.1 m $NaClO_4$	5.18 ± 0.06	8.87 ± 0.08
	0.30 m $NaClO_4$	4.88 ± 0.08	8.79 ± 0.09
	0.51 m $NaClO_4$	4.82 ± 0.09	8.76 ± 0.07
	1.03 m $NaClO_4$	4.73 ± 0.08	8.72 ± 0.10
	2.18 m $NaClO_4$	4.76 ± 0.07	8.70 ± 0.09
	3.44 m $NaClO_4$	4.87 ± 0.08	8.75 ± 0.08
	4 .92 m $NaClO_4$	5.02 ± 0.09	8.81 ± 0.09
	6.60 m $NaClO_4$	5.34 ± 0.08	8.99 ± 0.10
Eu^{3+}	0.1 m $NaClO_4$	5.12 ± 0.06	8.99 ± 0.07
	0.30 m $NaClO_4$	4.87 ± 0.07	8.91 ± 0.08
	0.51 m $NaClO_4$	4.77 ± 0.08	8.82 ± 0.09
	1.03 m $NaClO_4$	4.80 ± 0.08	8.76 ± 0.07
	2.18 m $NaClO_4$	4.78 ± 0.09	8.74 ± 0.09
	3.44 m $NaClO_4$	4.84 ± 0.08	8.78 ± 0.10
	4.92 m $NaClO_4$	4.91 ± 0.06	8.83 ± 0.09
	6.60 m $NaClO_4$	5.03 ± 0.08	8.93 ± 0.09

titration. Our pKa_2 values are close to those of Choppin and Chen (1996), while the pKa_1 values are constantly lower than the reference data. Our values of pKa_2 are also somewhat higher than the corresponding values

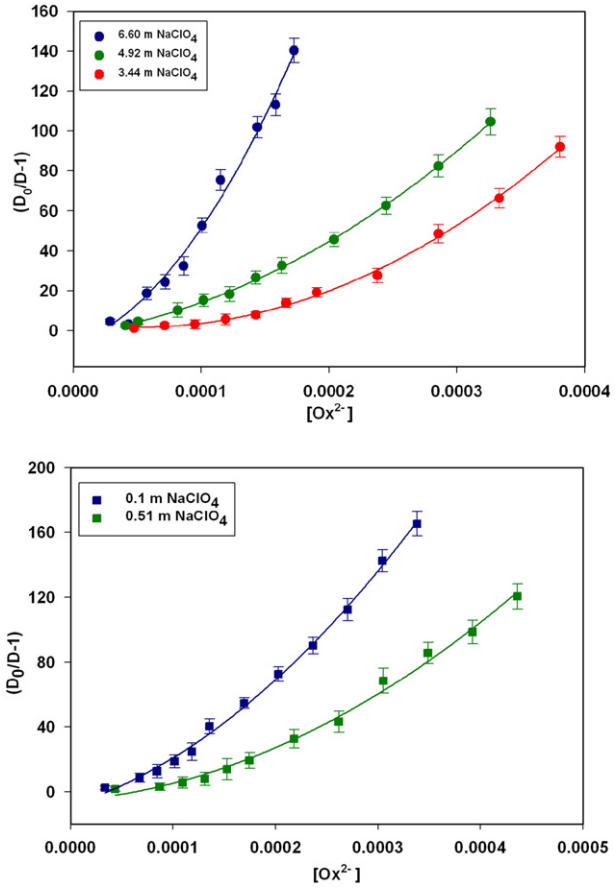


Fig. 1. Plot of (D_0/D − 1) as a function of free oxalate concentrations for Am^{3+} at different ionic strength, pcH = 3.6.

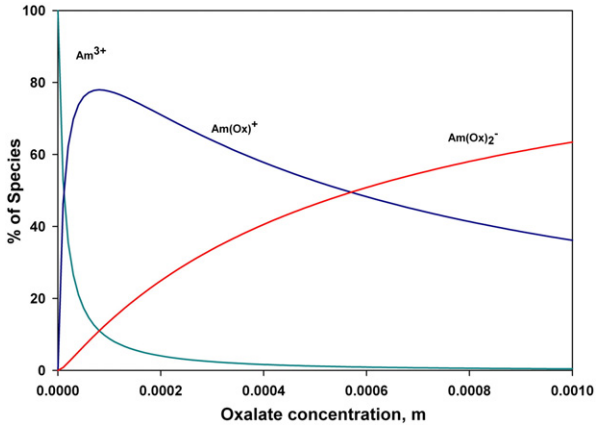


Fig. 2. The content of the different Am^{3+} species as a function of the oxalate concentrations for 6.6 m $NaClO_4$.

measured in NaCl medium by Kettler et al. (1998), and Mizera et al. (1999). The dissociation constant values are known to dependent significantly on ionic media. It has been reported (Mizera et al., 1999) that for background electrolytes with Na^{+} as cation and Cl^{-}, ClO_4^{-}, or I^{-} as anions, the differences in dissociation constant values are minimal at I < 0.1 m where Debye–Hückel limiting law is valid, and the SIT calculations yield comparable thermodynamic constants for the different electrolytes. At higher ionic strengths the difference in the "specific ionic interactions" become more pronounced, which results in an decrease in dissociation values in the approximate order: NaCl < $NaClO_4$ < NaI.

Ox is quite a strong complexing agent, because of its ability to form 5-membered chelate rings upon complexation with metal ions. Ox may coordinate metal ions with its two carboxylic groups. Complexes with stoichiometry >1:1 is common. However, the number of complex actually formed in aqueous solution depends on the charge and size of the metal ion. The stability constant of Am^{3+}, Cm^{3+} and Eu^{3+} with Ox reported in the literature by various methods such as solvent extraction, ion exchange, and electro-migration are summarized in Table 4.

There are large discrepancies (about one to two orders of magnitude) between the values from the various methods. As shown in Table 4, the formation of $M(Ox)^{+}$ and $M(Ox)_2^{-}$ complexes are the most common. Although several papers report the formation of $M(Ox)_2^{3-}$ complex as well for trivalent actinides (Pazukhin et al., 1987; Bykhovskii and Petrova, 1974), its presence is not observed in this work. The formation of protonated complexes with HOx^{-} is also reported in some studies. However, no reliable values for $Am(HOx)_n^{3-n}$ (n = 1) were recommended in the NEA report by Hummel et al. (2005). In solutions of higher pcH (pH > 7.0), the formation of hydrolysis complexes were reported by Caceci and Choppin (1983) and Choppin and Chen (1996). Since our experiments were conducted at pcH = 3.60, the hydrolysis reactions of Am^{3+}, Cm^{3+}, and Eu^{3+} were not included in the calculations.

Currently, most experimental work on stability constants of actinides with organic ligands that are present in the WIPP wastes is usually limited up to ionic strength of 1.0 m. Fortunately, there is one set of data available in the literature for Am–Ox complex measured in 0.1 to 5.0 m NaCl and $NaClO_4$ solutions that can be directly compared with data generated in this study. The reported log β_{101} values for Am^{3+} vary from 5.25–4.54 and the corresponding log β_{102}, from 7.91–9.42 in 0.1–9.0 M $NaClO_4$, while in NaCl medium log β_{101} values vary from 4.17–4.63 and the corresponding log β_{102}, from 7.77–8.6. Our log β_{101} value at 25 °C is higher than the value reported in (Borkowski et al., 2001), but the corresponding log β_{102} is in fair agreement with the literature data. The concentration range of our studies, the formation of only 1:1 and 1:2 complexes were observed. The stability constant values of the 1:1 complex increased in the order: $NpO_2^{+} < Am^{3+} < UO_2^{2+} < Th^{4+}$ in accordance with the metal charge density, reflecting strong ionic bonding.

Table 4
Literature data of log β_{101} and log β_{102} for the formation of $M(Ox)^{+}$ and $M(Ox)_2^{-}$ complexes at 25 °C for the reactions: $M^{3+} + Ox^{2-} \leftrightarrows M(Ox)^{+}$; $M^{3+} + 2Ox^{2-} \leftrightarrows M(Ox)_2^{-}$ (where M^{3+} = Am, Cm and Eu).

M^{3+}	Method	Ionic medium	Temp (°C)	log β_{101}	log β_{102}	References
Am^{3+}	cix	0.2 M $NH_4Cl \rightarrow 0$	20–25	5.99	10.15	Lebedev et al. (1960a)
	sol	0	25	6.89	9.73	Pazukhin et al. (1987)
	sol	0.2–0.7 M (H^+,K^+,ClO_4^-, Ox^{2-}, HOx^-) → 0	25	7.30 ± 0.06	11.46 ± 0.10	Lebedev et al. (1960b)
	em	0.2–0.3 M (H^+,NH_4^+,Cl^-, Ox^{2-}, Hox)	25	6.15 ± 0.16	10.54 ± 0.19	Stepanov and Makarova (1965)
	sx	1.0 M $NaClO_4$	25	4.63 ± 0.08	8.35 ± 0.09	Sekine (1964)
	cix	0.5 M $NaClO_4$	25	4.82 ± 0.03	8.60 ± 0.04	Aziz et al. (1968)
	em	0.1 M	25	5.25 ± 0.10	8.85 ± 0.10	Stepanov (1971)
	sx	0.7 M NaCl	21	4.58 ± 0.05	7.91 ± 0.10	Caceci and choppin (1983)
	em	0.01 $Na(H)ClO_4$	25	5.38 ± 0.18	8.96 ± 0.34	Rösch et al. (1990)
		0.05 $Na(H)ClO_4$	25	5.11 ± 0.13	8.30 ± 0.19	Rösch et al. (1990)
		0.10 $Na(H)ClO_4$	25	5.01 ± 0.13	8.16 ± 0.20	Rösch et al. (1990)
	sx	1.0 M $NaClO_4$	25	4.61 ± 0.06	8.39 ± 0.12	Choppin and Chen (1996)
		3.0 M $NaClO_4$		4.65 ± 0.04	8.67 ± 0.13	Choppin and Chen (1996)
		5.0 M $NaClO_4$		4.83 ± 0.06	9.24 ± 0.09	Choppin and Chen (1996)
		7.0 M NaClO4		4.93 ± 0.11	9.42 ± 0.06	Choppin and Chen (1996)
		9.0 M NaClO4		4.54 ± 0.06	8.77 ± 0.05	Choppin and Chen (1996)
	sx	0.3 m NaCl	25	4.53 ± 0.01	8.22 ± 0.02	Choppin et al. (2001)
		1 m NaCl		4.17 ± 0.05	7.77 ± 0.08	Choppin et al. (2001)
		2 m NaCl		4.40 ± 0.04	8.22 ± 0.03	Choppin et al. (2001)
		3 m NaCl		4.56 ± 0.04	8.42 ± 0.07	Choppin et al. (2001)
		4 m NaCl		4.63 ± 0.04	8.46 ± 0.02	Choppin et al. (2001)
		5 m NaCl		4.57 ± 0.06	8.6 ± 0.10	Choppin et al. (2001)
Cm^{3+}	em	0.1	25	5.25 ± 0.10	8.85 ± 0.10	Stepanov (1971)
		6.60 m $NaClO_4$		5.34 ± 0.08	8.99 ± 0.10	This work

sx = solvent extraction, ix = ion exchange, em = electromigration, cix = cation exchange, and sol = solubility.

5. Pitzer parameters calculation

Numerous models exist for accurately calculating equilibrium concentrations in low ionic strength solutions. Very few methods can adequately describe solution behavior in concentrated electrolytes. The activity coefficient formalism of Pitzer (1991) has been parameterized for concentrated aqueous electrolyte systems by Harvie et al. (1984) who have demonstrated the reliability of this formalism and database for predicting mineral solubility using chemical equilibrium in electrolyte from zero to high ionic strength. The Pitzer (1973, 1991) ion-interaction model is a semi-empirical model for calculating activity coefficients for high ionic strength, and has been proven to be the most accurate model for describing high ionic strength systems (e.g., Harvie et al., 1984). The Pitzer model expresses the excess energy of aqueous ion solution as a revised Debye–Hückel term plus the terms originating from possible ion interactions, with each described quantitatively by a specific parameter. In this model, the effect of an ion on the excess energy of another ion is proportional to the concentration of the former ion, thus only the terms for interactions with macro components are necessary to be retained in the calculation of the activity coefficient. The SIT (Specific Ion Interaction Theory) model, which is generally valid to ionic strength up to 3.5 m, has been recommended and widely used in the NEA reviews for evaluation of experimental data (e.g., Hummel et al., 2005). The SIT model, because of its less parameterized nature, is inherently less precise in reproduction of highly precise activity (and osmotic) coefficient data than the more parameterized Pitzer model, especially in high ionic strength region, even though it is advantageous in its mathematical simplicity. Therefore, the Pitzer formalism is the preferred method in treatment of activity (and osmotic) coefficients and other thermodynamic properties with high precision. Since our data is mainly in the high ionic strength region, we chose to estimate Pitzer parameters from regression analysis of our experimentally measured data. Parameters for use with the Pitzer equations are not unique; different sets of parameters can be used to provide an identical description of the same data. Therefore, it is imperative that parameters are not mixed and matched indiscriminately. Judicious selection of new parameters and careful referencing to a specified base model is required. For this and other work for the WIPP, the database developed by Harvie et al. (1984) and later extended by Felmy and Weare (1986) is the reference base model. The reference database is used for calculating new parameters values when additional species and ion interactions are included, maintaining and ensuring internal consistency with the reference database.

The Pitzer parameters and standard chemical potentials were calculated using the NONLIN version 2.0 software, which is a Gibbs energy minimization routine developed by A. Felmy at PNNL. For interested readers, its user's manual (Babb, 1996) in which numerous examples for fitting Pitzer parameters have been provided, is available from the WIPP Record Center at the address of the second author of this paper. The primary database, which was developed by Harvie and coworkers (Harvie and Weare, 1980; Harvie et al., 1984), contains basic parameters necessary to model the brine system at WIPP and it served as the reference database for the parameterization of other species in the WIPP model. The WIPP database includes standard chemical potentials (μ^o/RT) and Pitzer parameters to describe actinide interactions in the brine (Novak et al., 1996) and is continuously updated. Compilation of the database has been detailed in our previous publication (Thakur et al., 2014). The WIPP database formatted for the Fracture Matrix Transport (FMT) (Novak, 1996a) code, which was approved by U.S. EPA for predicting actinide solubilities for the WIPP Compliance Certification Application (CCA) in 1996 (U.S. DOE, 1996), and Compliance Re-Certification Applications in 2004 (CRA-2004) (U.S. DOE, 2004), and in 2009 (CRA-2009) (U.S. DOE, 2009). In September, 2011, U.S. EPA approved change of WIPP database format from the FMT code to EQ3/6 Version 8.0a, and the WIPP database subsequently changed to the EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011).

5.1. Modeling of dissociation constants of oxalic acid

A reliable model for the dissociation of Ox in dilute to concentrated $NaClO_4$ is required to interpret complexation of Am^{3+}, Cm^{3+} and Eu^{3+} with Ox in $NaClO_4$ media. For evaluation of ion interaction parameters related to the Ox ligand, the most suitable data are the experimentally measured dissociation constant values obtained at different ionic

strengths. In the work of Choppin et al. (2001), the authors reported Pitzer binary interaction parameters for Na^+–HOx^-, and Na^+–Ox^{2-} ion pairs using their dissociation constant values as a function of ionic strength in NaCl media. In the fitting process, they set $\beta^{(1)}$ for each of the above interaction pairs to certain values and derive the rest of the interaction parameters (i.e., $\beta^{(0)}$, and C^{Φ}). In this work, we combine our dissociation constant data obtained in $NaClO_4$ media with the dissociation data of Choppin and Chen (1996) also measured in $NaClO_4$, and that of Mizera et al. (1999) and Choppin et al. (2001) dissociation data in NaCl media and then, simultaneously fitted these four sets of data (Tables 3 and 4, Figs. 3–4). As shown in Figs. 3–4, the model provides a good representation of the dissociation constant values of Ox in both NaCl and $NaClO_4$ media. It is important to note that the first dissociation constant model presented by Choppin et al. (2001) was based on the studies extending only up to 1.0 m NaCl. In combination with our data, a significant improvement of the modeling was obtained. The log Ka_1 value calculated by Choppin et al. (2001) was −1.39, which is significantly different from the value obtained in this work −1.71 ± 0.15. This difference can be attributed to the lack of sufficient data points in Choppin et al. (2001) for extrapolation to infinite dilution. In contrast, the log Ka_2 values obtained from this work are consistent with those determined by Choppin et al., 2001.

It should be mentioned that the interaction parameters, i.e., lambda parameters, for all fully protonated organic acid neutral species in the WIPP database are set to zero (e.g., Novak, 1996b; Novak and Moore, 1996; Borkowski et al., 2000, 2003; Choppin et al., 2001; Wolery et al., 2010; Xiong, 2011; Thakur et al., 2014). In the present modeling, the lambda parameters for the interactions with neutral species, $H_2Ox(aq)$, are also set to zero to maintain the internal consistency of the WIPP database. Qafoku and Felmy (2007) parameterized the lambda parameters with non-zero values for interactions of $H_2Ox(aq)$ with Na^+, Cl^-, NO_3^-, HSO_4^- and $H_3PO_4(aq)$ for extremely high acidity conditions with total acidity up to ~13 m. Then, they re-fit the apparent equilibrium constant data for dissociation of oxalic acid in NaCl medium from Mizera et al. (1999) to obtain the binary interaction parameters for Na^+–HOx^- and Na^+–Ox^{2-}. Those binary interaction parameters were applied for their subsequent investigation of aluminum speciation in acidic range (Boily et al., 2007).

5.2. Modeling of formation constants of Am^{3+}, Cm^{3+}, and Eu^{3+} with oxalic acid

In modeling complexation of Am^{3+}, Cm^{3+}, and Eu^{3+} with Ox^{2-}, ternary interaction parameters (theta and psi parameters) of Ox^{2-} with ClO_4^- and Na^+ are set to zero, in consistent with the model approach of Choppin et al. (2001). The log β_{101} value of 6.16 for

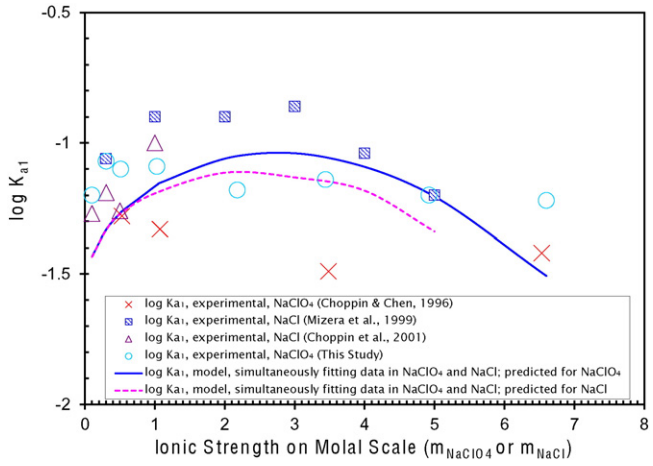


Fig. 3. A plot showing the first dissociation constants of oxalic acid as a function of molality of $NaClO_4$ or NaCl.

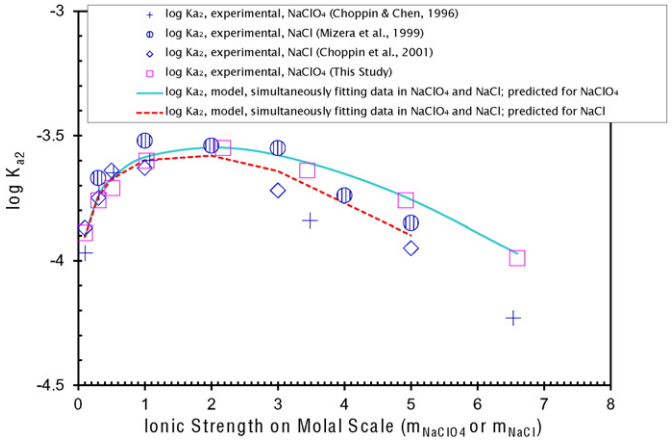


Fig. 4. A plot showing the second dissociation constant of oxalic acid as a function of molality of $NaClO_4$ or NaCl.

$Am(Ox)^+$ in NaCl medium (Table 6) is similar to the value 6.30 ± 0.06 obtained in this work by simultaneously fitting experimental data in both NaCl and $NaClO_4$ media (Fig. 5). The log β_{102} for $Am(Ox)_2^-$ evaluated by this combine approach is 10.84 ± 0.06 (Table 6 and Fig. 6). Further, the log β_{101} for $Cm(Ox)^+$ and $Eu(Ox)^+$, and β_{102} for $Cm(Ox)_2^-$ and $Eu(Ox)_2^-$ evaluated from our data in $NaClO_4$ media only are consistently higher than the respective log β_{101} for $Am(Ox)^+$ and β_{102} for $Am(Ox)_2^-$. This difference can be attributed to the complexation of Am^{3+} with chloride in NaCl solutions. The complexation of Am^{3+} by Cl^- has been studied by a variety of methods (Fuger et al., 1992; Barbanel and Mikhailova, 1969), and values of stability constant ranging from −0.2 to 0.3 were reported from the solvent extraction and cation exchange experiments. However, a much lower value (log $\beta_1 \sim -2$) was reported by Barbanel and Mikhailova for Am–Cl complex from absorption spectra in presence of 0.1–12.6 M or 0–10.75 M HCl. This contradiction has also been observed in Np(V)–Cl (Neck et al., 1995; Fanghänel et al., 1995) and Cm(III)–Cl (Fanghänel et al., 1999) systems and has been discussed in terms of the difference between these methods in the measurements of various factors (Neck et al., 1995; Choppin, 1997). The spectroscopic method usually measures inner sphere complexation only, while methods such as solvent extraction and ion exchange may take into account an overall effect from many factors such as the activity coefficient,

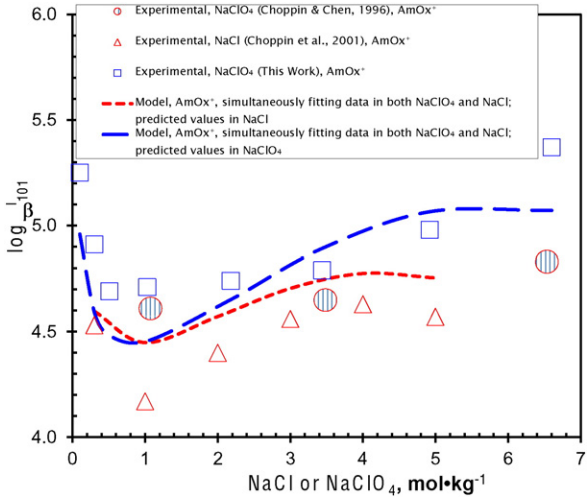


Fig. 5. A plot showing the formation constant of $Am(Ox)^+$ as a function of molality of $NaClO_4$ or NaCl The size of errors bars is equal to or smaller than that of symbols.

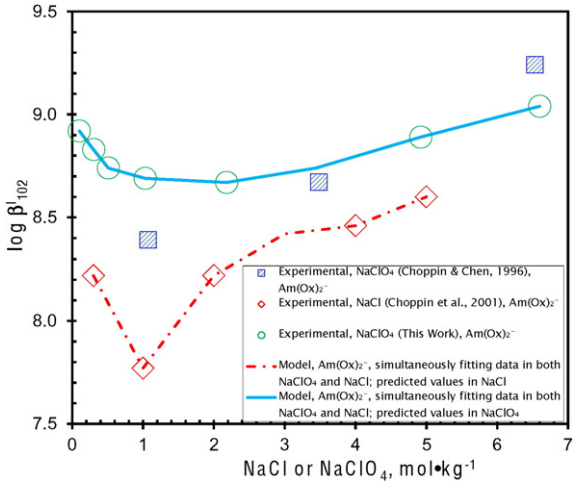


Fig. 6. A plot showing the formation constant of $Am(Ox)_2^-$ as a function of molality of $NaClO_4$ or NaCl The size of errors bars is equal to or smaller than that of symbols.

inner sphere complexation, and outer sphere complexation. Since it is common practice to incorporate the weak interactions (such as outer sphere complexation) into the activity coefficient, the spectroscopic method should provide a relatively reliable evaluation of the extent inner sphere metal complexation. In Fig. 7, experimental and model-predicted apparent stability constants of Cm–Ox and Eu–Ox systems are plotted as a function of $NaClO_4$ molality. The model-predicted values calculated using the interaction parameters are listed in Table 5 and μ^o/RT values are presented in Table 6. The plot in Fig. 6 demonstrates that the proposed model reasonably reproduces experimental values over the entire ionic strength range up to 6.6 m.

In NEA database, Hummel et al. (2005) calculated log β_{101} value of 6.51 ± 0.12 for the complex $Am(Ox)^+$, and log β_{102} value of 10.71 ± 0.20 for the complex $Am(Ox)_2^-$ using the SIT model for extrapolation. Most of the experimental data used for the extrapolation in that study was taken from Choppin et al. (2001) determined in NaCl medium. Our log β_{101} value is slightly lower than the value obtained by Hummel et al. (2005), but our log β_{102} value is pretty close to their value.

5.3. Interactions of other environmentally important metal cations with oxalic acid

The organic ligands such as oxalate present in the WIPP waste may complex with actinides, which may lead to increased dissolved actinide concentrations. Therefore, potential effect of organic ligands is important for WIPP PA. In addition to actinides, the WIPP repository contains high concentrations of a number of other environmentally important metal cations, such as Pb^{2+} that can complex with the organic ligands, possibly mitigating the ability of the organic ligands to impact repository performance with respect to actinide solubility. Further, industrial grade MgO is currently being emplaced in the WIPP (it is estimated that over 75,000 tons will be emplaced in the WIPP by the time of repository closure) as an engineered barrier to reduce solubility of actinides by buffering brine pH in the mildly alkaline range and to sequester CO_2 that could be produced by the microbial consumption of cellulosic, plastic and rubber materials. Besides, one of the WIPP brine, GWB contains 1.16 m Mg^{2+} (Xiong and Lord, 2008). In addition, Ca^{2+} present in the brines could also compete for soluble oxalate (e.g., Qafoku and Felmy, 2007). The competition of these metals with the actinides for binding to Ox must be considered in an assessment of the possible role of the ligands in actinide solubility. Given the comparable complexation strength of non-actinides as well as that of actinides with Ox, it is safe to assume that the displacement of Am–Ox complex by non-actinides–Ox complex may be highly likely. The complexation and solubility data for the competing metals are being collected (e.g., Pb, Xiong et al., 2013) to support our assumptions and to interpret the data using the thermodynamic formalism of Pitzer. The Pitzer ion interaction parameters so obtained would be included in the WIPP actinide solubility database.

6. Conclusion

The present investigation is continuation of the work previously carried out by Choppin and Coworkers at Florida State University on the determination of Pitzer parameters of the major actinides species applicable to the performance assessment of the WIPP. Our main goal was to construct a more universal thermodynamic model, which can provide an improved set of Pitzer parameters for the interaction of actinides species important to the WIPP. The "combined fitting model approach" has

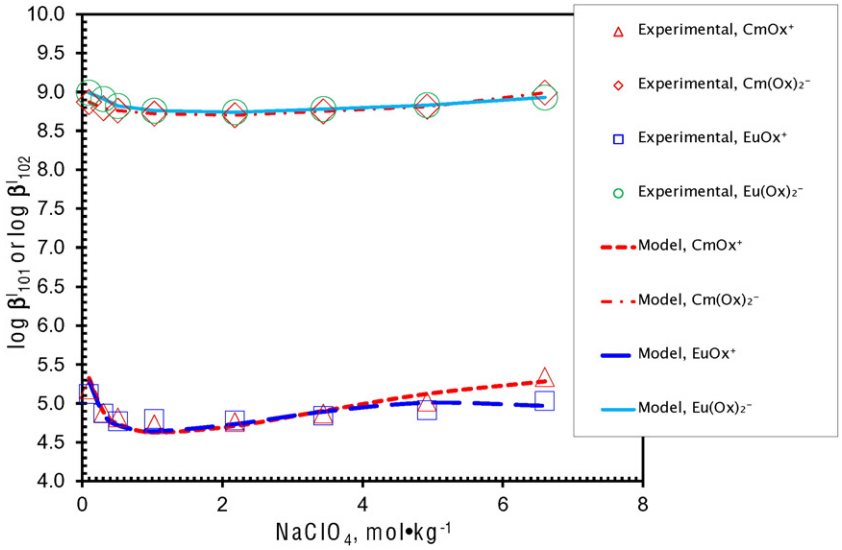


Fig. 7. A plot showing the formation constants of $Cm(Ox)^+$, $Cm(Ox)_2^-$, $Eu(Ox)^+$ and $Eu(Ox)^{2-}$ as a function of molality of $NaClO_4$. The size of errors bars is equal to or smaller than that of symbols.

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)

demonstrated to provide superior Pitzer parameters and it better reflects the effect of ionic strengths than the parameters that currently exist in the WIPP database. Furthermore, an ionic strength range was extended to 6.6 m and more data points were added in the lower ionic strength regions. In the concentration range adopted in this study, the formation of 1:1 and 1:2 complexes of Ox with trivalent metal ions was observed. The experimentally determined dissociation constants and the stability constants were successfully modeled using the Pitzer formalism with $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} interaction parameters. The Pitzer model developed in this study gives an excellent representation of the data over the entire range of ionic strengths. The Pitzer parameters determined in this work can be used to describe speciation of trivalent actinides in the presence of oxalate in a wide range of environments, including concentrated brine solutions specific to the WIPP. The work is also applicable to the accurate modeling transport of rare earth elements in various environments under the surface conditions.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2015.07.029.

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).

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