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Study of a ternary Am(III)-ISA-OH system under alkaline conditions

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1. Introduction

Physicochemical behaviors of actinides in natural environments should be understood for the long-term performance assessment of radioactive waste repository. Isosaccharinic acid (ISA) is a concerned small organic ligand that can increase the mobility of radionuclides by reducing mineral uptakes and increasing solubility [1-3]. ISA is a major cellulose degradation product in highly alkaline Ca^{2+} rich environment of cementitious materials [4], which are used for the fixation of low to intermediate level radioactive wastes and for constructions of repositories.

In our previous study, the formation of Am(III) complexes with α-D-ISA was studied by combined use of spectrophotometry, time-resolved laser fluorescence spectroscopy (TRLFS), and density functional theory (DFT) calculations [5]. First, aqueous Am(III)-ISA complexes were studied using absorption and TRLFS of Am(III) in weakly acidic condition of pH~5.5. The reaction enthalpy and entropy changes were measured from the formation constants determined at various temperatures in the range of 15–70 °C. Formation of 1:1 Am(III)-ISA complex is driven by entropy increase, while 1:2 complex formation is exothermic with much less increase in entropy. DFT calculations predicted that C2 and C4-hydroxyl groups, along with the carboxyl group, participate in the tridentate chelate binding of the primary ISA as shown in Figure 1. The thermodynamic, TRLFS, and DFT results collectively suggested tridentate binding of the primary ISA to Am(III) via a carboxylate and C2 and C4-hydroxyl groups in the protonated state and reduced dentate binding of the secondary ISA, such as a bidentate binding, forming a four-membered ring structure via the carboxylate group.

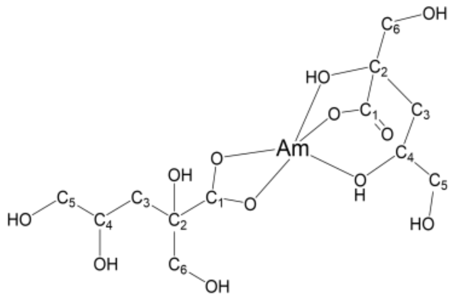

Fig. 1. A geometry of $Am(ISA)_2^+$ suggested under a weak acidic condition of pH 5.5 [5].

In this study, we extended the study to alkaline conditions upto pH 13, where ISA becomes concerned due to high efficiency of cellulose degradation reactions. We discuss the effects of deprotonated hydroxyl groups of ISA on the binding structures and the stability. Probable formation of colloidal particles are examined and aqueous ternary complexes of Am(III)-OH-ISA are discussed.

2. Methods

2.1 Sample preparation

A series of Am(III) samples (1–12 μM) were prepared either by varying pH (5.3–13) at a constant ISA concentration of 30 mM, or by varying the ISA concentration (0-30 mM) at a constant pH of ~ 12.5. The background electrolyte was maintained at 1 M $NaClO_4$. All samples were prepared in an Ar-filled glovebox to prevent CO_2 interference. For the solubility experiments, samples were filtered twice through membrane filters (1 kDa cutoff), and only the third filtrate was collected to minimize Am(III) loss due to adsorption during the filtration process. Aqueous Am(III) concentrations were measured by a liquid scintillation counter (LSC, TriCarb4910TR, PerkinElmer).

2.2 Absorption spectroscopy

UV-Vis absorption spectra were collected using a spectrophotometer (Cary 5000, Agilent) with a 0.1 nm resolution, 0.5 nm spectral bandwidth, and 1 s averaging time. Quartz cells (Hellma) with a 1 cm optical path legnth were used. Samples were equilibrated in a thermostat at 25 °C prior to measurements. To monitor the long-term stability of the solutions, absorption spectra were measured periodically over the course of one month.

2.2 Time-resolved luminescence spectroscopy

TRLFS was employed to investigate the luminescence properties of the Am(III)-ISA samples. A nanoseccond-pulsed Nd:YAG pumped OPO system (Vibrant B, OPOTEK Inc.) served as the excitation source. The excitation wavelengths were tuned between 503 and 510 nm to account for the absorption shifts induced by varying ISA concentrations. Time-resolved luminescence spectra were collected using a spectrograph (Andor Technology) coupled with a gated intensified CCD (ICCD).

3. Results and discussion

Fig. 2 illustrates the changes in the absorption spectra of Am(III) in the presence of 30 mM ISA as the pH increases from 5.3 to 12.8. The absorption spectrum of Am^{3+} (at pH 1) is co-plotted as a reference. In weakly acidic to neutral pH conditions (pH 5.3–7.6), the absorption spectra exhibit the same maximum absorbance at approximately 506 nm, which was confirmed as the absorbance of $Am(ISA)_2^+$ complex in our previous study [5]. Above pH 8, abrupt shifts and a decrease in absorbance were observed. Stable absorption spectra were obtained once the pH reached above 12. TRLFS results showed a decrease in luminescence intensity without changes in the maximum luminescence positions or decay rates. These results indicate that the Am(III)-ISA complex(es) formed under alkaline conditions are non-luminescent.

Fig. 3 shows absorption spectra of Am(III) at pH 12.5 before and after ultrafiltration (1 kDa). The Am(III) sample in the presence of 30 mM ISA showed no change in the absorption spectra after ultrafiltration, whereas a concentration of 10 mM ISA led to a significant decrease in absorbance. These results suggest that Am(III) forms aqueous species in the presence of 30 mM ISA. This is further supported by the fact that the absorption spectra of the Am(III) sample remained almost unchanged over a month in the presence of 30 mM ISA.

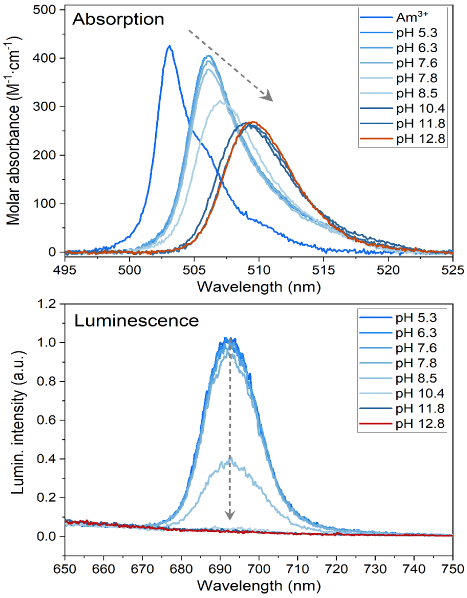

Fig. 2. Absorption and luminescence spectra of Am(III) in the presence of 30 mM ISA in the pH variation from 5.3 to 12.8.

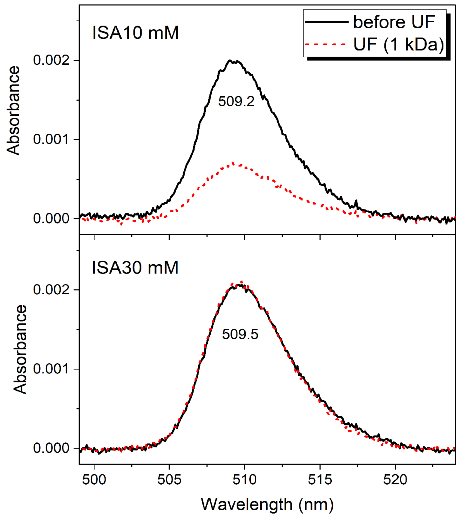

Fig. 3. Comparisons of absorption spectra of Am(III) before and after ultrafiltration (1 kDa).

Slope analysis of a series of solubility experiments as function of eiter pH or ISA concentrations suggests the formation of $Am(ISA)_2(OH)_3^{2-}$, which is indistinguishable from $Am(ISA_{-nH})(ISA_{-mH})(OH)_{3-n-m}^{2-}$. This is also supported by TRLFS results on the Eu(III)-ISA system, which indicate an additional displacement of the inner-sphere hydration number by two or more at alkaline pH conditions. The optimal species and their probable geometries will also be presented based on the DFT calculations.

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