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Laser-Induced Fluorescence Studies of Sm(III) and Cm(III) in HNO_3/DHDECMP Extraction System

Dong Yong Chung and Jae Hyung Yoo
Korea Atomic Energy Research Institute
P.O. Box 105, Yusong, Taejon, Korea 305-600

Takaumi Kimura
Japan Atomic Energy Research Institute
Tokai-mura, Ibaraki, Japan 319-1195

Abstract

Laser-induced fluorescence(LIF) studies of Sm^{3+} and Cm^{3+} complexes in 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^{3+} and Cm^{3+} in the nitric acid solution and in DHDECMP phase. The hydration number of Sm^{3+} and Cm^{3+} in nitric acid solution decreased linearly with an increasing nitric acid concentration. The hydration numbers of Sm^{3+} and Cm^{3+} in DHDECMP phase decreased with an increase of nitric acid concentration. The water molecules in the inner coordination sphere of Sm^{3+} and Cm^{3+} extracted into the DHDECMP from nitric acid solution were not completely removed at the low nitric acid concentration and decreased with an increase of nitric acid concentration.

1. 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 a similar range of ionic radii and show strong similarities in chemical behavior. Many efforts have been devoted to develop 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 at the molecular level the species extracted to the organic phase.

Time resolved laser-induced fluorescence(LIF) has been a powerful means for studying some complexed lanthanide and actinide ions in aqueous solution. However, few LIF studies of lanthanide or actinide ion-extractant complexes have been reported, and a few attempts were made to determine the presence of water, either qualitatively or quantitatively, in the extracted complexes. LIF spectra 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^{3+} extracted from nitric acid using HDEHP and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) as extractants. The results showed that there was no water in the inner coordination sphere of the Eu^{3+} 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 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.

In the present study, experimental research was conducted in order to provide further evidence for water molecules coordinated to the extracted lanthanide complexes. Luminescence lifetime measurements together with LIF spectra were measured to determine the number of water molecules coordinated to Sm^{3+} and Cm^{3+} in aqueous solution and in DHDECMP phase.

2. Experimental

Sm^{3+} stock solution was prepared by dissolving an appropriate amount of the lanthanide oxides (Wako Pure Chem. Ind., Ltd.) in perchloric acid. Cm^{3+} stock solution used in this experiments has been prepared by Kimura as described follows.[7] $^{244}Cm(t_{1/2}=18.1y)$ supplied by C.E.A., France was purified from its daughter nuclide ^{240}Pu by passage through anion exchange resin(AG 1X8) with elution by 7M HNO_3. The Cm fraction in effluent was fumed to dryness after addition of concentrated $HClO_4$. The residue obtained was dissolved in 0.01M $HClO_4$ to yield the Cm^{3+} stock solution. The concentration of the Cm^{3+} stock solution was determined by α-ray spectrometry and liquid scintillation counting.

Analytical reagent grade nitric acid were used. DHDECMP purified by Kimura after purchasing from Columbia Organic Chemical Company, South Carolina, USA was used.[8] DNO_3(99.9%) and D_2O(99.9%) was obtained from Aldrich and Merck, Canada. Solutions of the nitric acid complexes of Sm^{3+} were prepared from Sm^{3+} and nitric acid stock solutions of a 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 deuterated aqueous solution, the DHDECMP was contacted with D_2O two times. The initial concentration in the aqueous phase, before extraction, was $5x10^{-3}$ M for Sm^{3+} and $1x10^{-7}$ M for Cm in HNO_3/DHDECMP system. 5 mm- ID quartz tubes were used for luminescence measurements at room temperature. Extractions were carried out using equal volumes of aqueous and organic phases.

The Sm^{3+} and Cm^{3+} in the samples were excited to the excited states of Sm ($^6P_{3/2}$, 401 nm), 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., $^5G_{5/2} \rightarrow {}^6H_{7/2}$ (594 nm) for Sm^{3+}, $^6D_{7/2} \rightarrow {}^8S_{7/2}$ (596 nm) for Cm^{3+}, was measured to obtain the luminescence lifetime.[9-12]

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 a 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. 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, a digital pulse generator turned on the optical multichannel analyzer prior to externally triggering the laser. Fluorescence data were recorded at room temperature.

3. Results and discussions

The mechanisms which lead to changes in the luminescence lifetime of Ln^{3+} or Cm^{3+} species are similar to those which affect the intensities in the emission spectra. High-energy vibrations are efficient deactivators of the excited lanthanide ions, and are effective quenchers of the emission lifetime. The –OH stretching mode of coordinated water molecules is particularly effective in this regard.[13] Most ligands do not contain groups with vibrational frequencies required to effectively quench the excited state, and therefore do not reduce the luminescence lifetimes of Ln^{3+} and Cm^{3+}. Since the direct binding of ligand results in the expulsion of some of the coordinated water molecules, it affects the degree of excited state quenching. As a result, the emission lifetimes of Ln^{3+} and Cm^{3+} provide direct information on residual hydration states of the metal ion.

The existence of a deuterium isotope effect in luminescence lifetimes of lanthanides has been known for some time.[14,15] While the –OH stretching mode of coordinated water(3500 cm^{-1}) is effective at quenching the Eu^{3+} excited $^5D_0$ state and the Tb^{3+} excited $^5D_4$ state, the analogous –OD stretching mode of coordinated deuterium oxide(2800 cm^{-1}) is far less effective. Horrocks and Sudnick[13] have used this phenomenon to develop a spectroscopic method suitable for determination of the water molecules bound at the inner coordination sphere of either Eu^{3+} and Tb^{3+}. The luminescence lifetime of a given species is measured in both H_2O and D_2O, and the observed rate for luminescence decay obtained in each solvent system. The difference between the rate constants, Δk, obtained in H_2O and D_2O is directly proportional to number of coordinated water molecules, N_{H2O}, and can be calculated using the relationship developed by Horrocks and Sudnick[13] 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) as measured in H_2O and D_2O solution, respectively. According to Kimura's results[16-19], it appears as the value of 2.54×10^{-5} for Sm^{3+}, 0.65×10^{-3} for Cm^{3+}. The uncertainty associated with the deduced N_{H2O} values is approximately ±0.5 water molecules.

The luminescence emission spectra of Sm^{3+} in nitric acid solutions and DHDECMP phases after the excitation at 401 nm as a function of nitric acid concentration are shown in Figures 1 and 2. The spectra are attributed to emission from the $^4G_{5/2}$ state of Sm^{3+} to components of the lower-lying ^6H manifold. The primary emission band of Sm^{3+}-nitrate complex and DHDECMP phase is shown at near 595 nm and 596 nm in the range of 0-13M nitric acid concentration.

Figures 3 and 4 show the emission spectra of Cm^{3+} in the aqueous solutions and the organic phases after the excitation at 397 nm as a function of the nitric acid concentration. The Cm^{3+} was excited to the excited states of Cm ($^6I_{17/2,11/2}$, 397 nm) and then the emission from the lowest luminescent level to the ground state, $^6D_{7/2} \rightarrow {}^8S_{7/2}$ (596 nm) for Cm^{3+}, was measured to obtain the luminescence lifetime.[12]

The peak wavelength of Cm^{3+} emission increases due to the formation of Cm^{3+}-nitrate complexes 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^{3+}. It is of interest that complexation of Cm^{3+} results in shifting of the emission peak to longer wavelengths in comparison with luminescence from aquo Cm^{3+}.

Figure 5 also shows the number of water molecules, N_{H2O}, associated with the Sm^{3+} and Cm^{3+}. N_{H2O} was calculated by the equation (1) with the C=2.54x10^{-5} for Sm and 0.65x10^{-3} for Cm. The hydration numbers of Sm^{3+} and Cm^{3+} have about 9 in the 0.01M perchloric acid solutions. It agrees with the previous measured values of Kimura's.[7,19]

In 0 – 13.0 M HNO_3, the N_{H2O} values of Sm^{3+} and Cm^{3+} decreased similarly with increasing HNO_3 concentration, indicating inner-sphere complexation of both ions with the nitrate ion, with similar stability constants.[20] Approximately 4 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[7], suggesting the formation of $[M(NO_3)_2(H_2O)_5]^+$ with the nitrate ion functioning as a bidentate ligand in 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^{3+} and Ln^{3+} may be written

$$M^{3+} + 3NO_3^-(aq.) + xCMP(org.) \longleftrightarrow M(NO_3)_3CMP_x(org.) \qquad (2)$$

where x = the number of extractant molecules, CMP represents DHDECMP

The hydration number of Sm^{3+} and Cm^{3+} in 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^{3+} extracted by CMPO, which has 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^{3+} and Cm^{3+} be extracted into DHDECMP from nitric acid through the equation (2), the value of x is not exactly 3, if DHDECMP is a bidentate ligand.

4. Conclusions

LIF studies of Sm^{3+} and Cm^{3+} complexes in DHDECMP phase have been carried out. The fluorescence transitions of Sm^{3+} and Cm^{3+} in the nitric acid solution and DHDECMP phase are summarized in below.

The hydration number of Sm^{3+} and Cm^{3+} in nitric acid solution decreased linearly with increasing nitric acid concentration. The hydration number of Sm^{3+} and Cm^{3+} in DHDECMP phase decreased with an increase of nitric acid concentration. The water molecule in the inner coordination sphere of Sm^{3+} extracted into the DHDECMP from nitric acid solution was not completely removed at the low nitric acid concentration and decreased with the increase of nitric acid concentration. Cm^{3+} extracted into the DHDECMP phase from nitric acid solution represented the same results with Sm^{3+}.

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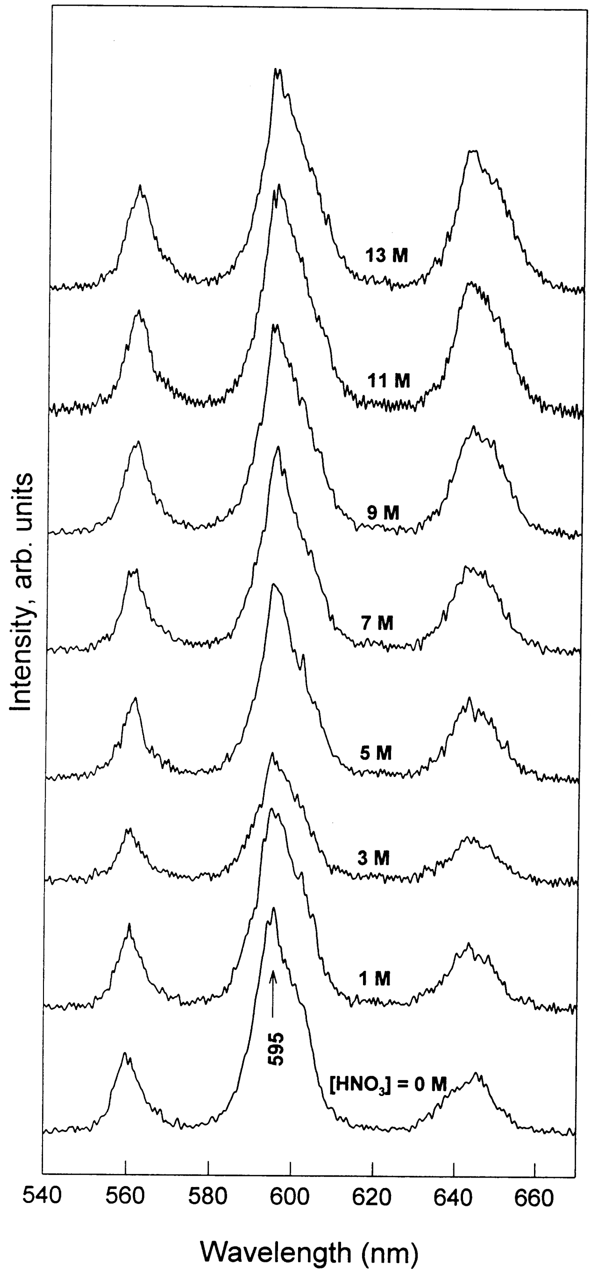

Fig. 1 Luminescence emission spectra of Sm^{3+} in nitric acid soluions following excitation at λ_{ex}=401nm.

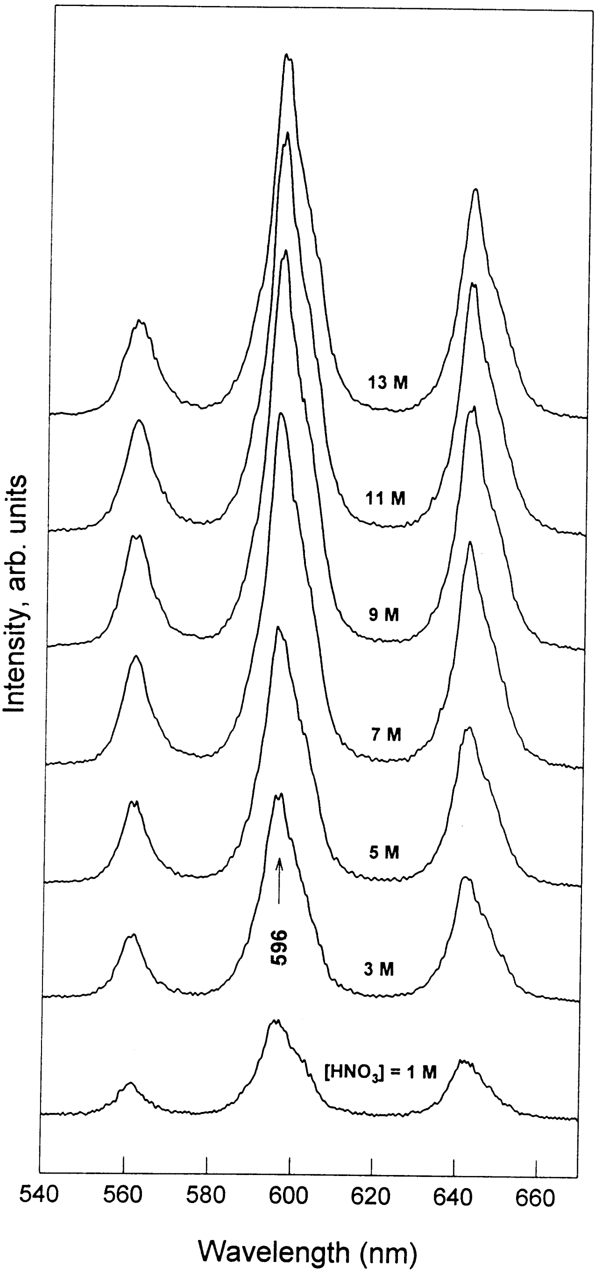

Fig. 2 Luminescence emission spectra of Sm^{3+} extracted into the DHDECMP phase from nitric acid following excitation at λ_{ex}=401nm.

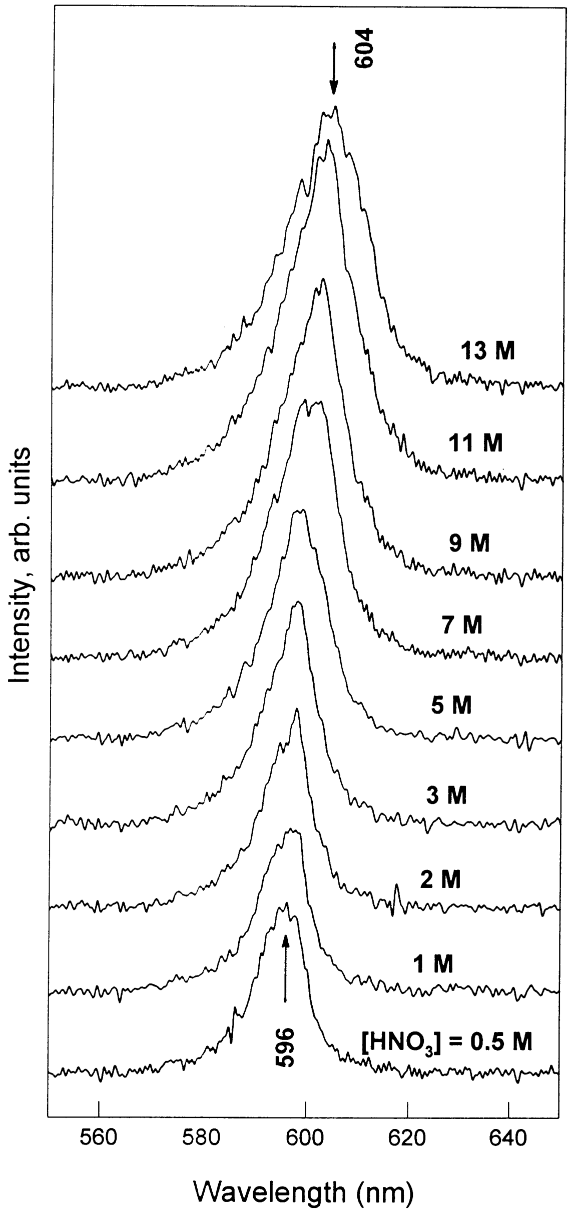

Fig. 3 Luminescence emission spectra of Cm^{3+} in nitric acid soluions following excitation at λ_{ex}=397nm.

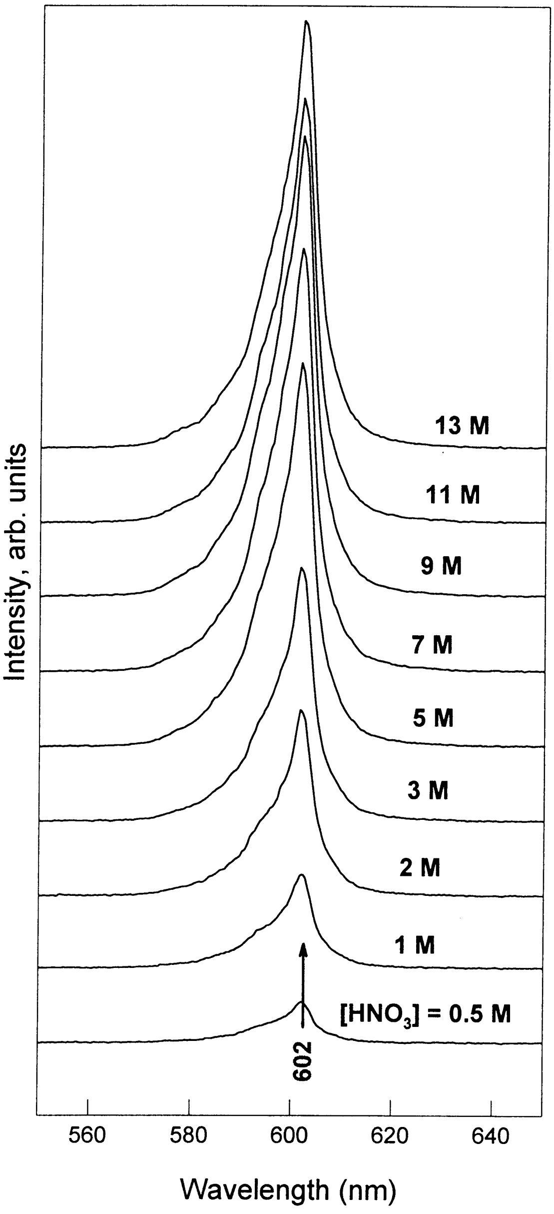

Fig. 4 Luminescence emission spectra of Cm^{3+} extracted into the DHDECMP phase from nitric acid following excitation at λ_{ex}=397nm.

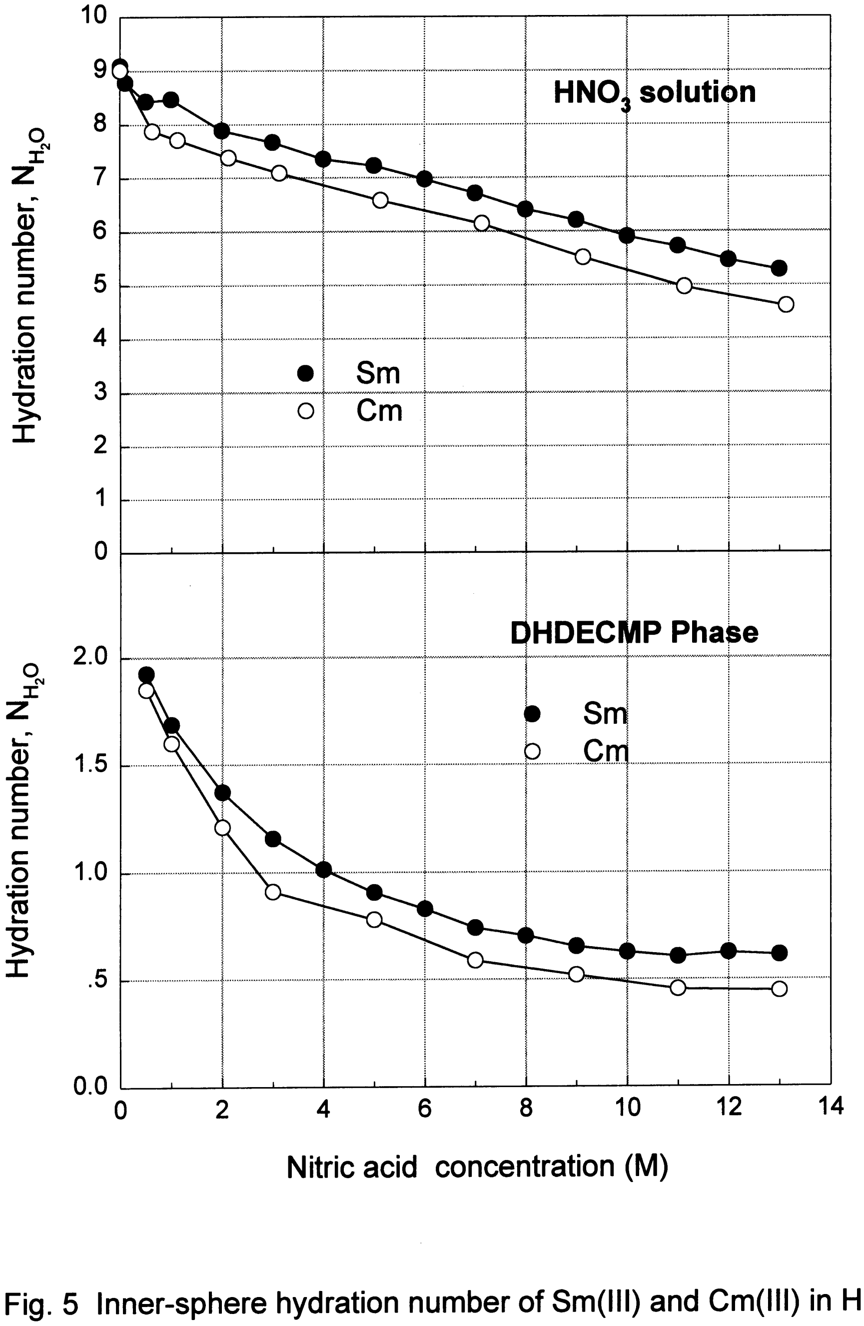

Fig. 5 Inner-sphere hydration number of Sm(III) and Cm(III) in HNO_3 solutions and DHDECMP phases with nitric acid concentration.