Impact of f-element complexation on the radiolytic robustness of separations ligands

May 2022

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INL/CON-22-67196
Reprocessing used nuclear fuel

Solvent Extraction Reprocessing
Ligands/organic diluent: HNO$_3$/H$_2$O
(± additives)

Gaseous Phase

Organic Phase

Aqueous Phase

Precipitation
Oxide Layer
Structural Materials

Uranium mine
Conversion to fuel
Reactor

Spent fuel
Plutonium and recovered uranium
Reprocessing

Waste management and storage
Reprocessing radiation challenges

- Destruction of active molecules
- Degradation product formation
- Metal ion redox chemistry

- Horne, Zarzana, Rae, Cook, Mezyk et al., PCCP, 2020, 22, 24978.
Reprocessing radiation chemistry

**Water Radiolysis**

\[ \text{H}_2\text{O} \rightarrow e^-, H^+, \cdot OH, H_2, H_2\text{O}_2, \text{H}_{\text{aq}}^+ \]

**Indirect Radiation Effects**

\[ \text{HNO}_3 + \cdot \text{OH} \rightarrow \cdot \text{NO}_3 + \text{H}_2\text{O} \]
\[ \text{NO}_3^- + e^- \rightarrow \text{NO}_3^{2-} \]
\[ \text{NO}_3^{2-} + \text{H}_2\text{O} \rightarrow \cdot \text{NO}_2 + 2\text{OH}^- \]
\[ \text{NO}_3^- + H^+ \rightarrow \text{HNO}_3^- \rightarrow \cdot \text{NO}_2 + \text{OH}^- \]
\[ \cdot \text{NO}_2 + \cdot \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \]
\[ \text{N}_2\text{O}_4 \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

**Direct Radiation Effects**

\[ \text{NO}_3^- \rightarrow \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O} \]
\[ \text{HNO}_3 \rightarrow \text{HNO}_3^+ \rightarrow \text{HNO}_2 + \text{O} \]
\[ \text{NO}_3^- \rightarrow \cdot \text{NO}_3 + e^- \]
\[ \text{HNO}_3 \rightarrow \cdot \text{NO}_3 + H^+ \]

**Alkane Radiolysis**

\[ \text{R-CH}_3 \rightarrow e^-, \text{RH}^+, \text{RH}^+, \cdot \text{CH}_3, H^+, H_2 \]

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Reprocessing radiation chemistry

Water Radiolysis

\[ \text{H}_2\text{O} \rightarrow e^{-}, \text{H}^{\cdot}, \text{•OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}^{\cdot}\text{aq}^{+} \]

Indirect Radiation Effects

\[ \text{HNO}_3 + \text{•OH} \rightarrow \text{•NO}_3^{\cdot} + \text{H}_2\text{O} \]
\[ \text{•NO}_3^{\cdot} \rightarrow \text{NO}_3^{-} + \text{e}^{-} \rightarrow \text{•NO}_3^{2-} \]
\[ \text{•NO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{•NO}_2^{\cdot} + 2\text{OH}^{-} \]
\[ \text{•NO}_3^{\cdot} \rightarrow \text{HNO}_3^{-} \rightarrow \text{•NO}_2^{\cdot} + \text{OH}^{-} \]
\[ \text{•NO}_2^{\cdot} + \text{•NO}_2^{\cdot} \leftrightarrow \text{N}_2\text{O}_4 \]

\[ \text{N}_2\text{O}_4 \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

Direct Radiation Effects

\[ \text{NO}_3^{-} \rightarrow \text{NO}_3^{-}^{\ast} \rightarrow \text{NO}_2^{\cdot} + \text{O} \]
\[ \text{HNO}_3 \rightarrow \text{•NO}_3^{\cdot} + \text{H}^{\cdot} \]
\[ \text{•NO}_3^{\cdot} \rightarrow \text{•NO}_3^{\cdot} + \text{e}^{-} \]

Key Transient Species

- \( e_{\text{aq}}^{-}, \text{H}^{\cdot}, \text{•OH} \) from \( \text{H}_2\text{O} \)
- \( \text{•NO}_3 \) from \( \text{HNO}_3 \)
- \( \text{RH}^{\cdot\ast} \) from \( n\)-dodecane

Complexation effects

Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å³. (a) [Nd(TEDGA)₃][NO₃]₃, (b) [Nd(TEDGA)₃]Cl₃, (c) [Am(TEDGA)₃][NO₃]₃, and (d) [Am(TEDGA)₃]Cl₃.

“...in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products.” Kimberlin et al., PCCP, 2022.

- Ilan and Czapski, Biochimica et Biophysica Acta, 1977, 498, 386.
- Kimberlin, Saint-Loius, Guillaumont, Cames, Guibal, and Berthon, PCCP, 2022, 24, 9213.
Electron pulse radiolysis

Transients are detected by optical absorption changes.

Time

Light Intensity

0 V

It all started with HONTA

- Complexation of HONTA with either Eu\(^{3+}\) of Am\(^{3+}\) afforded an order of magnitude increase in rate coefficient \(k\):
  - \(k(\text{HONTA} + \text{RH}^{•}) = (7.6 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\).
  - \(k(\text{Am(HONTA)}_2 + \text{RH}^{•}) = (7.1 \pm 0.7) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}\).
  - \(k(\text{Eu(HONTA)}_2 + \text{RH}^{•}) = (9.5 \pm 0.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}\).
Then the HEH[EHP] saga

- **Methodology:** $\Delta [\text{HEH[EHP]}]/[\text{M((HEH[EHP])}_2]_3$ in 0.5 M DCM/n-dodecane; RH•+ decay measured at 800 nm over 200 ns using the Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF).

Size Matters…

**Computations:** Geometry optimization using ADF2020 (*GGA OPBE functional + ZORA/STO-TZP basis set for all atoms*); Wave functions using ORCA (*Hybrid PBE0 functional + DKH-def2-SVP/DKH-def2-TZVP/SARC-DKH-TZVP*); and QTAIM metrics obtained from DFT wave functions using the AIMALL software.

Size matters…

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Is there a ligand dependence?

- $\text{UO}_2^{2+}$ complexation had negligible effect on the reaction of TBP with $\text{RH}^{\bullet+}$, $k(\text{TBP} + \text{RH}^{\bullet+}) = (1.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

- For DEHBA and DEHiBA, $\text{UO}_2^{2+}$ complexation afforded a $2.6\times$ and $1.4\times$ increase in their respective rate coefficients, respectively.

Is there a ligand dependence?

\[
\text{[UO}_2\text{(NO}_3\text{)}_2\text{(TBP)}_2\text{]}^{\text{2+}} \quad \text{[UO}_2\text{(NO}_3\text{)}_2\text{(DEHBA)}_2\text{]}^{\text{2+}} \quad \text{[UO}_2\text{(NO}_3\text{)}_2\text{(DEHiBA)}_2\text{]}^{\text{2+}}
\]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(\Delta G_{\text{electron/hole transfer (eV)}})</th>
<th>(\Delta G_{\text{proton transfer (eV)}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>0.16</td>
<td>-0.36</td>
</tr>
<tr>
<td>DEHBA</td>
<td>-0.88</td>
<td>-0.60</td>
</tr>
<tr>
<td>DEHiBA</td>
<td>-0.90</td>
<td>-0.57</td>
</tr>
</tbody>
</table>

**Electron/Hole Transfer**

\[\text{RH}^{\bullet^+} + \text{Ligand} \rightarrow \text{RH} + [\text{Ligand}]^{\bullet^+}\]

**Proton Transfer**

\[\text{RH}^{\bullet^+} + \text{Ligand} \rightarrow \text{R}^\bullet + [\text{Ligand}(+\text{H})]^+\]
Conclusions

- Chemical kinetics were measured for the reaction of RH•+ with f-element complexes with HONTA, HEH[EHP], TBP, DEHBA, and DEHiBA.
- Complexation has a profound effect on reaction kinetics, from changes in electron distribution to size.
- Understanding the impact of complexation on the radiation-induced degradation mechanisms of reprocessing ligands is essential for accurate estimates of process viability.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Rate coefficient ((k, \text{M}^{-1} \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>e\text{aq}^- ((10^{10}))</td>
<td>3.17 ± 0.04 \hspace{1cm} 11.4 ± 0.1</td>
</tr>
<tr>
<td>H• ((10^9))</td>
<td>5.5 ± 0.2 \hspace{1cm} 5.5 ± 0.2</td>
</tr>
<tr>
<td>*OH ((10^{10}))</td>
<td>1.66 ± 0.06 \hspace{1cm} 1.05 ± 0.02</td>
</tr>
<tr>
<td>*NO₃ ((10^9))</td>
<td>3.79 ± 0.10 \hspace{1cm} 2.61 ± 0.03</td>
</tr>
</tbody>
</table>

Acknowledgements