Selective Separation of Am(III) using the Hydrophilic Complexing Agent SO$_3$Ph-BTPhen

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The innovative-SANEX concept

- Co-extraction of An(III) and Ln(III) by TODGA
- Selective separation of An(III) from the loaded phase

The innovative-SANEX process

Process demonstrated in a spiked test at FZ-Jülich

Properties:
- Centrifugal contactors
- Counter current flow
- 32 stages

<table>
<thead>
<tr>
<th>Component</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am</td>
<td>&gt; 99.8%</td>
</tr>
<tr>
<td>Cm</td>
<td>&gt; 99.8%</td>
</tr>
<tr>
<td>Ln</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>An</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Y</td>
<td>~ 99%</td>
</tr>
<tr>
<td>other</td>
<td>&lt; 0.5%</td>
</tr>
</tbody>
</table>

Selective Americium(III) separation

Concept based on the innovative-SANEX process

Realization:
- Hydrophilic complexing agent SO$_3$Ph-BTPhen
- Developed by the University of Reading
TODGA + SO₃Ph-BTPhen

- Application with TODGA
- SF(Cm/Am) rises to 3.6

organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
aqueous: diff. c(HNO₃) with (PhSO₃Na)₂-BTPhen
T= 22°C; 5 min centrifuge
TODGA

- An(III) and Ln(III) co-extraction
- $S_F_{(Cm/Am)} = 1.6$
- D (An) in between D (Ln)
- No separation of Am(III) from Cm(III) and Ln(III) possible

organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
aqueous: diff. c(HNO$_3$) with $10^{-4}$ mol/L Ln(III) and tracers,
$T=22^\circ C$; 5 min centrifuge
TODGA + SO$_3$Ph-BTPhen

organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
aqueous: diff. c(HNO$_3$) with (PhSO$_3$Na)$_2$-BTPhen
T= 22°C; 5 min centrifuge

- Application with TODGA
- SF$_{(Cm/Am)}$ rises to 3.6
- An(III) stripped from Ln(III)
- Americium selective strip possible
SO₃Ph-BTPhen concentration variation

Slope analysis against TODGA

\[ \begin{align*}
  L₃M(NO₃)₃ + A & \xrightleftharpoons[k]{} MA(NO₃)₃ + 3L \\
  \log(D) & = -0.8 \times \log(\text{SO₃Ph-BTPhen}) - 1.9 \\
  \log(D) & = 0.8 \times 1.3
\end{align*} \]

Slope of -0.8 indicates 1:1 complexes for Am(III) and Cm(III)

organic: 0.2 mol/L TODGA in TPH + 5 vol-% 1-octanol
aqueous: diff c(SO₃Ph-BTPhen) in 0.5 mol/L HNO₃
T=22°C; t= 30 min; 5 min centrifuge
Comparison to lipophilic BTPhen

- CyMe₄-BTPhen also shows selectivity for Am(III)
- Literature of lipophilic BTBP and BTPhen shows 1:2 complexes

Information about stoichiometry of [An(III)(SO₃Ph-BTPhen)ₓ] complexes is missing

Applied speciation method: TRLFS in the aqueous phase

**Curium TRLFS**

TRLFS = Time Resolved Laser Fluorescence Spectroscopy

- excitation by monochromatic laser-pulse at excitation energy of central ion
- de-excitation by fluorescence
- fluorescence shift related to complex environment
- measurement of Cm(III) fluorescence
- information on complex stoichiometry and inner coordination shell
Cm(III)-TRLFS with SO$_3$Ph-BTPPhen

Fluorescence spectra during titration
- First formation of a 1:1 complex
- Afterwards formation of a 1:2 complex
- 1:1 completely disappearing

Speciation diagram
- Solvent species (black)
- 50 % of 1:1 species at about 1:2 Cm/Ligand (red)
- >90 % 1:2 species at 1:100 Cm/L (blue)

Conditions: titration of SO$_3$Ph-BTPPhen in 10$^{-3}$ mol/L HClO$_4$
Initial c(Cm(III)): 10$^{-7}$ mol/L; c(SO$_3$Ph-BTPPhen): 0 - 7.07·10$^{-5}$ mol/L
Cm(III)-TRLFS with SO$_3$Ph-BTPhen

Titration in HNO$_3$

Fluorescence spectra during titration
- Formation of a 1:2 complex
- Less formation of a 1:1 complex

Speciation diagram
- Solvent species (black)
- Less than 10% of 1:1 species (red)
- Changing to 1:1 species at 1:1000 Cm/L (blue)

Conditions: titration of SO$_3$Ph-BTPhen in 0.5 mol/L HNO$_3$
Initial c(Cm(III)): 10$^{-7}$ mol/L; c(SO$_3$Ph-BTPhen): 0 - 7.1e$^{-4}$ mol/L
Comparison of $\text{SO}_3\text{Ph}$-BTPhen and $\text{SO}_3\text{Ph}$-BTBP

- 1:1 and 1:2 complex found with Cm(III)
- 1:1 complex suppressed with HNO$_3$
- Similar stability constants to $\text{SO}_3\text{Ph}$-BTBP

**Comparison with $\text{SO}_3\text{Ph}$-BTBP measurements of Christoph Wagner, KIT, presented this morning.**

**Ligand** | **log($K$)$_{01}$** | **log($K$)$_{02}$** | **log($\beta$)$_{02}$**
--- | --- | --- | ---
BTPhen | 6.2 | 4.5 | 10.7
BTBP | 4.2 | 4.6 | 10.4

Wagner, C., Master thesis; University of Heidelberg, 2013
Conclusion and outlook

SO$_3$Ph-BTPhen for selective separation of Americium

- Separation of Am(III) from Cm(III) and Ln(III) possible
- Slope of ~ -1 observed
- Fast stripping kinetics
- 1:1 and 1:2 complex found by TRLFS-studies
- 1:2 complex preferred in 0.5 mol/L HNO$_3$
- Stability constants similar to the SO$_3$Ph-BTBP system
- Fluorescence-lifetime showed quenching of SO$_3$Ph-BTPhen

For the details I like to invite you to my Poster this afternoon.
Acknowledgement

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Thank you for your attention!