



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



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ARTICLE INFO

Article history:

Received 25 January 2015

Received in revised form 21 July 2015

Accepted 22 July 2015

Available online 30 July 2015

Keyword:

Oxalic acid dissociation constants

Am–Cm–Eu–oxalic acid complexation

Pitzer parameters

Extraction

High ionic strength

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, $\text{M}(\text{Ox})_n^{3-2n}$, where ($\text{M} = \text{Am}^{3+}$, 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 $> 3700 \text{ Bq/g}$ ($> 100 \text{ nCi/g}$). 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 = $6.5 \times 10^{-5} \text{ M}$, Ac = $1.9 \times 10^{-2} \text{ M}$, Ox = $1.7 \times 10^{-2} \text{ M}$, and Cit = $2.4 \times 10^{-3} \text{ M}$ (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/NaClO₄ 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 NaClO₄ media up to 9.0 M NaClO₄. Erten et al. (1994) measured the stability constants of Th(IV) and U(VI) with Ox in 0.1 to 9.0 M NaClO₄. 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 NaClO₄) 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, $\text{Am}(\text{EDTA})^-$ 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 NaClO₄ were measured using solvent extraction and potentiometric titration techniques, respectively. Stability constant data collected in 0.1 m to 6.60 m NaClO₄ were used for the Pitzer interaction parameter calculations. The thermodynamic data obtained from this study, measured in non-complexing NaClO₄ 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 NaClO₄ 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 NaClO₄ (from this study) and NaCl data (from Choppin et al., 2001) were fitted simultaneously. In contrast to the earlier model, the model developed in 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

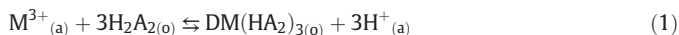
2.1. Materials

All of the reagents were ACS certified grade. NaClO₄ (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 N₂, 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 NaClO₄ 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 ²⁴¹Am, ²⁴⁴Cm and ¹⁵², ¹⁵⁴Eu radionuclides were obtained from Oak Ridge National Laboratory and their purity checked by α- and/or γ-spectrometry. The ²⁴⁴Cm was purified from its daughter nuclide ²⁴⁰Pu by anion exchange (Dowex 1 × 4) in 7.5 M HNO₃. The working stock of the tracer was prepared in a solution of pCh = 3.0 (HClO₄) 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 ²⁴¹Am, ²⁴⁴Cm and ¹⁵², ¹⁵⁴Eu 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 NaClO₄) and the organic phase (HDEHP, represented as H₂A₂, in the dimeric form) can be expressed as:



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:



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:

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

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

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