Mixed Lanthanide-CO$_3^-$-Fulvic Complex: Spectroscopic Evidence

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The formation of mixed complexes between lanthanides and actinides(III), complexing inorganic anions, and humic substances is still not completely settled, particularly, the competition, or mixed complex formation, with CO$_3^-$ [5,6]. To propose answers on this topic, time-resolved laser-induced luminescence spectroscopy (TRLS) experiments in the system Eu(III)-CO$_3^-$-FA at pH 7 are done, using Suwannee River fulvic acid (SRFA). Starting from former characterization of the Eu-SRFA system [1], the evolution of both the fluorescence spectra and lifetimes of Eu(III) at pH 7 and varying concentrations of carbonate and FA are obtained. With the use of an optic parametric oscillator, several excitation wavelengths ($\lambda_{\text{exc}}$) were used either to excite selectively Eu(III) through the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition ($\lambda_{\text{exc}}$ = 394.7 nm), to take advantage of the antenna effect from the SRFA ($\lambda_{\text{exc}}$ = 390 nm), or to minimize the excitation of the fulvic complex ($\lambda_{\text{exc}}$ = 532 nm).

The evolutions of the Eu(III) luminescence spectra from the $^5\text{D}_0 \rightarrow ^7\text{F}_{1,2}$ transitions are showing modifications of the asymmetry ratio (area ratio of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition) that indicates the presence of several species in addition to the EuCO$_3^+$ and Eu-FA complexes. The occurrence of bi-exponential decay times, with a faster than Eu$^{3+}$ component, is typical of the occurrence of fulvic complex [8] even in the presence of carbonates.

The analyses of the undirect excitation of the Eu-CO$_3^-$-SRFA systems are used to build the complexation isotherms varying both SRFA or total carbonate concentrations in the framework of the NICA-Donnan modeling of the Eu(III)-SRFA system [1,2]. In view of the restricted pH span, no strict attribution to the different possible types of sites can be done. Different complex formation are considered and discussed.