RadChem 2022



Contribution ID: 914

Type: Verbal

## Multi-technique study of the complexation of Np(V)/Pa(V) with mellitate

Tuesday, 17 May 2022 14:00 (20 minutes)

Activities related to nuclear energy are at the origin of a dissemination of actinides in the environment. The migration of actinides in the environment is strongly dependent on their speciation and consequently on the pH, the ionic strength, the redox potential but also on the presence of ligands which can promote their mobility. The An(V) ions are, in general, highly soluble leading to a high mobility in waters and are for some actinides (Pu, Np and Pa) the most stable oxidation state in natural waters. The knowledge of fundamental data, both thermodynamic and structural, on actinide complexes formed with ligands of interest is essential to improve models of actinide migration in the geosphere and biosphere. Among the pentavalent actinides, Pa(V) is the unique An(V) without actinyl moiety [1,2], and data on the protactinium chemistry remain incomplete.

Thus, this study focuses on the behavior of Np(V) and Pa(V) in aqueous solution in the presence of mellitic acid, derived from minerals having organic origins. Mellitic acid is also used as a model ligand of natural organic matters [3]. This is an aromatic acid with six carboxyl groups, that displays a high solubility in aqueous phase.

The complexation of Np(V) was studied using ultraviolet visible near infrared spectroscopy (UV-VIS-NIR) and attenuated total reflection Fourier transform infrared (ATR FT-IR) at mM scale and pH =4 and 6. Because of the high tendency of Pa(V) to hydrolyze and polymerize at high concentration, its complexation with mellitic acid was carried out combining partition methods at ultra-trace level (liquid-liquid extraction) with  $\gamma$ -spectrometry measurements ([233Pa(V)] total=10-10M, I=1.0M NaClO4, pH=1). In the extraction experiment, the distribution coefficient D was determined in the system NaClO4/HClO4/ligand||TBP/Toluene, according to the ligand concentration.

Two different behaviors have been observed for each An(V). By varying the mellitic concentration, a stoichiometry of 1:1 has been observed in presence of Np(V), whereas, for Pa(V), complexes of stoichiometry 1:1 and 1:2 were observed. The structure of the complexes of Np(V) and Pa(V) was investigated using x-rays absorption spectroscopy and ATR-FTIR spectroscopy. The coordination with carboxylate can be monodentate with one O atom of one COO-group, bidentate with both O atoms of the same one COO- group (end-on), or monodentate with two O-atom of two neighboring COO- group form chelate rings (side-on) [4,5]. For Np(V), the spectroscopic techniques seem to indicate that the coordination of the carboxylate groups from the mellitic ligand is in a bidentate fashion.

Primary author: LUO, Meng (Université Paris-Saclay)

**Co-authors:** LE NAOUR, Claire (Université Paris-Saclay, CNRS/IN2P3-IJCLab); MALOUBIER, Melody (Université Paris-Saclay, CNRS/IN2P3-IJCLab)

Presenter: LUO, Meng (Université Paris-Saclay)

Session Classification: Environmental Radioactivity

Track Classification: Radionuclides in the Environment, Radioecology