

Laser-Based Spectroscopic Studies of Actinide Complexes: Americium

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1. Introduction

In the last year, a new book titled “The Heaviest Metals: Science and Technology of the Actinides and Beyond” was designed by John Wiley & Sons to cover both the fundamentals and recent advances in the science and technology of the “heaviest metals,” i.e., the actinide and transactinide elements, starting with actinium, up to the current end of the periodic table [1]. This book will also be published online as part of the Encyclopedia of Inorganic & Bioinorganic Chemistry. We contribute one chapter entitled “Laser-Based Spectroscopic Studies of Actinide Complexes” and we would like to present description of the techniques and several representative application studies introduced in the chapter in a series of three poster presentations. Each poster presentation is specific to uranium, plutonium and americium.

The chemical speciation of actinide complexes is considered to be a key concept for the safe management of spent nuclear fuels in the back-end of a nuclear fuel cycle. Methodological approaches for chemical speciation have been reported in detail in several studies [2, 3]. However, it appears that most nuclear and chemical engineers who work in nuclear industries are not familiar with laser-based spectroscopic techniques. In this presentation, applications of the laser-based spectroscopic techniques to the chemical speciation of actinide complexes are introduced for those who are interested in the highly sensitive analytical techniques applicable in the nuclear industry.

In the americium part, spectroscopic properties of dicarboxylate complexes of Am(III) are investigated by using UV-Vis absorption spectroscopy coupled with a liquid waveguide capillary cell (LWCC) and

time-resolved laser fluorescence spectroscopy (TRLFS). We demonstrate here that UV-Vis-LWCC and TRLFS are sensitive and specific techniques, enabling the speciation of Am(III)-organic ligand complexes.

2. Experimentals

Am³⁺ and dicarboxylate solutions (sodium oxalate (Ox), sodium malonate (Mal), sodium succinate (Suc), Sigma-aldrich) were prepared in 0.1 M NaClO₄ and pH were adjusted to be in the range of pH 6 - 6.3. Am(III)-dicarboxylate samples were prepared by adding concentrated dicarboxylate solutions (10-400 mM) into the Am³⁺ solutions (1-10 μM). UV-Vis absorption spectra were measured by using Cary3 (Varian) coupled with a LWCC (WPI) with a path length of 100 cm. Luminescence spectra were collected by TRLFS equipped with a nanosecond pulsed laser (OPO, Vibrant B, OPOTEK Inc.) as an excitation source (503 nm, 3.5 mJ). Detailed experimental setups can be found elsewhere [4, 5]. All the measurements were carried out at 25-26 °C.

3. Results and Discussion

Am³⁺ exhibits relatively strong absorption properties with an absorption peak at 503 nm ($\epsilon = 424 \pm 8 \text{ cm}^{-1}\text{M}^{-1}$) in comparisons to other actinide ions (Fig. 1 (a), black). Am³⁺ is also luminescent with a maximum luminescence peak at 689 nm ($^5\text{D}_1 \rightarrow ^7\text{F}_1$), although the luminescence is very weak with a short lifetime of 23 ns (Fig. 1 (b) and (c), black). Additions of dicarboxylates (Ox, Mal, Suc) into the

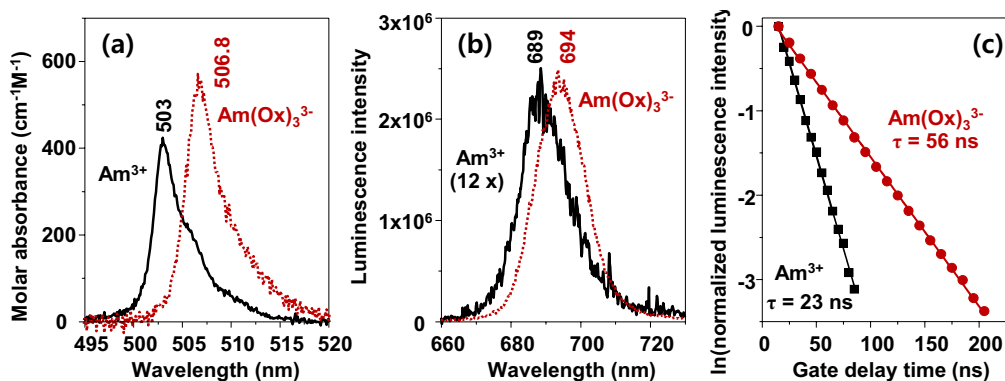


Fig. 1. Spectroscopic speciation of $\text{Am}(\text{Ox})_3^{3-}$ complexes by using (a) UV-Vis absorption spectra and (b) luminescence spectra. (c) Luminescence lifetime measurements by TRLFS. The sample is $8.35 \mu\text{M Am}^{3+}$ in 0.1 M NaClO_4 , $\text{pH} \sim 6$.

Am^{3+} samples induced gradual shifts of the absorption and luminescence spectra towards the longer wavelength directions as a function of the dicarboxylate concentrations. Representative spectral changes induced by the presence of 50 mM Ox are shown in Fig. 1 (red dots). Luminescence intensities and lifetimes are also gradually increased as increasing the ligand concentrations. Deconvolution of the absorbance spectra suggest that $\text{Am}(\text{Ox})_n^{3-3n}$ ($n = 1 - 3$) species are formed with increasing the higher complexes distributions as increasing the Ox concentration. $\text{Am}(\text{Ox})_3^{3-}$ complex becomes the major species in the presence of 50 mM Ox . Mal and Suc were also examined for the systematic investigation of the Am (III) interactions with dicarboxylates. Detailed spectral speciations including deconvolution results will be presented. Formation constants and probable molecular structures of the complexes will also be discussed in the presentation.

4. Conclusion

Absorption and luminescence property changes upon $\text{Am}(\text{III})$ -dicarboxylate complexations are investigated by using UV-Vis-LWCC and TRLFS. The observed distinct spectral changes and deconvolution of them using a calculation program enable speciation of the complexes. We demonstrate here that UV-Vis-LWCC and TRLFS are powerful in the study of $\text{Am}(\text{III})$ -organic ligand complexations. These techniques can be applied further to the study

of chemical speciation of $\text{Am}(\text{III})$ interacting with organic matters in groundwater system.

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