Determination of Thermodynamic and Kinetic Parameters for Complexation of Tc(IV) with F⁻, Cl⁻, Br⁻, I⁻, SO₂⁻ and PO₃⁻, acetate, citrate and EDTA

SSAA Grant DE-NA0002916

PI: Nathalie A. Wall
Co-PI: Donald Wall

Washington State University
Department of Chemistry
Lindsey Lecrivain: Ph.D. 2017
Trevor Omoto: Ph.D. 2017
Mitchell Friend: PhD Summer 2018
Cecilia Eroa Lledo: PhD candidate
Publications


• Complexation of Tc(IV) with SO$_4^{2-}$ in NaCl Medium. Parker, Omoto, Dickens, Wall, and Wall. Journal of Solution Chemistry. Submitted (2017)

• Comparison of the Solvent Extraction Behavior of ReO4- and TcO4-. Parker, Lecrivain, Lledo Eiroa Lledo, Tabada, Wall, Wall. In preparation.

• Solubility of Technetium(IV) in presence of complexing ligands. Omoto, Wall. In preparation.

• Thermodynamic parameter for the complexation of Tc(IV) with EDTA. Friend, Wall, and Wall. In preparation

• …More in preparation…

https://nawall.chem.wsu.edu/
Presentations

• Complexation of Tc(IV) with sulfate in NaCl Medium. Wall; Parker; Omoto; and Wall. Methods and Applications of Radioanalytical Chemistry, Kailua-Kona, HI 04/08-13/2018.

• Thermodynamic parameters for the complexation of Tc(IV) with EDTA. Friend, Eiroa Lledo, Lecrivain, Wall, and Wall. Methods and Applications of Radioanalytical Chemistry, Kailua-Kona, HI 04/08-13/2018.


• Method comparison for the determination of Pitzer parameters for HTcO, HReO and V₂O₃ in aqueous systems. Eiroa Lledo, Parker, Wall, Wall. ACS 253th National Meeting, San Francisco, Ca, 04/02-06/2017


Student Achievements

Gannon Parker
• Post doc 2015-2017. Now at LANL since Nov. 2017

Lindsey Lecrivain
• Ph.D. Spring 2017 (now PD at WSU)

Trevor Omoto
• PhD Spring 2017 (now staff at Hanford)

Mitchell Friend
• Ph.D. summer 2018
• Fellowship at Lawrence Livermore National Laboratory (2017)
• First Place winner in the 2017 Innovations Awards (Innovations in Nuclear Technology R&D Awards) for his paper “Hafnium(IV) complexation with oxalate at variable temperatures” and invited to present his award-winning paper at the ANS Winter Meeting 10/29-11/02/2017 in Washington DC. (2017)

Cecilia Eiroa Lledo – Ph.D. candidate
• U.S. NRC certified nuclear reactor operator
• Seaborg Fellowship at Los Alamos National Laboratory (2018)
• Invited by Stanford Center for International Security and Cooperation to participate to the Young Professionals Nuclear Forum (YPNF) with MEPhI-Stanford University. Moscow, Russia, 24-26 April, 2017

https://nawall.chem.wsu.edu/
Tc(IV)

Organic Ligands
- Stability constant determination (ΔG)
- Thermodynamic parameters (ΔH, ΔS)
- V(IV) as a cold analogue
- Solubility studies

Halide Ligands
- Stability constant determination (ΔG)
- Thermodynamic parameters (ΔH, ΔS)
- V(IV) as a cold analogue
- Solubility studies

Polyatomic Ligands

Tc(VII)

Re(VII) as a cold analogue
Extraction system for Tc(IV) complexes

With no ligand ($D_0$):
- Tc(IV) will be extracted by extractant to the organic phase
- Determine extraction mechanisms

With ligand ($D$):
- Tc(IV) will be held in the aqueous phase due to interactions with the ligands
- Only some will be extracted to the organic phase

https://nawall.chem.wsu.edu/
Tc(IV) as a cold analogue

- Stability constant determination ($\Delta G$)
  - Thermodynamic parameters ($\Delta H$, $\Delta S$)
  - Organic Ligands
    - Solubility studies
    - V(IV) as a cold analogue

Halide Ligands

- Stability constant determination ($\Delta G$)
  - Thermodynamic parameters ($\Delta H$, $\Delta S$)
  - V(IV) as a cold analogue
    - Solubility studies

Polyatomic Ligands

- Stability constant determination ($\Delta G$)
  - Thermodynamic parameters ($\Delta H$, $\Delta S$)

Tc(VII) as a cold analogue

https://nawall.chem.wsu.edu/
Tc(IV) with organic ligands

IDA
Iminodiacetic acid

NTA
Nitrilotriacetic acid

EDTA
Ethylenediaminetetraacetic acid

HEDTA
(Hydroxyethyl)ethylenediaminetriacetic acid

DTPA
Diethylenetriaminepentaacetic acid

https://nawall.chem.wsu.edu/
The stability constants for Tc(IV) at $I = 0.5$ M NaNO$_3$ and pH 2.3 reported as $\beta_{\text{app}}$ and $\beta_{1,-1,1}$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\log \beta_{\text{app}}$</th>
<th>$\log \beta_{1,-1,1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDA</td>
<td>3.9 ± 0.1</td>
<td>11.4 ± 0.3</td>
</tr>
<tr>
<td>NTA</td>
<td>4.8 ± 0.1</td>
<td>12.5 ± 0.3</td>
</tr>
<tr>
<td>HEDTA</td>
<td>6.6 ± 0.1</td>
<td>17.6 ± 0.3</td>
</tr>
<tr>
<td>DTPA</td>
<td>6.8 ± 0.1</td>
<td>22.3 ± 0.6</td>
</tr>
</tbody>
</table>


https://nawall.chem.wsu.edu/
Tc(IV) with EDTA: $\Delta H, \Delta G, \Delta S$

Plot of $1/D$ vs. concentration of free EDTA at variable $p_{C^H}$ and $T = 25.0 \pm 0.1$ °C.

\[
\frac{1}{D} = \frac{1}{D_0} + \frac{\beta_{app}}{D_0}[\text{Ligand}]
\]

\[
TcO^{2+} + EDTA^{4-} \rightleftharpoons TcOEDTA^{2-}
\]

\[
\beta_{101} = \frac{[TcOEDTA^{2-}]}{[TcO^{2+}][EDTA^{4-}]}
\]

\[
TcO^{2+} + H^+ + EDTA^{4-} \rightleftharpoons TcO(HEDTA)^-
\]

\[
\beta_{111} = \frac{[TcO(HEDTA)^-]}{[TcO^{2+}][H^+][EDTA^{4-}]}
\]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\log \beta_{app}$</th>
<th>$\log \beta_{1,1,1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>16.2 ± 0.2</td>
<td>19.48 ± 0.04</td>
</tr>
</tbody>
</table>


https://nawall.chem.wsu.edu/
V(IV) as analog of Tc(IV)?
Tc(IV) and V(IV) with organic ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Tc(IV) log(β_{app})</th>
<th>V(IV) log(β_{app})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDA</td>
<td>3.4 ± 0.1</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>NTA</td>
<td>3.7 ± 0.1</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>HEDTA</td>
<td>3.9 ± 0.1</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>DTPA</td>
<td>4.6 ± 0.1</td>
<td>5.4 ± 0.2</td>
</tr>
</tbody>
</table>

\( \beta_{app} \) stability constants for the selected ligands with Tc(IV) and V(IV) pH 2.3 in 0.5 M NaCl. reported errors: 3\( \sigma \).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Tc(IV) log(\beta_{1,-1,1})</th>
<th>V(IV) log(\beta_{1,0,1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDA</td>
<td>10.9 ± 0.1</td>
<td>9.3 ± 0.1</td>
</tr>
<tr>
<td>NTA</td>
<td>11.4 ± 0.1</td>
<td>11.6 ± 0.2</td>
</tr>
<tr>
<td>HEDTA</td>
<td>14.9 ± 0.1</td>
<td>15.8 ± 0.1</td>
</tr>
<tr>
<td>DTPA</td>
<td>20.1 ± 0.1</td>
<td>20.8 ± 0.2</td>
</tr>
</tbody>
</table>

\( \beta_{1,-1,1} \) and \( \beta_{1,0,1} \) stability constants for the selected ligands with Tc(IV) and V(IV) pH 2.3 in 0.5 M NaCl. reported errors: 3\( \sigma \).


https://nawall.chem.wsu.edu/
Tc(IV)

Organic Ligands

Stability constant determination ($\Delta G$)
Thermodynamic parameters ($\Delta H, \Delta S$)
V(IV) as a cold analogue
Solubility studies

Halide Ligands

Stability constant determination ($\Delta G$)
Thermodynamic parameters ($\Delta H, \Delta S$)
V(IV) as a cold analogue
Solubility studies

Polyatomic Ligands

Stability constant determination ($\Delta G$)
Thermodynamic parameters ($\Delta H, \Delta S$)

Tc(VII)

Re(VII) as a cold analogue

https://nawall.chem.wsu.edu/
Tc(IV) dissolution with organic ligands

The soluble Tc(IV) concentration in solutions of 10 mM of each ligand, and in ligand free control solution. Ionic strength 0.5 M (NaCl) at pH 2.3. Error: 1σ of replicate measurements.

Predicted solubility based on stability constants match experimental solubility.


https://nawall.chem.wsu.edu/
Tc(IV) as a cold analogue

Stability constant determination (ΔG)
Thermodynamic parameters (ΔH, ΔS)

Organic Ligands

V(IV) as a cold analogue
Solubility studies

Halide Ligands

Stability constant determination (ΔG)
Thermodynamic parameters (ΔH, ΔS)

V(IV) as a cold analogue
Solubility studies

Polyatomic Ligands

Stability constant determination (ΔG)
Thermodynamic parameters (ΔH, ΔS)

Tc(VII)

Re(VII) as a cold analogue

https://nawall.chem.wsu.edu/
Tc(IV) with Halides


\[
\frac{1}{D} = \frac{1}{D_0} + \frac{\beta_{\text{app}}}{D_0}[\text{Ligand}]
\]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\beta_{\text{app}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsuperscript{-}</td>
<td>0.4 ± 0.3</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>Br\textsuperscript{-}</td>
<td>2.7 ± 0.2</td>
</tr>
</tbody>
</table>

Plot of $1/D$ vs. concentration of halide
pH 2.0, T = 25.0 ± 0.1 °C

https://nawall.chem.wsu.edu/
D\textsubscript{0}/D - 1 vs. [Na\textsubscript{2}SO\textsubscript{4}] collected using 50 mM TOPO
pH = 1.51 ± 0.05. I = 1.0 m (NaCl).

Complexation of Tc(IV) with SO\textsubscript{4}\textsuperscript{2-} in NaCl Medium. T. G. Parker®, T. Omoto, S. M. Dickens, D. E. Wall, and N. A. Wall*. Journal of Solution Chemistry. Submitted (2017)

Determination of thermodynamic parameters associated with Tc(IV) Sulfate Complexation. Parker, Wall, Wall. ACS 253\textsuperscript{th} National Meeting, San Francisco, Ca, 04/02-06/2017

Complexation of Tc(IV) with sulfate in NaCl Medium. Wall; Parker; Omoto; and Wall. Methods and Applications of Radioanalytical Chemistry, Kailua-Kona, HI 04/08-13/2018

https://nawall.chem.wsu.edu/
**Tc(VII) and Re(VII) extractions**

Efficiency of extraction (log $K_{ex}$) of Tc(VII) and Re(VII) by triphenylphosphonium chloride (TPPC) with varying pH.

Efficiency of extraction of Tc(VII) and Re(VII) by triphenylphosphonium chloride (TPPC) with varying electrolytes.

Comparison of the Solvent Extraction Behavior of ReO$_4^-$ and TcO$_4^-$. T. Gannon Parker®, Lindsey Lecrivain®, Lledo Eiroa Lledo®, Diana L. Tabada, Donald E. Wall, Nathalie A. Wall*. In preparation

Comparison the Solvent Extraction Behavior of Re(VII) with Tc(VII). Lecrivain, Parker, Wall, Wall. 255th ACS National Meeting, New Orleans, LA, 03/18-22/2018

https://nawall.chem.wsu.edu/
Determination of Thermodynamic and Kinetic Parameters for Complexation of Tc(IV) with F⁻, Cl⁻, Br⁻, I⁻, SO₂⁻ and PO₃⁻, acetate, citrate and EDTA

SSAA Grant DE-NA0002916

Nathalie A. Wall; Donald Wall
Washington State University

Publications
• 3 papers published; 1 paper submitted; > 3 papers in preparation

Presentations
• 7 conference presentations 2016-2018

Achievements
• 2 Ph.D. 2017; 1 Ph.D. 2018; 1 Ph.D. 2020
• Fellowships with LANL and LLNL
• ANS award

https://nawall.chem.wsu.edu/