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Laser-induced Fluorescence Studies on Sm(III) and Cm(III) Complexes in the HNO_3/DHDECMP Extraction System

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Laser-induced fluorescence(LIF) studies of Sm(III) and Cm(III) complexes in the HNO_3/DHDECMP solvent extraction system have been carried out. Luminescence lifetime together with LIF spectra were measured to determine the number of water molecules coordinated to Sm(III) and Cm(III) in a nitric acid solution and in the DHDECMP phase. The hydration number of Sm(III) and Cm(III) in the nitric acid solution decreased linearly with an increasing nitric acid concentration. The hydration numbers of Sm(III) and Cm(III) in the DHDECMP phase decreased with an increase of nitric acid concentration and the water molecules in the inner coordination sphere were not completely removed at the low nitric acid concentration.

KEYWORDS: Sm(III), Cm(III), luminescence lifetime, inner-sphere hydration number, coordination number, DHDECMP extraction

I. Introduction

Efficient separation of trivalent actinides from lanthanides has been an important and rather difficult subject in the fields of inorganic chemistry and nuclear technology because the two f-element series have similar range of ionic radii and show strong similarities in chemical behavior. Many efforts have been devoted to developing trivalent actinide/ lanthanide separation using solvent extraction, ion exchange, and other techniques.[1,2] For an in-depth understanding of the separation mechanisms in the application of solvent extraction, it is necessary to identify and characterize the species extracted to the organic phase at the molecular level.

Time resolved laser-induced fluorescence(LIF) has been powerful means for studying some complexed lanthanide and actinide ions in aqueous solution. LIF studies of lanthanide or actinide ion-extractant complexes have been reported, however, only a few attempts have been made to determine the presence of water, either qualitatively or quantitatively, in the extracted complexes. Luminescence lifetime measurements were used to determine the number of water molecules coordinated to the lanthanide ions in extraction by di-2-ethylhexyl phosphoric acid(HDEHP)[3], tributyl phosphate (TBP)[4] and thenoyltrifluoroacetone (HTTA), mixtures of HTTA+TBP, TTA+TOPO as well as HTTA+crown ethers[5]. Beitz and Sullivan[3] reported the LIF studies of Eu(III) extracted from nitric acid using HDEHP and octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO) as extractants. The results showed that there was no water in the inner coordination sphere of the Eu(III) extracted by 0.01 M HDEHP and by 2M CMPO from nitric acid.

Dihexyl N,N-diethylcarbamoylmethyl phosphonate (DHDECMP) is an extractant for not only tetravalent and hexavalent metal ions but also trivalent metal ion from acid solutions. DHDECMP is a neutral extractant in which the primary interaction is between the trivalent ion and the phosphoryl oxygens, partially the carbonyloxygens, of the three DHDECMP molecules surrounding it. Charge neutrality is achieved by the co-extraction of anions from the aqueous phase. Horwitz, *et al.*[6] examined the extraction of trivalent actinides and lanthanides by DHDECMP from nitric acid and lithium nitrate solutions.[7]

In the present study, experimental research was conducted in order to provide further evidence for water molecules coordinated to the extracted lanthanide and trivalent actinide complexes. Luminescence lifetimes together with LIF spectra were measured to determine the number of water molecules coordinated to Sm(III) and Cm(III) in the nitric acid solution and in the DHDECMP.

II. Experimental

Sm(III) stock solution was prepared by dissolving an appropriate amount of the samarium oxide (Wako Pure Chem. Ind., Ltd.) in perchloric acid. The Cm(III) stock solution used in this experiment was prepared by Kimura and Kato.[8] ^{244}Cm($t_{1/2}$=18.1y) supplied by C.E.A., France was purified from its daughter nuclide ^{240}Pu by passage through anion exchange resin(AG 1X8) by eluting with 7M HNO_3. The Cm fraction in the effluent was fumed to dryness after the addition of concentrated $HClO_4$. The residue obtained was dissolved in 0.01M $HClO_4$ to yield the Cm(III) stock solution. The concentration of the Cm(III) stock solution was determined by α-ray spectrometry and liquid scintillation counting.

Analytical reagent grade nitric acid and purified DHDECMP (Columbia Organic Chemical Company, South

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Carolina, USA) were used.[9)] DNO_3(99.9%) and D_2O(99.9%) were obtained from Aldrich and Merck, Canada. Solutions of the nitric acid complexes of Sm(III) were prepared from Sm(III) and a nitric acid stock solution of known concentration. The D_2O solutions were prepared by evaporating an aliquot of H_2O solution to dryness and then adding an equal volume of D_2O. This evaporation-addition cycle was repeated two times. Pure DHDECMP was used for all extractions. Before the extraction from the deuterated aqueous solution, the DHDECMP contacted D_2O two times. The initial concentration in the aqueous phase, before extraction, was 5x10^{-3} M for Sm(III) and 1x10^{-7} M for Cm in HNO_3/DHDECMP system. Five mm ID quartz tubes were used for luminescence measurements. Extractions were carried out using equal volumes of aqueous and organic phases. The range of nitric acid concentration in the aqueous phase is from 0 M to 13 M.

The Sm(III) and Cm(III) in the samples were excited to the excited states of Sm ($^6P_{3/2}$, 401 nm) and Cm ($^6I_{17/2,11/2}$, 397 nm) by a pulsed laser beam. Subsequently, the emission from the lowest luminescent level to the ground state manifold, i.e., $^5G_{5/2} \rightarrow {}^6H_{7/2}$ for Sm(III) and $^6D_{7/2} \rightarrow {}^8S_{7/2}$ for Cm(III), was measured to obtain the luminescence lifetime.[10-13)]

The 355 nm (third harmonic) laser beam was obtained directly from a pulsed (10 Hz) output of a Spectron SL-803 Nd:YAG laser. The 390-410 nm laser beam was obtained from a pulsed (10 Hz) 308 nm output of a Lambda Physik COMPex201 XeCl excimer laser pumping PBBO (Lambda Physik) in dioxane solution in a Lambda Physik SCANmate2 dye laser head. The pulse power was typically 3-7 mJ per pulse and the pulse width was about 15 ns. The emission light was collected at 90° into an Oriel 77257 monochromator using an optical fiber and detected by a Hamamatsu 3896 photomultiplier tube. The whole emission wavelength range (12.8 nm width) was observed. The signal was fed into a Hewlett Packard 54510A digitizing oscilloscope which was connected to a personal computer through a GP-IB interface. The luminescence decay curves observed in this work were fitted to single-exponential curves. An optical multichannel analyzer (Princeton Instruments) was also used to acquire time gated emission spectra. Emission lines from a mercury lamp were used to calibrate the optical multichannel analyzer system. In most cases, the optical multichannel analyzer was gated on after a fixed time delay following the laser pulse, and a digital pulse generator was turned on by the optical multichannel analyzer prior to externally triggering the laser. Fluorescence data was recorded at room temperature.

III. Results and discussions

The luminescence lifetime of a given species is measured in both H_2O and D_2O; thus the hydration number, N_{H2O}, of the corresponding Sm(III) and Cm(III) complexes were obtained from the luminescence decay constants measured in H_2O and D_2O media. N_{H2O} can be calculated using the relationship developed by Horrocks and Sudnick[14)] as follows:

$$N_{H2O} = C \{k_{obs}(H_2O) - k_{obs}(D_2O)\} \qquad (1)$$

where $k_{obs}(H_2O)$ and $k_{obs}(D_2O)$ are the observed luminescence rate constants(reciprocal lifetime, sec^{-1}) as measured in the H_2O and the D_2O solutions, respectively. The values of C are 4.2x10^{-3} for Tb(III) and 1.05x10^{-3} for Eu(III). Also, according to Kimura and Choppin,[15)] Kimura, *et al.*,[16)] and Kimura and Kato,[17,18)] the C values are 2.54x10^{-5} for Sm(III) and 0.65x10^{-3} for Cm(III). The uncertainty associated with the deduced N_{H2O} values is approximately ±0.5 water molecules.

The luminescence emission spectra of Sm(III) in nitric acid solutions and DHDECMP phases after the excitation at 401 nm as a function of nitric acid concentration are shown in **Fig. 1**. The spectra are attributed to emission from the $^4G_{5/2}$ state of Sm(III) to components of the lower-lying ^6H manifold. The primary emission band of the Sm(III)-nitrate complex and DHDECMP phase is shown at near 595 nm and 596 nm in the range of 0-13M nitric acid concentration.

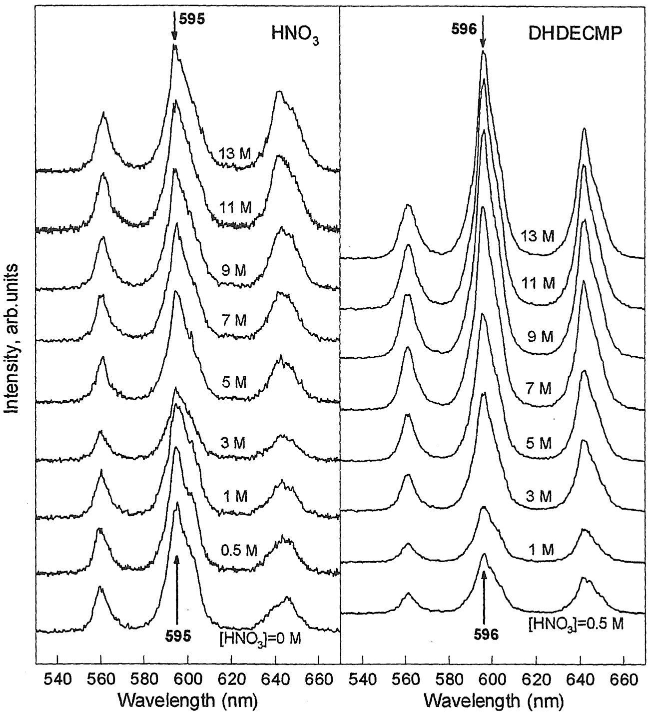

Fig. 1 Luminescence emission spectra of Sm(III) in the HNO_3 solution and DHDECMP phases following excitation at $\lambda_{ex} = 401$ nm.

Figure 2 shows the emission spectra of Cm(III) in the aqueous solutions and the organic phases after the excitation at 397 nm at various nitric acid concentrations.

Due to the formation of Cm(III)-nitrate complexes, the peak wavelength of Cm(III) emission change was from 596 nm at 0.5M HNO_3 to 604 nm at 13.0 M. It is readily evident that the counter ion (NO_3^-) and extractant (DHDECMP) significantly influence the emission spectrum of Cm(III). It is of interest that complexation of Cm(III) results in a shift of the emission peak to longer wavelengths in comparison with luminescence from aquo Cm(III).

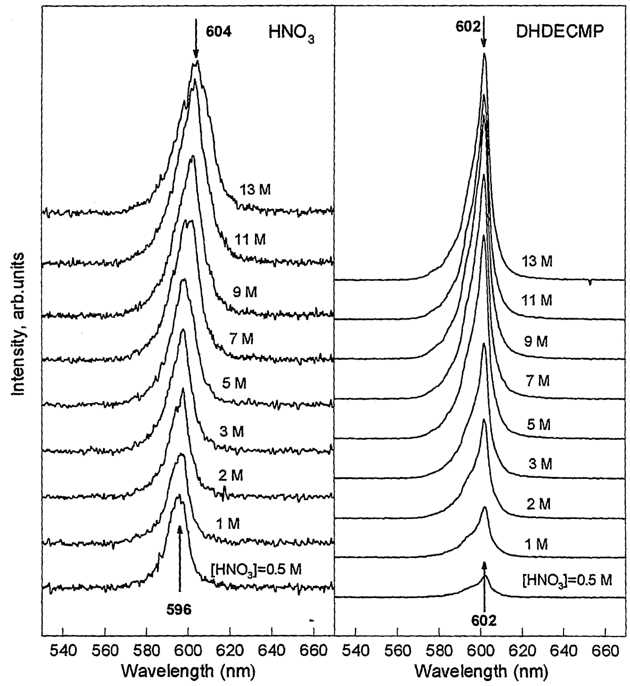

Fig. 2 Luminescence emission spectra of Cm(III) in the HNO_3 solution and DHDECMP phases following excitation at $\lambda_{ex} = 397$ nm.

The luminescence decay constants, $k_{obs}(s^{-1})$ of the Sm(III) and Cm(III) in the HNO_3 solutions and in DHDECMP phases after extraction from H_2O and D_2O solutions are given in **Table 1**. **Figure 3** also shows the number of water molecules, N_{H2O}, associated with Sm(III) and Cm(III). N_{H2O} was calculated by equation (1) with $C=2.54 \times 10^{-5}$ for Sm and 0.65×10^{-3} for Cm. The hydration numbers of Sm(III) and Cm(III) are about 9 in the 0.01M perchloric acid solutions. This agrees with the previous measured values of Kimura's.[8,18]

In 0 – 13 M HNO_3, the N_{H2O} values of Sm(III) and Cm(III) decreased similarly with increasing HNO_3 concentration, indicating inner-sphere complexation of both ions with the nitrate ion, with similar stability constants[19]. Approximately 4 water molecules are removed from the first coordination sphere of the ions at 13 M HNO_3, This is in agreement with the experimental results of Kimura[8], suggesting the formation of $[M(NO_3)_2(H_2O)_5]^+$ with the nitrate ion functioning as a bidentate ligand in an aqueous solution.

Since DHDECMP does not ionize when extracting trivalent actinides or lanthanides, three nitrate ions must be extracted along with the metal ion to maintain electroneutrality. Hence, the equation for the extraction of Cm(III) and Sm(III) may be written

$$M^{3+} + 3NO_3^-(aq.) + xCMP(org.) \longleftrightarrow M(NO_3)_3 \cdot CMP_x(org.) \quad (2)$$

where M = Cm(III) and Sm(III), x = the numbers of extractant molecule and CMP represents DHDECMP.

Table 1 Luminescence decay constants of Sm(III) and Cm(III) in the HNO_3 and extracted into DHDECMP phases from H_2O and D_2O solutions.

(a) Nitric acid solution

$[HNO_3]$ (M)	Sm, $k_{obs}(\times 10^{-3}sec^{-1})$ H_2O	Sm, $k_{obs}(\times 10^{-3}sec^{-1})$ D_2O	Cm, $k_{obs}(\times 10^{-3}sec^{-1})$ H_2O	Cm, $k_{obs}(\times 10^{-3}sec^{-1})$ D_2O
0	375.27	17.51	15.06	1.1
0.5	465.27	16.92	13.07	0.95
1	466.4	16.35	12.84	0.97
2	434.63	15.27	12.36	1.0
3	421.7	14.27	11.95	1.04
5	396.57	12.7	11.27	1.14
7	367.2	11.19	10.72	1.27
9	339.1	9.99	9.88	1.41
11	312.27	9.19	9.19	1.55
13	288.37	8.56	8.8	1.72

(b) DHDECMP phase

$[HNO_3]$ (M)	Sm, $k_{obs}(\times 10^{-3}sec^{-1})$ H_2O	Sm, $k_{obs}(\times 10^{-3}sec^{-1})$ D_2O	Cm, $k_{obs}(\times 10^{-3}sec^{-1})$ H_2O	Cm, $k_{obs}(\times 10^{-3}sec^{-1})$ D_2O
0.5	89.49	13.73	4.5	1.65
1	80.16	13.73	4.15	1.69
2	67.48	13.43	3.6	1.74
3	58.78	13.17	3.27	1.86
5	48.48	12.72	2.99	1.79
7	41.66	12.47	2.7	1.8
9	38.08	12.36	2.52	1.72
11	36.27	12.4	2.39	1.69
13	36.75	12.59	2.42	1.73

The hydration number of Sm(III) and Cm(III) in the DHDECMP phase decreases from about 1.8 at 0.5M HNO_3 to near 0.5 at 13M HNO_3 with an increase of nitric acid concentration. Beitz and Sullivan[3] reported there was no water in the inner coordination sphere of Eu(III) extracted by CMPO, which has a bidentate ligand like DHDECMP, from 2M nitric acid. Our results are different from theirs.

From the results, it will be expected that when the Sm(III) and Cm(III) be extracted into DHDECMP from nitric acid through equation (2), the value of x will not exactly be 3, if DHDECMP is functioning as a bidentate ligand.

IV. Conclusions

LIF studies of Sm(III) and Cm(III) complexes in a nitric acid solution and the DHDECMP phase have been carried out.

The hydration number of Sm(III) and Cm(III) in nitric acid solutions decreased linearly with increasing nitric acid concentration. The hydration number of Sm(III) and Cm(III) in the DHDECMP phase decreased with an increase of nitric acid concentration.

The water in the inner coordination sphere of Sm(III) extracted into the DHDECMP from nitric acid solutions was not completely removed at a low nitric acid concentration and decreased with an increase of nitric acid concentration. Cm(III) extracted into the DHDECMP phase from nitric acid solution represented the same results as Sm(III).

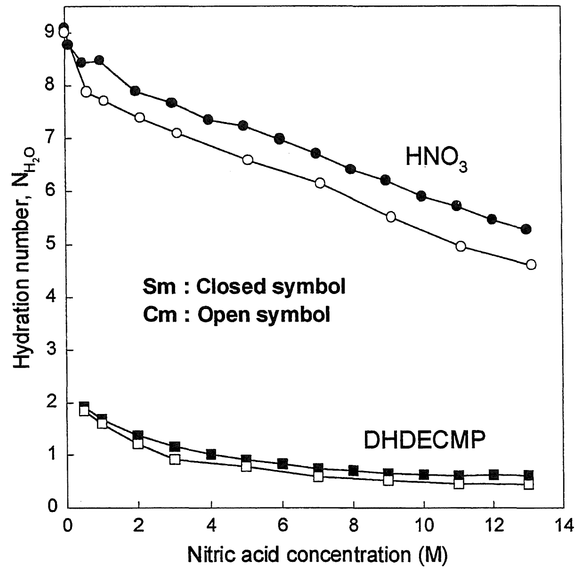

Fig. 3 Inner-sphere hydration number of Sm(III) and Cm(III) in HNO_3 solution and DHDECMP phase as a function of nitric acid concentration.

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