A TRLFS Study on the Interactions of Am(III) at the Interface of Water and Silica Nanoparticles

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1. Introduction

Actinides including Am(III) are the long-lived radionuclides present in the spent nuclear fuel wastes. Thorough understanding on the migration behaviors of the actinides in groundwater is critical for the safety assessments of the long-term radio-active waste managements. Physicochemical interactions of the actinides with mineral surfaces at the water-solid interface are important factors that determine their migration behaviors in groundwater. Understanding the interactions at a molecular level is essential in establishing the reaction mechanisms of the actinides at the interface. While there are many luminescence spectroscopic studies on the adsorption of Cm(III) or Eu(III) as an analog of Am(III) [1], only a few studies were reported on the Am(III) incorporated into solid phases rather than surface adsorbed species [2]. In this study, we employed time-resolved laser-induced fluorescence spectroscopy (TRLFS) to characterize Am(III) interactions with SiO_2 nanoparticles at a molecular level. TRLFS results show that adsorption of Am(III) onto the silica broadens the luminescence spectra with red-shifts of 2-3 nm. Luminescence lifetime measurements show the increase in the lifetime from 23.5 ± 0.3 ns to ~37 ns as the pH increases from 2.5 to 8 or above. The observations indicate that adsorption takes place via inner-sphere bindings by displacing about four inner-sphere bound water molecules. At the pH 7 and above, additional longer lifetime (> 100 ns) component was identified, which corresponds to displacing all the inner-sphere water molecules. We will discuss more details on the spectral characteristics of the adsorbed Am(III) and their implications.

2. Experimental

2.1. Adsorption of Am(III) onto SiO_2

Adsorption of Am(III) onto SiO_2 nanoparticles was carried out under the Ar condition with 6.5 μM Am(III) and 1 g/L SiO_2 (Aerosil 200, d 16 nm, BET 200) in 0.1M $NaClO_4$. The pH was adjusted by adding small amount of NaOH or $HClO_4$, and the samples were let equilibrated by rotating for 2-3 days. The samples were centrifuged at 18000 rpm for 30 min and 10 μL of the supernatant was subjected to liquid scintillation counting (TriCarb, PerkinElmer) of [241]Am for the measurement of the adsorption ratios. Two mL of re-agitated samples were withdrawn for the TRLFS study. After luminescence measurements, samples were combined back to the rest of the samples and subjected to pH measurements. The pH was increased by adding more NaOH for the next round of experiments.

2.2. TRLFS

Samples were excited at 503 nm (3.5 mJ) by Nd:YAG pumped OPO laser (Vibrant, Opotek Inc.) while continuously being stirred. Luminescence was collected at 90° direction from the excitation by an optical fiber bundle connected to a spectrometer (Semrock). Gated detection of the luminescence was performed by an ICCD camera (Andor Tech.). A delay generator triggered by the flashlamp of the laser was set to control the timing of the Q-switch of the OPO laser and the ICCD detection, so that luminescence with such short lifetimes can be detected [3].

3. Results and discussion

3.1. Distribution coefficient, K_d

Adsorption ratios of Am(III) onto the silica and corresponding distribution coefficients were measured by the liquid scintillation counting of [241]Am.
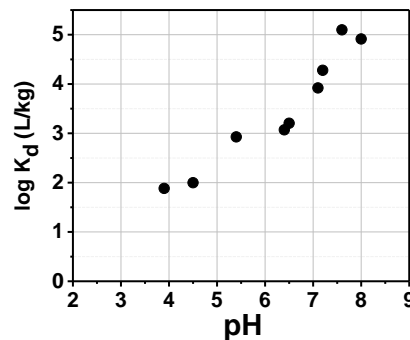

Fig. 1. Distribution coefficients (K_d) of Am(III) onto silica nanoparticles in 0.1M $NaClO_4$.

Distribution coefficients were calculated according to the equation (1).

$$K_d = \frac{C_{total} - C_{eq}}{C_{eq}} \cdot \frac{V}{m} \qquad (1)$$

where c_{total} is the initial aqueous metal ion concentration (M), c_{eq} is the metal ion concentration in the supernatant at an equilibrium (M), V is the volume of the liquid phase (L) and m is the mass of the solid phase (kg). As shown in Fig. 1, Am(III) started being

adsorbed at around the pH 4 and most of them (> 99%) were adsorbed at around the pH 7 and above.

3.2. Luminescence spectra of Am(III)

Fig. 2 shows Am(III) luminescence spectra of $^5D_1 \rightarrow$ $^7F_1$ transition from the adsorbed Am(III) (pH 8.0) and the aqueous Am(III) (pH 2.5). Two major differences of the adsorbed Am(III) luminescence compared to that of the aqueous Am(III) are the considerably broadened luminescence spectrum and the red-shifts (2-3 nm) of the peak maxima. Changes in the spectral shape will be discussed in relation to the adsorption ratio.
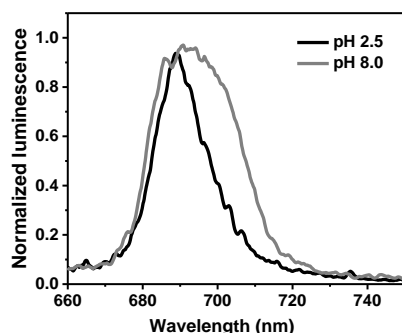

Fig. 2. Luminescence spectra of 6.5 μM Am(III) in the presence of silica nanoparticle (1 g/L) in 0.1 M NaClO$_4$. Adsorption efficiencies are 0 and 99% at the pH 2.5 and the pH 8.0, respectively. Spectra were averaged over 2000 shots at a 30 ns delay from the excitation at 503 nm (3.5 mJ) with a gate width of 150 ns (pH 2.5) or 1000 ns (pH 8.0).

3.3. Luminescence lifetimes and hydration numbers

Lifetimes of the Am(III) luminescence were measured depending on the pH and corresponding inner-sphere hydration numbers, n (H$_2$O), were calculated according to the equation (2) [4]

$$n \ (H_2O) = 2.56 \times 10^{-7} \cdot k_{obs} - 1.43 \qquad (2)$$

where k_{obs} (s^{-1}) is the decay rate of the luminescence, corresponding to the inverse of the lifetime.

At the pH below 4, where all the Am(III) are present as aqueous Am^{3+} ions, lifetimes were measured to be 23.5 ± 0.3 ns. It is in good agreements with previously reported values [4, 5]. Between the pH 6 and pH 8, adsorption increased significantly as described in Fig. 1, and lifetimes also increased accordingly (Fig. 3). Above the pH 7, the luminescence decay curves were described well by double exponential decay curves rather than single exponential curves. The measured lifetimes are ~37 ns and > 100 ns. In Fig. 3, short lifetime values are plotted as a function of the pH. The short lifetime of ~37 ns corresponds to around 5 water molecules bound on the inner-sphere, indicating around 4 water molecules were displaced upon adsorption of Am(III) onto the silica. We will discuss more details regarding the spectral changes upon adsorption onto the silica and

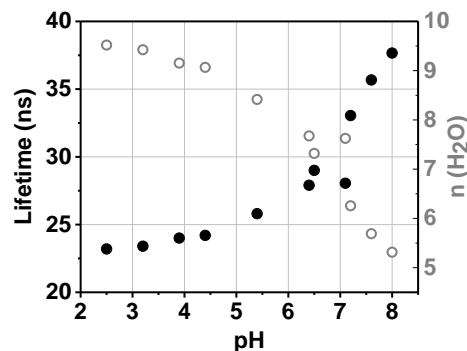compare them to other trivalent ions including Cm(III) and Eu(III).

Fig. 3. Luminescence lifetimes (black squares) of Am(III) in the presence of silica nanoparticles and corresponding inner-sphere hydration numbers (gray circles) as a function of the pH. Lifetimes were measured from the fittings the luminescence decay curves to single (pH < **7**) or double exponential (pH > **7**) curves

4. Conclusions

Adsorption of Am(III) onto silica nanoparticles was studied as a function of the pH by using batch-sorption experiments and TRLFS. TRLFS results show that adsorbed Am(III) displays broadened luminescence spectra with longer lifetimes compared to those of the aqueous species, indicating that adsorption takes place via formation of inner-sphere surface complexes. Our data also suggest that at least two different types of Am(III)-silica species are present at the pH above 7. Details on the spectral characteristics will be described in relation to the molecular structural implications.

REFERENCES

[1] T. Kupcik, T. Rabung, J. Lützenkirchen, N. Finck, H. Geckeis, T. Fanghänel, Macroscopic and spectroscopic investigation on Eu(III) and Cm(III) sorption onto bayerite (β-Al(OH)$_3$) and corundum (α-Al$_2$O$_3$), J. Colloid Interface Sci. Vol. 461, pp. 215-224, 2016
[2] T. Stumpf, M.M. Fernades, C. Walther, K. Dardenne, Th. Fanghänel, Structural characterization of Am incorporated into calcite: A TRLFS and EXAFS study, J. Colloid Interface Sci., Vol. 302, pp. 240-245, 2006
[3] E.C. Jung, H.-R. Cho, M.H. Baik, H. Kim and W. Cha, Time-resolved laser fluorescence spectroscopy of UO$_2$(CO$_3$)$_3^{4-}$, Dalton Trans., Vol. 44., pp. 18831-18838, 2015.
[4] T. Kimura, Y. Kato, Luminescence study on determination of the inner-sphere hydration number of Am(III) and Nd(III), J. Alloys Comp., Vol. 271-273, pp. 867-871, 1988
[5] J.V. Beitz, f-State luminescence of trivalent lanthanide and actinide ions in solution, J. Alloys Comp., Vol. 207-208, pp. 41-50, 1994