

Speciation of Curium (III) Humate by Time-Resolved Laser Fluorescence Spectroscopy

Hichung Moon

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejeon 305-701

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The understanding of actinide behaviour in natural aquifer systems is of great importance for the safety assessment of nuclear industry. In particular, complexation reactions of actinide ions of higher oxidation states ($Z \geq 2$) with natural organic ligands such as humic/fulvic acids present in aquifer systems play a significant role, because humic substances form strong complexes with these cations^{1,2}. Humic substances commonly found in nature are structurally similar, but number or type of functional groups vary depending on their origin and age³. Because of these differences, there is a need to investigate the complexation reactions of humic acid (HA) from one area and compare it with the data of other humic acids of differing origins⁴. Although a number of experimental techniques such as ultrafiltration⁵, ion exchange⁶, solvent extraction⁷, and spectrophotometry⁸ have been used in such studies in the past, these techniques do not allow direct work at trace levels.

Recently, time-resolved laser fluorescence spectroscopy (TRLFS) is showing a great promise for direct speciation of some actinide ions (e.g., Cm^{3+}) and their complexes at trace levels in aqueous media⁹⁻¹¹, showing that it can be applied to such interlaboratory comparative study. The time-resolved laser fluorescence spectroscopy used in such studies consists of an excimer pumped dye laser system (Lambda Physics, EGM 201 E, and FL 2002), with an average operational pulse energy of 5 mJ and pulse duration of 10 ns, and a fluorescence spectrometer (Jobin Yvon H320 polychromator and Spectroscopic Instrument OSMA IRY 700 G optical multichannel analyzer). The detector system consists of a time-gating microchannel plate and an array of 1024 Si-photodiodes coupled to a control unit, and for most applications the time-gate is set approximately 2 μs after the laser pulse.

The absorption spectra of hydrated Cm^{3+} ion are characterized by three strong f-f transition from the Z-groundstate ($^8S_{7/2}$) to the excitation states G, H and F, as is illustrated by Beitz¹¹. Subsequently, a non-radiative deexcitation processes populate the first excited A state ($J=7/2$), from which a radiative decay occurs down to the Z-groundstate with a relatively high quantum efficiency¹², yielding an emission peak at 593.5 nm. The life-time of the radiative emission is determined to be $T=63 \mu\text{s}$ for hydrated Cm^{3+} ion in 1 M HClO_4 ¹¹. In contrast, humic acids emit a broad fluorescence signals over a wide range (400 to 700 nm) with a short life-time of 50 ns or less^{13,14}. Because of the differences in the life-time, the complexation reactions of humate with Cm^{3+} can be investigated without significant background signal from free humic acid by setting a suitable time-gate of TRLFS. Since selection of light energies occurs during both

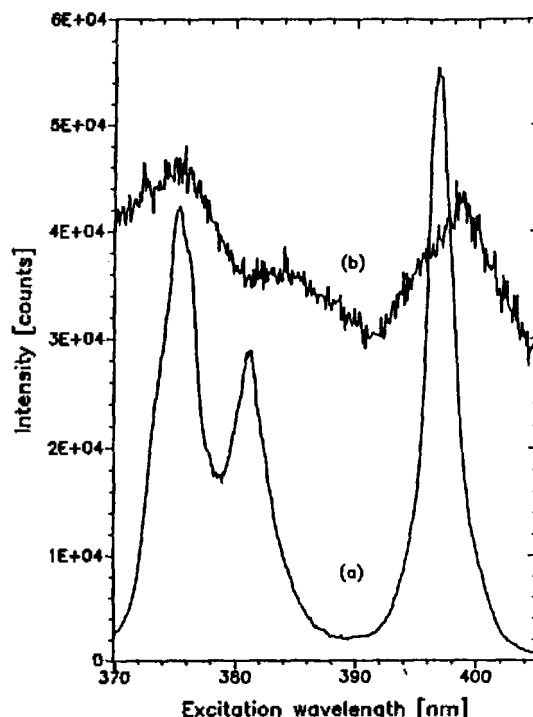


Figure 1. Excitation spectra of (a) hydrated Cm^{3+} ion ($[\text{Cm}] = 8.2 \times 10^{-8} \text{ mol/l}$, $\text{pH} = 6$) in 0.1 M NaClO_4 solution and (b) Cm humate ($[\text{Cm}] = 6.7 \times 10^{-8} \text{ mol/l}$, $[\text{HA-T1}] = 9.36 \text{ mg/l}$, $\text{pH} = 6$).

the excitation and emission processes for measuring a fluorescence spectrum and this coupled with high light intensity of a laser beam, makes TRLFS a highly sensitive method, and can be used to study Cm-humate complexation down to a very low concentration range ($< 10^{-8} \text{ mol/l}$). By this method three different spectroscopic characteristics of the Cm-humate can be measured namely, excitation spectra, emission spectra and life-time of Cm-humate fluorescence.

The stock ^{244}Cm solution used in this experiment is prepared by removing its daughter nuclide ^{240}Pu by Dowex 1 \times 4 anion exchange in 7 M HNO_3 , and contains some 10% ^{241}Am impurity. Because ^{241}Am are known to have a much lower fluorescence yield, this does not seem disturb the Cm-humate fluorescence measurement¹⁵. The humic acids (T1 and T2) are extracted and purified chemically from soils collected from the uranium bearing blackshale regions of Kyue San, Korea. One other humic acid (T3) is similarly extracted from the soil of the neighbouring greyshale region for comparison. The characterization work of these humic acids are given elsewhere¹⁶.

Excitation Spectra

The excitation spectra of the hydrated Cm^{3+} ion and Cm-humate (T1), measured in the spectral range 370-405 nm by setting a 40 nm window on the emission peak maximum, is shown in Figure 1. The hydrated Cm^{3+} ion ($[\text{Cm}] = 8.2 \times 10^{-8} \text{ mol/l}$), represented by the spectrum (a), displays the characteristic peaks of H (375.4 nm), G (381.4 nm) and F (396.5 nm) bands respectively, showing that the excitation spectra has the spectroscopic feature same as the absorption spectra.

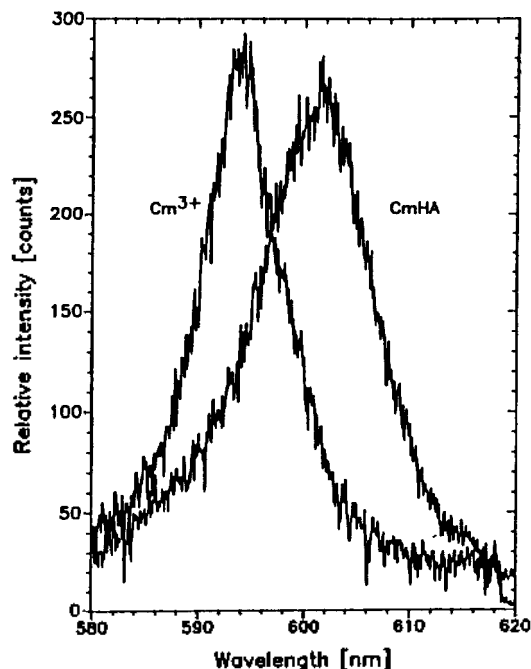


Figure 2. Emission spectra of hydrated Cm^{3+} ion ($[\text{Cm}] = 6.06 \times 10^{-8}$ mol/l, pH=6) and Cm humate ($[\text{Cm}] = 6.26 \times 10^{-8}$ mol/l, $[\text{HA-T1}] = 9.36$ mg/l, pH=6).

The spectroscopic feature is changed considerably by the addition of excess humic acid ($[\text{Cm}] = 6.7 \times 10^{-8}$ mol/l, $[\text{HA}] = 9.36$ mg/l) to a 0.1 M NaClO_4 solution and pH adjusted to 6 with 10^{-3} M MES buffer (2-morpholineethane sulfonic acid). The excitation spectra of Cm-humate is shown as the spectrum (b) in Figure 1. The peaks of the absorbing states show a broadening and increase in the baseline between the states. In particular the clearly resolved F band shows a small but significant peak shift from 396.5 nm to 398.3 nm. This phenomena maybe attributable to a non-selective energy transfer from excess humic acid present in the solution, and has been reported for other Cm complexes, namely Cm complex of β -diketonates¹⁷.

Emission Spectra

The emission energy of the A band is strongly affected by the complexing ligand. The sample is excited by tuning the dye laser to the peak maximum of the H band at 375.4 nm and the spectral resolution of polychromator is set to 0.8 nm. The emission spectra obtained for the hydrated Cm^{3+} ion and Cm-humate complex are shown in Figure 2. The reference solution of the hydrated Cm^{3+} ions ($[\text{Cm}] = 6.06 \times 10^{-8}$ mol/l, pH=6) in 0.1 M NaClO_4 gave a characteristic emission peak maximum at 593.8 nm with a peak width of 9.0 nm (FWHM). The peak is somewhat broader than that reported by Beitz¹³, which may be caused by a weak complexation with MES buffer or a partial Cm^{3+} hydrolysis reaction⁹.

On addition of a large excess of humic acid (T1, blackshale humic acid) to a similar solution, ($[\text{Cm}] = 6.26 \times 10^{-8}$ mol/l, $[\text{HA}] = 9.36$ mg/l, pH=6) a peak shift occurs, and a new emission spectra obtained has a single peak maximum at 601.4 nm with a peak width of 11 nm, as is shown in Figure 2. Replicate experiments using other humic acids, one from

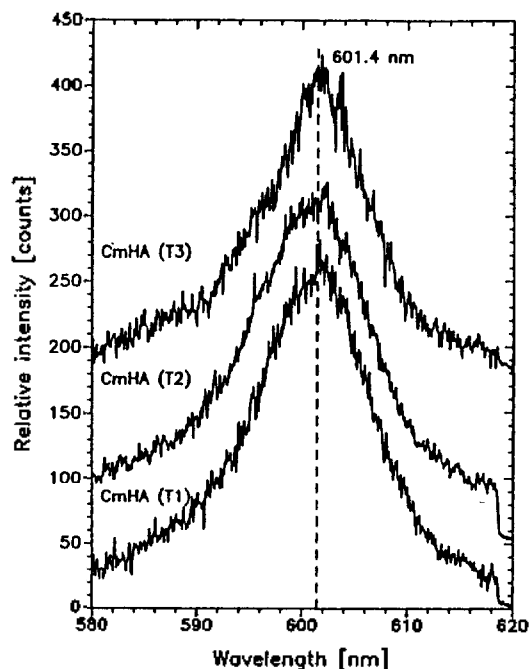


Figure 3. Emission spectra of Cm complexed to humic acids of different origins (T1, T2 and T3).

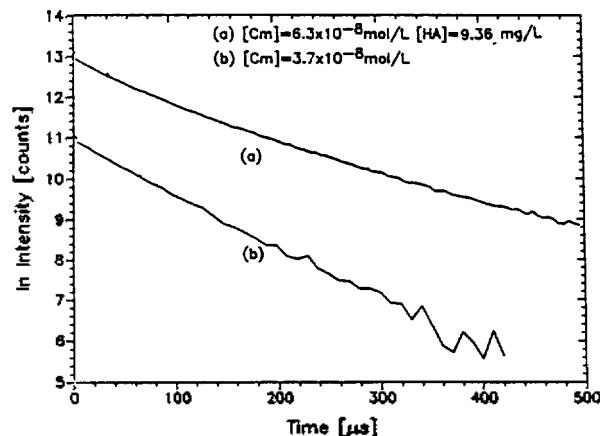


Figure 4. Life-time measurement of the fluorescence of hydrated Cm^{3+} ion ($[\text{Cm}] = 3.7 \times 10^{-8}$ mol/l, pH=6) and Cm humate ($[\text{Cm}] = 6.3 \times 10^{-8}$ mol/l, $[\text{HA-T1}] = 9.36$ mg/l, pH=6).

the same blackshale region (T2) and another from the neighbouring greyshale region (T3), gave the identical emission peak maxima with the same peak width. This result is shown in Figure 3. The peak shift is due to an increase in the crystal field splitting of the A state, showing that the Cm^{3+} ions are complexed almost completely to humates and, furthermore, all three humates from Kuye San seem to form the same Cm humate complexes. Such peak shift and broadening has also been reported for Cm carbonate complex¹⁴.

Life-Time Measurement

Life-time of the fluorescence emission can also provide an additional information about Cm humate complexation. Life-time of an excited state is affected in parts by a non-radiative decay pathway; energy transfer from electronic to

vibronic modes of the coordinated ligands. Therefore, replacement of inner sphere water molecules of the hydrated Cm^{3+} ion by other complexing ligands can cause changes in the life-time of the fluorescence emission, and for a Cm humate an increase of life-time is expected.

In Figure 4, the life-time measurement of Cm humate (T1) complex {plot (a), $[\text{Cm}] = 6.3 \times 10^{-8}$ mol/l, $[\text{HA}] = 9.36$ mg/l}, and hydrated Cm^{3+} ion {plot (b), $[\text{Cm}] = 3.7 \times 10^{-8}$ mol/l} are shown. The life-time of the reference hydrated Cm^{3+} ion is found to be 72 μs , which is slightly longer than that reported by Beitz, and this maybe caused by MES buffer. The life-time measurement of Cm humate gave two different time components: 47 μs (minor) and 146 μs (major), as seen by the plot (a) in Figure 4 which shows a discrepancy from the linear line. The minor component of the life-time, 47 μs , is not clearly understood at present and is being further investigated. However, the major life-time component, 146 μs , is comparable to that obtained for the Cm carbonate complex¹⁴, 141 μs .

This preliminary results seem to suggest that the complexation behaviour of humates of differing origins with Cm^{3+} can be investigated at very low concentration for both constituents by TRFLS, thus avoiding the humus aggregation phenomena. All three applications of TRFLS (excitation spectra, emission spectra and life-time of the fluorescence measurement) conclusively show the formation of Cm humate complex. The measured peak shift in the emission spectra and the difference of life-time between the hydrated Cm^{3+} ion and Cm-humate implies a strong inner sphere complexation almost exclusively by the carboxylic groups of the humic acid at pH 6.

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Substituent and Solvent Effects on the Excited States of 4,4-Disubstituted Cyclohex-2-enones

Hwa Sung Lee, Kye Sook Namgung, Jung Kyou Sung, and Woo Ki Chae*

Department of Chemistry Education,
Seoul National University, Seoul 151-742

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4,4-Disubstituted cyclohex-2-enones can undergo a variety of reactions upon excitation. The choice of reaction pathway by such compounds appears to be dependent upon the character of low-lying triplet states.¹⁻⁷

The rearrangement of 4,4-diphenylcyclohex-2-enone (1) to give bicyclo (3,1,0) hexan-2-one (2) is thought to occur from the n, π^* triplet state,² whereas skeletal rearrangement such as 4,4-dimethylcyclohex-2-enone (3) to 6,6-dimethylbicyclo (3,1,0) hexan-2-one (4) have been attributed to the π, π^* triplet state.^{3,4}

In order to evaluate these suggestions, Dauben⁴ studied solvent effect on the excited states of 4-methyl-4-phenylcyclohex-2-enone (5). Irradiation of 5 in benzene, a nonpolar solvent, gave products arising from n, π^* triplet state. The photochemistry of 5 was also investigated in a polar solvent which would lower the energy of the π, π^* triplet state.

These studies of compound 5 supports the suggestions that rearrangement of the type 1 to 2 results from n, π^* triplet state, while rearrangement of the type 3 to 4 results from π, π^* triplet state.

Since the compound 5 is potentially capable of phenyl migration and methyl migration processes, a proximity of n, π^* and π, π^* triplet states would also be expected.

