



Contribution ID: 638

Type: Verbal

Thermodynamic and Structural study of uranyl phosphonate-based ligands as potential uranium decorporation agents

Thursday, 17 May 2018 14:45 (15 minutes)

Éric Simoni¹, Jérôme Roques¹, Christophe Den Auwer², Loïc J. Charbonnière³, Pier-Lorenzo Solari⁴
¹Institut de Physique Nucléaire d'Orsay, CNRS-IN2P3, Université Paris-Sud, Université Paris-Saclay, Orsay, France
²Institut de Chimie de Nice, Université Côte d'Azur, CNRS, Nice, France
³IPHC, UMR 7178 CNRS/ Université de Strasbourg, Strasbourg, France
⁴MARS beamline, Synchrotron SOLEIL, Gif sur Yvette, France

ABSTRACT: Because of the widely use of uranium in fuel cycle, especially in the reprocessing process, the environmental and occupational exposure opportunities have increased. Although uranium has very limited radioactive dose impact, its chemical toxicity still need to consider, e.g. uranyl ion (UO₂²⁺, U(VI)) could cause renal injury. The only way to remove or prevent the internally deposited uranium is by using decorporation agents to accelerate excretion. It is known that phosphonate group has a really strong affinity to complex U(VI). Two phosphonate-based ligands were synthesized and tested for its uranium-binding properties.

Fig.1 structure of bisphosphonate-based ligands

The two ligands could provide 5 coordination at equatorial planar, 3N & 2O, for the uranyl. L3 was designed only for uranyl with relatively high lipophilic property due to the 3 aromatic group, meanwhile L4 could donate 7 coordination totally, 3N & 4O, which should also has high affinity to chelate minor actinide. 1

Due to the hydrolysis of uranium, low pH is required to have a major free uranyl species in solution, thus pH 3 was chosen. Then for physicochemical study for blood serum, pH 7.4 was suggested.

Then ligand uranyl complex was preliminary studied with TRLFS. Due to formation of precipitation at pH 3 with NaClO₄ or NaNO₃ as ionic strength, although Cl⁻ will quench the fluorescence of uranyl, NaCl was been used. For L3 at pH 3, the uranyl ligand complex has a strong fluorescence with a red shift about 7 nm, the time constant is 0.48 μs. For L3 at pH 7.3, the uranyl ligand complex has no fluorescence no matter with NaCl or NaNO₃ which suggests there is a configuration change. The same study was done with L4. At pH 3, the uranyl L4 complex fluorescence spectra have a red shift about 5 nm, the time constant is 0.83 μs. At pH 7.3, the uranyl L4 complex fluorescence spectra have a red shift about 9 nm, the time constant is 25 μs. Thus, the coordination mode for two pH shouldn't be the same.

Then ATR-FTIR was been used to study the uranyl ligand complex at two pH. At pH 3, each phosphonic acid group has deprotonate one proton. At pH 7.4, there is no proton for the phosphonic acid group.

Fig.2 FT-IR spectra in absorption mode of free L4 and L4-U, pH = 3 & 7.4. Normalization was performed on the band at 1600 cm⁻¹ (not shown) and spectra were shifted in ordinates

Three type of phosphonate-based ligands /uranyl complexes mode under pH 3 and 7.4 had calculated with DFT. Then EXAFS was implement.

Fig.3 Minimum energy conformation obtained from DFT calculations (B3LYP) in aqueous solution for [UO₂(H₄L₄)] at pH 3(left) & [UO₂(H₄L₄)] at pH 7.4(right) system

Fig.4 U LIII edge k³-weighted EXAFS spectra (left) and the corresponding Fourier transforms(right) of the ligand-U complexes formed. The experimental spectra are given in line and the fits are given in dash line.

Table 1. Structural parameters of the ligand-U complex formed at different conditions
 samples path Ndeg sigma²(× 10⁻³ Å²) RFIT

UO2-L3-PH3 U-Oyl 2 3.67 1.79508
U-Op 2 2.92 2.30471
U-Npyr 1 2.08 2.43804
U-Namine 2 9.93 2.95359
U-P 2 14.95 3.69177
UO2-L3-PH7.4 U-Oyl 2 3.03 1.79963
U-Op 2 7.42 2.32334
U-OOH 1 7.42 2.32334
U-Npyr 1 0.72 2.47119
U-Namine 2 14.81 2.97252
U-P 2 10.23 3.76969
UO2-L4-PH3 U-Oyl 2 3.87 1.80601
U-Op 2 4.04 2.31739
U-Npyr 1 2.92 2.49759
U-Namine 2 27.17 2.8262
U-P 2 19.48 3.68678
UO2-L4-PH7.4 U-Oyl 2 4.02 1.78448
U-Op 2 8.2 2.28005
U-Npyr 1 8.2 2.31105
U-OOH 1 4.85 2.93286
U-Namine 2 10.46 2.23852
U-P 2 9.14 3.56492

1. Abada, S. et al. Highly relaxing gadolinium based MRI contrast agents responsive to Mg²⁺ sensing. Chem. Commun. 48, 4085 (2012).

Primary authors: Prof. SIMONI, Eric; Mr YE , Gaoyang (Université Paris-Sud)

Presenter: Mr YE , Gaoyang (Université Paris-Sud)

Session Classification: TAN 3

Track Classification: Chemistry of Actinide and Trans-actinide Elements