# ランタノイドの発光寿命について

## 「時間分解蛍光分光法によるアクチノイドおよびランタノイドの溶液化学に関する研究」からの抜粋を使って、ガドリニウムについて考察

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福島研究開発部門

JNRS Award

# *Studies on Solution Chemistry of Actinides and Lanthanides by Time-resolved Laser-induced Fluorescence Spectroscopy (TRLFS)*

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# Scope of the TRLFS study

## Environment

Speciation and Behavior Prediction/Control

Precipitation, Sorption, Colloid formation, Complexation, etc.

## Separation

Elucidation of Mechanism Novel Method Creation

Solvent extraction, Ion exchange, Electrolysis, etc.

## Time-resolved Laser-induced Fluorescence Spectroscopy

Highly Sensitive & Selective Method

## Coordination

Coord. Structure and Reaction Control

Oxidation state, Chemical bond, Structure, Hydration/Solvation, etc.

# Luminescent ions of Ln and An

## Lanthanides

| 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **La** | **Ce** | **Pr** | **Nd** | **Pm** | **Sm** | **Eu** | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** |
| | | | | | 2 | **2** | (2) | | | (2) | (2) | 2 | 2 | |
| **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** | **3** |
| | 4 | 4 | (4) | | | | | 4 | (4) | | | | | |

## Actinides

| 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ac** | **Th** | **Pa** | **U** | **Np** | **Pu** | **Am** | **Cm** | **Bk** | **Cf** | **Es** | **Fm** | **Md** | **No** | **Lr** |
| | | | | | | | | | | | | 1? | | |
| | | | | | | (2) | | | (2) | (2) | 2 | 2 | **2** | |
| **3** | (3) | (3) | 3 | 3 | 3 | **3** | **3** | **3** | **3** | **3** | **3** | **3** | 3 | **3** |
| | **4** | 4 | **4** | 4 | **4** | 4 | 4 | 4 | (4) | 4? | | | | |
| | | **5** | 5 | **5** | 5 | 5 | 5? | | 5? | | | | | |
| | | | **6** | 6 | 6 | 6 | 6? | | | | | | | |
| | | | | 7 | (7) | 7? | | | | | | | | |

Bold type= most stable; ( )= unstable; ?= claimed but not substantiated.

# Contents

1. Hydration studies of An(III) and Ln(III) and its applications to the solution chemistry

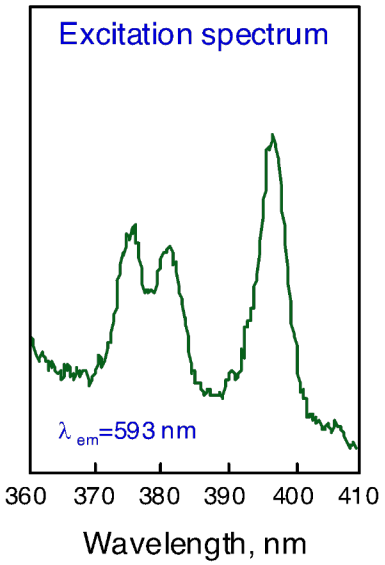
2. Speciation study of U(VI) hydrolysis at high temperatures and pressures

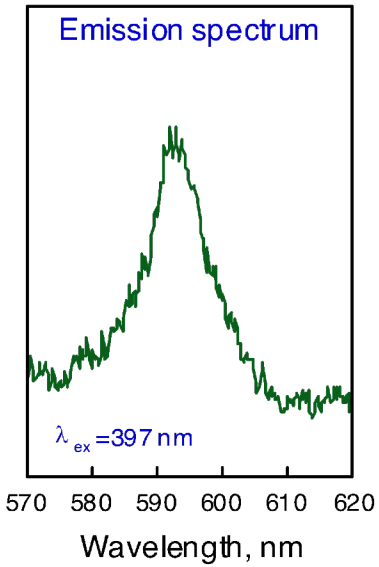
3. Luminescence properties of U(IV) in aqueous solution

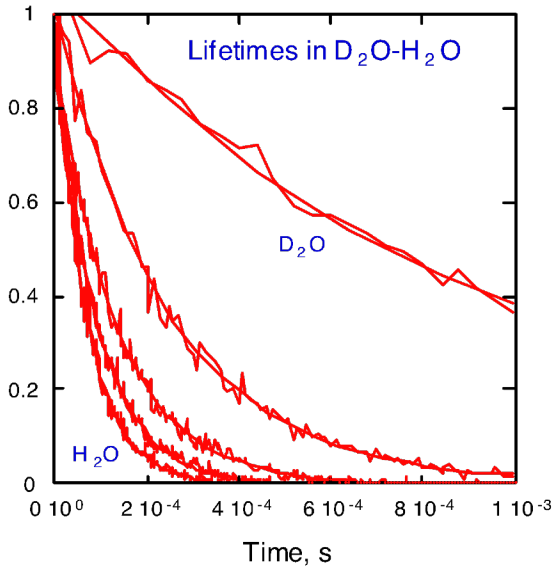
# TRLFS data

Excitation spectrum
Emission spectrum
Lifetime ⇛ Determination of Hydration Number $N_{H2O}$
⇛ Characterization of Chemical Species
⇛ Direct Comparison of 5f- vs. 4f-elements

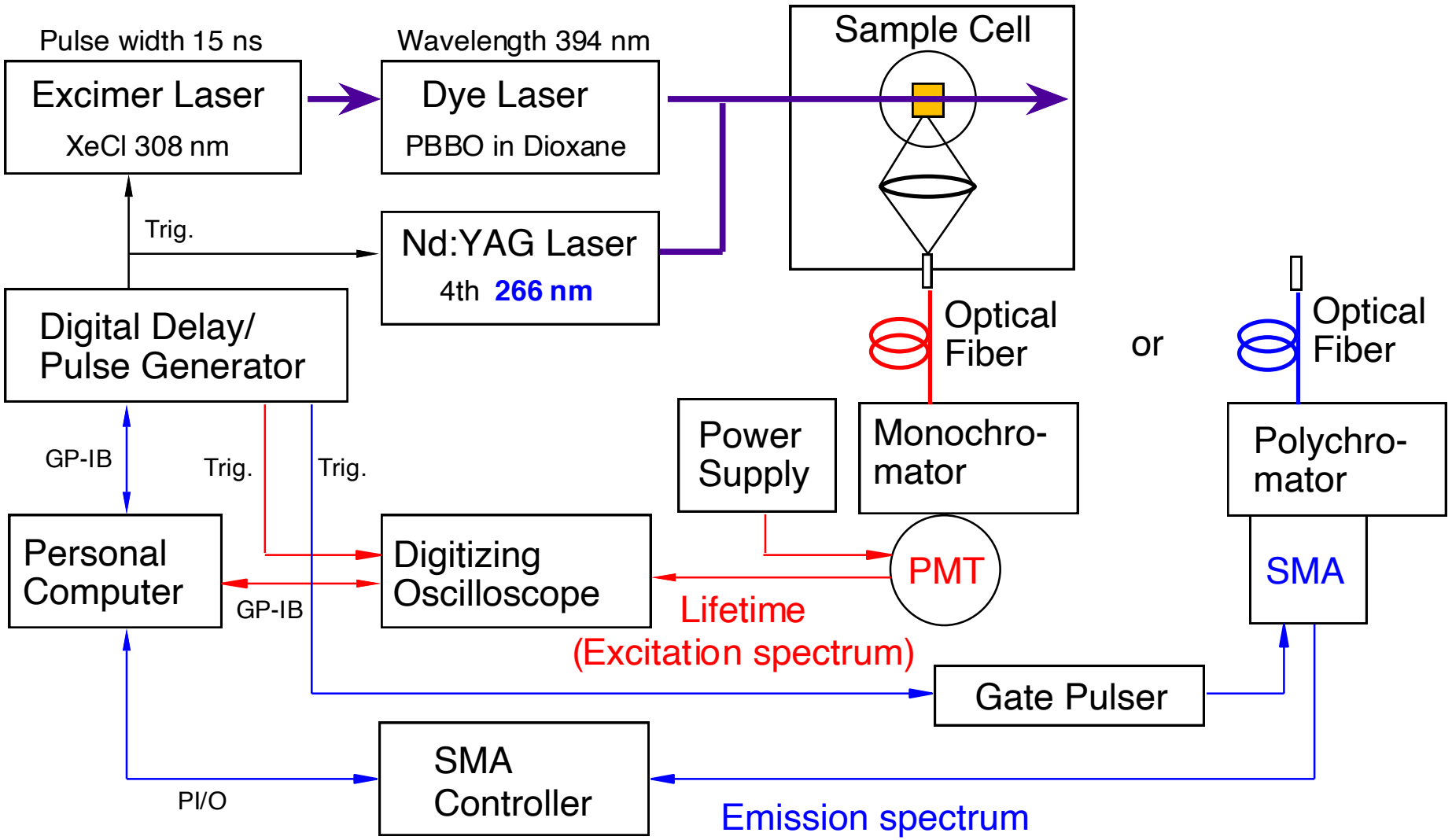
Examples of Cm(III)



# TRLFS system



# Calibration of $k_{obs}$ vs. $N_{H2O}$ for Cm(III)

J. Alloys Compd., **213/214**, 313 (1994).

$$k_{obs}(H_2O) = k_F + \Sigma k_i^{nr} + k_{H2O} \cdot \chi_{H2O}$$

$$k_{obs}(D_2O) = k_F + \Sigma k_i^{nr}$$

$k_F$ : emission

$k_i^{nr}$ : quenching by ligand, etc.

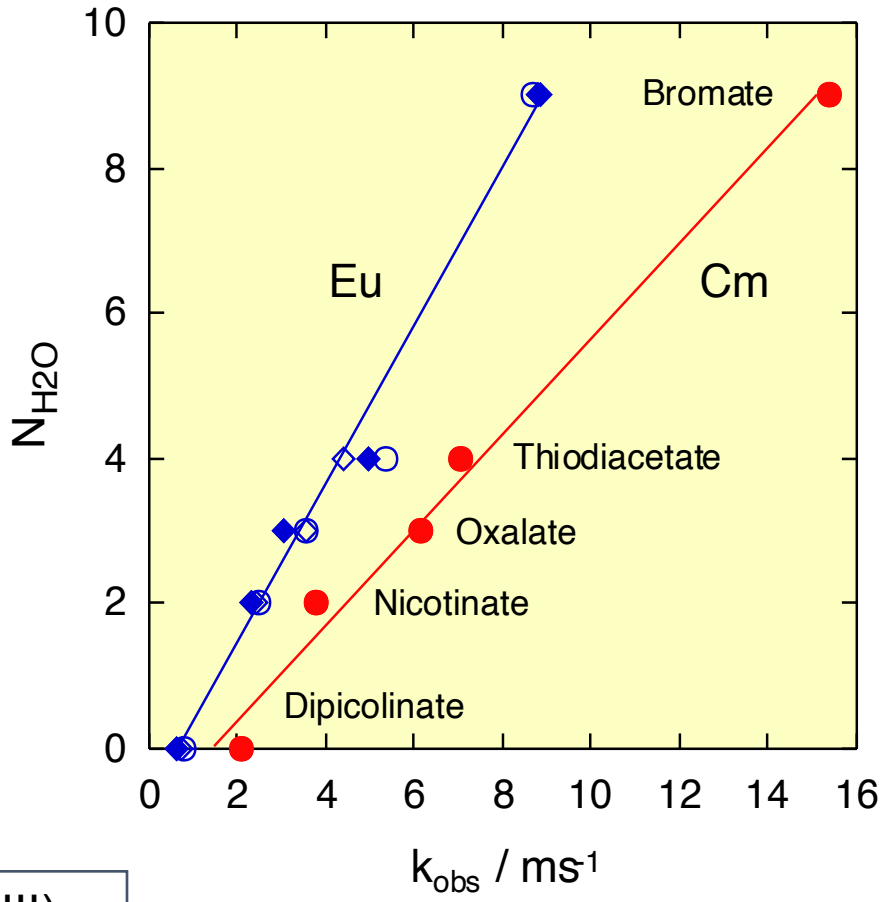
$k_{H2O}$: quenching by $H_2O$

$\chi_{H2O}$: mole fraction of $H_2O$

$$N_{H2O} = A\,[k_{obs}(H_2O) - k_{obs}(D_2O)]$$

$k_{obs}(H_2O) >> k_{obs}(D_2O)$ = constant

$$N_{H2O} = A \cdot k_{obs}(H_2O) - B$$




Comparison of $\Delta E$ among Ln(III) and Cm(III)

Eu($1.22 \times 10^4$ cm$^{-1}$)

**Gd($3.20 \times 10^4$ cm$^{-1}$)** ⇔ Cm($1.68 \times 10^4$ cm$^{-1}$)

Tb($1.48 \times 10^4$ cm$^{-1}$)

$N_{H2O} = 0.65 k_{obs}(Cm) - 0.88$

$N_{H2O} = 1.07 k_{obs}(Eu) - 0.62$

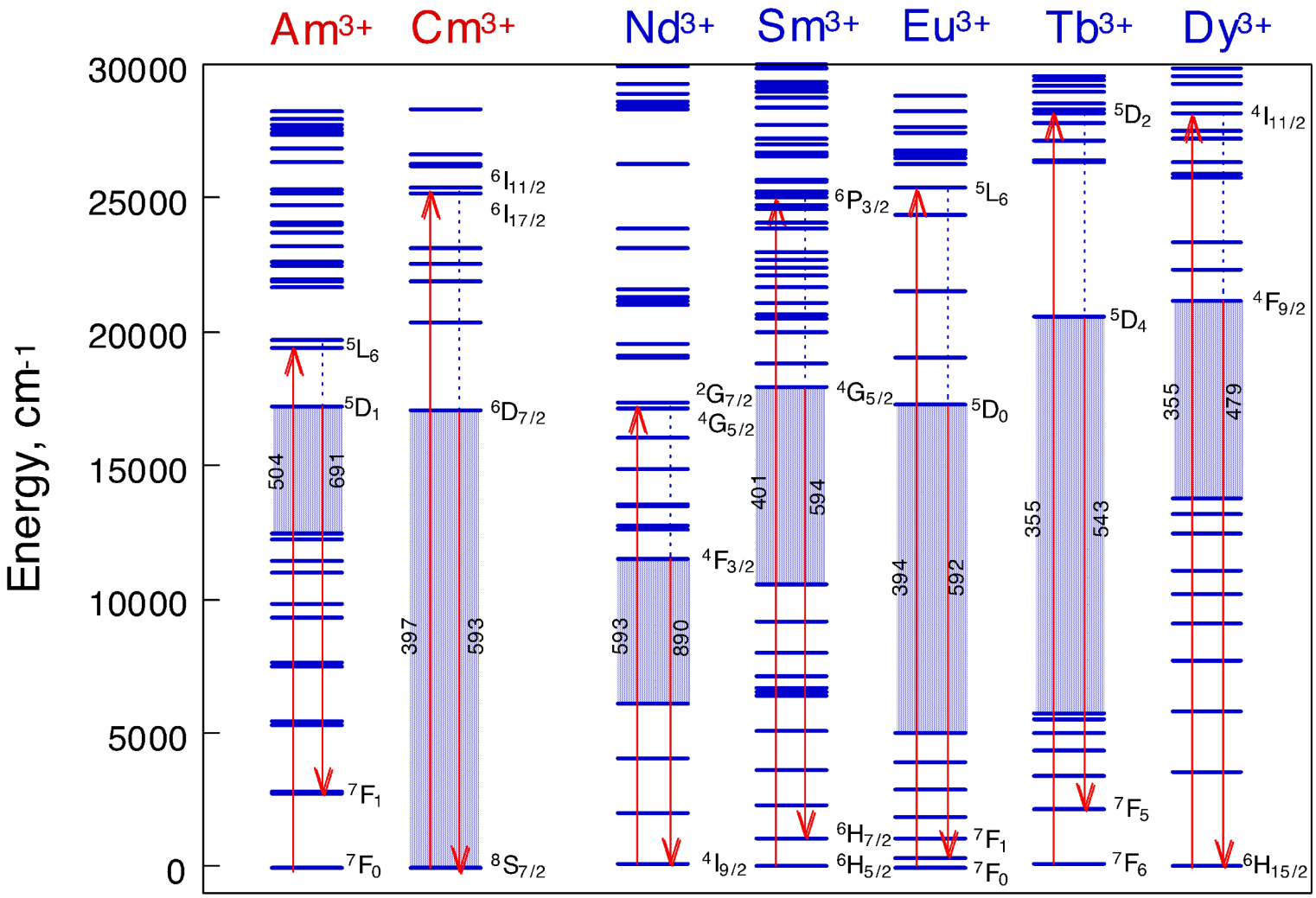
# Spectroscopic characteristics of Cm(III)

| Species | Excitation (nm) | Emission (nm) | Lifetime (μs) | $N_{H2O}$[a] |
|---|---|---|---|---|
| $Cm^{3+}$ | 375.4, 381.3, 396.5 | 593.8 | 65±2 | **9.1±0.3** |
| $Cm(OH)^{2+}$ | 376.0, 381.6, 397.5 | 598.8 | 72±2 | **8.2±0.3** |
| $Cm(OH)_2^{+}$ | 377.4, 384.2, 399.2 | 603.5 | 81±10 | **7.3±1.1** |
| $Cm(CO_3)^{+}$ | 376.5, 382.5, 397.5 | 598.0 | 85±4 | **6.8±0.4** |
| $Cm(CO_3)_2^{-}$ | 377.5, 384.5, 398.9 | 605.9 | 105±5 | **5.3±0.3** |
| $Cm(CO_3)_3^{3-}$ | 377.5, 384.1, 399.9 | 607.6 | 215±6 | **2.1±0.1** |
| Cm humate | 376, 383, 398 | 601 | 72±5(80%)<br>145(20%) | **8.2±0.7**<br>**3.6** |
| Cm fulvate | 374, 382, 398.5 | 600.3 | 70±5(80%)<br>142(20%) | **8.4±0.7**<br>**3.7** |

[a] $N_{H2O}=0.65k_{obs}(ms^{-1}) - 0.88$

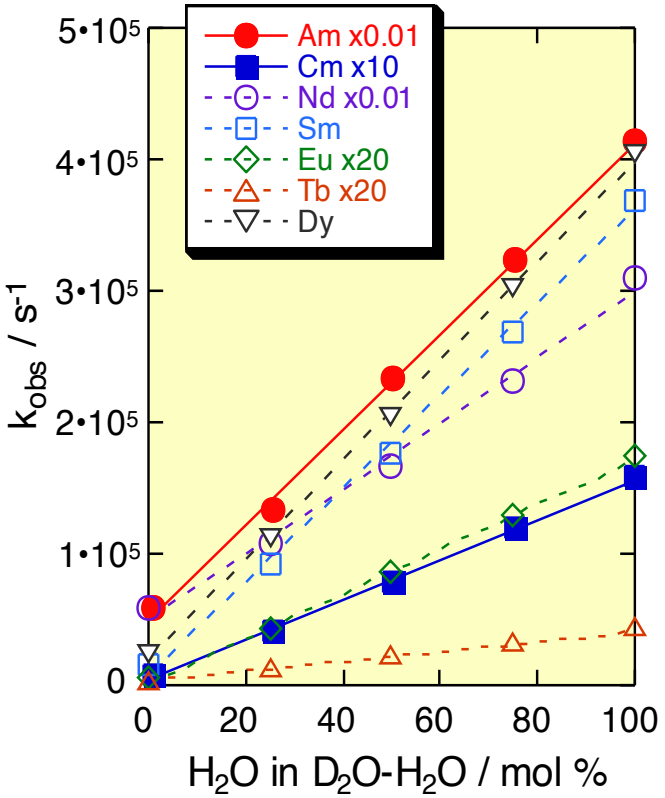
Radiochim. Acta, **72**, 61 (1996).

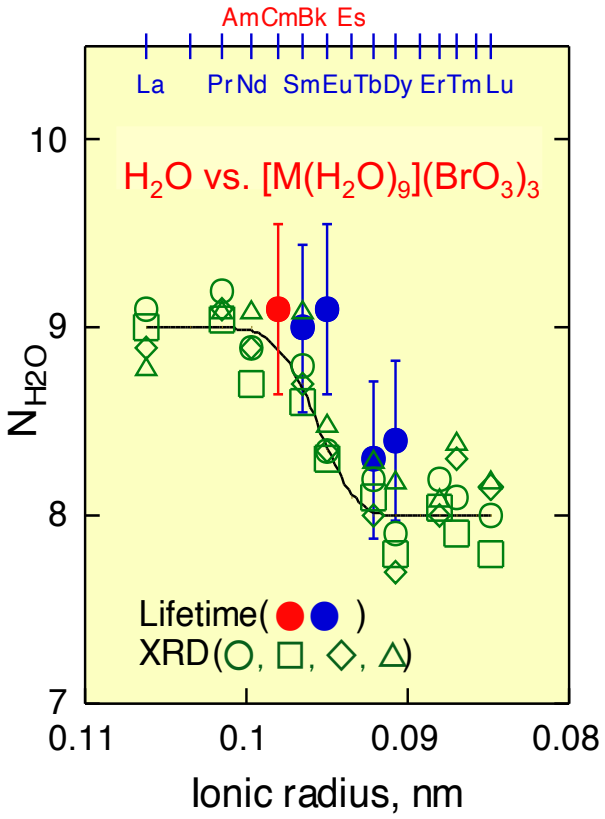
# Selection of $\lambda_{ex}$ and $\lambda_{em}$




Energy levels of luminescent Ln(III) and An(III) ions in aqueous solution and excitation and emission wavelengths used in the experiments.

# Calibration of $k_{obs}$ vs. $N_{H2O}$




Calibration relations

$N_{H2O} = 6.12 \times 10^{-4}\, k_{obs}(Cm) - 0.48$

$N_{H2O} = 4.03 \times 10^{-3}\, k_{obs}(Tb) - 0.87$

$N_{H2O} = 1.05 \times 10^{-3}\, k_{obs}(Eu) - 0.44$

$N_{H2O} = 2.54 \times 10^{-5}\, k_{obs}(Sm) - 0.37$

$N_{H2O} = 2.11 \times 10^{-5}\, k_{obs}(Dy) - 0.60$

$N_{H2O} = 3.58 \times 10^{-7}\, k_{obs}(Nd) - 1.97$

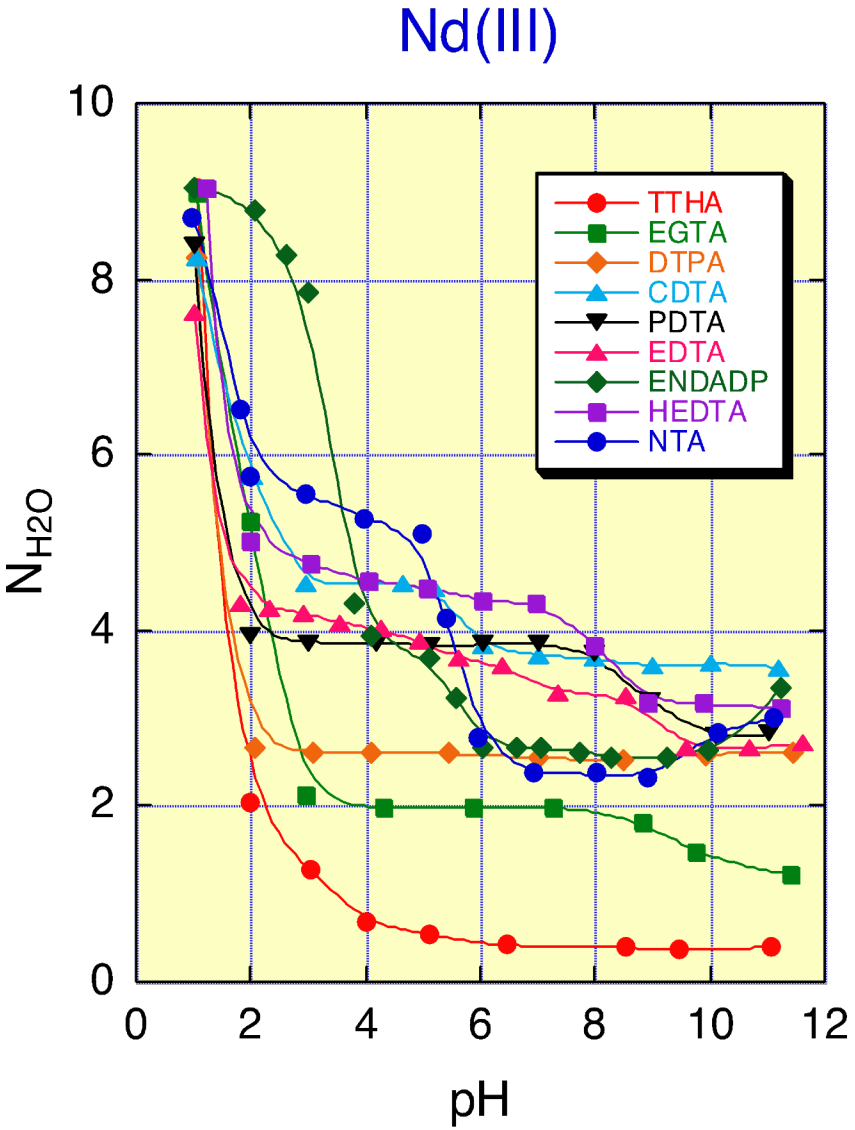
$N_{H2O} = 2.56 \times 10^{-7}\, k_{obs}(Am) - 1.43$

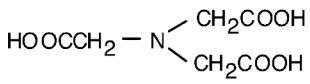
Linear relation of $k_{obs}$ - $H_2O$ % $\Rightarrow$ Correlation of $k_{obs}$ - $N_{H2O}$

$N_{H2O}$ in $H_2O$ $\quad N_{H2O} = A.k_{obs}(s^{-1}) - B$

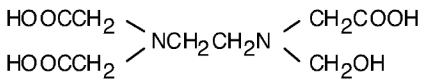
# Complexes with aminopolycarboxylates

J. Alloys Compd., **271-273**, 867 (1998).
Ibid., **275-277**, 806 (1998).

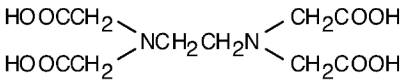


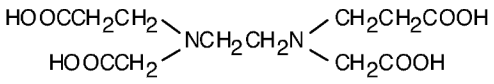

NTA (4)



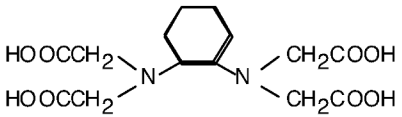

HEDTA (6)



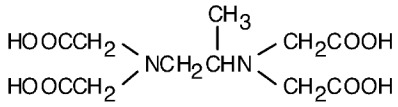

EDTA (6)



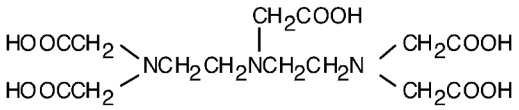

ENDADP (6)



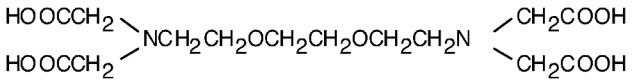

CDTA (6)



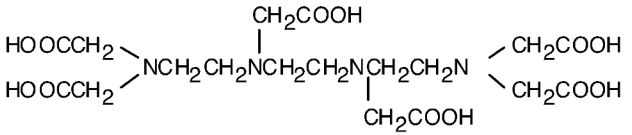

PDTA (6)




DTPA (8)




EGTA (8)




TTHA (10)

# Evaluation of $CN_T$ of An(III) and Ln(III)

Average numbers of hydration number $N_{H2O}$, ligand coordination number $CN_L$, and total coordination number $CN_T$ for actinide(III) complexes ($CN_T = CN_L + N_{H2O}$)

| Ligand | $CN_L$ | Am(III) $N_{H2O}$ | Am(III) $CN_T$ | Cm(III) $N_{H2O}$ | Cm(III) $CN_T$ |
|---|---|---|---|---|---|
| NTA | 4 | **6.5** | 10.5 | **6.3** | 10.3 |
| HEDTA | 5-6 | **5.1** | 10.6 | **4.3** | 9.8 |
| ENDADP | 6 | **4.9** | 10.9 | --- | --- |
| EDTA | 6 | **4.8** | 10.8 | **3.9** | 9.9 |
| PDTA | 6 | **4.8** | 10.8 | --- | --- |
| CDTA | 6 | **7.3** | 13.3* | **3.9** | 9.9 |
| DTPA | 7-8 | **3.1** | 10.6 | **1.9** | 9.4 |
| EGTA | 8 | **3.0** | 11.0 | --- | --- |
| TTHA | 8-9 | **1.6** | 10.1 | **0.9** | 9.4 |
| **av. $CN_T$** | | | **10.7** | | **9.8** |

| | $CN_T$ |
|---|---|
| **Am(III)** | **10.7 ± 0.3** |
| **Cm(III)** | **9.8 ± 0.3** |
| **Nd(III)** | **9.9 ± 0.3** |
| **Sm(III)** | **10.2 ± 0.5** |
| **Eu(III)** | **8.9 ± 0.2** |
| **Tb(III)** | **8.6 ± 0.4** |
| **Dy(III)** | **9.1 ± 0.2** |

**$CN_T$: Am(III), Cm(III), Nd(III), Sm(III) > Eu(III), Tb(III), Dy(III)**

# Applications of the hydration study

-Hydration number of Ln(III) in concentrated aqueous salt solution in fluid and frozen states

**- Solvation of An(III) and Ln(III) in non-aqueous and binary mixed solvents**

**- Hydration states of Cm(III) and Eu(III) in solution and in cation exchange resin**

- Hydration states of Ln(III) and Cm(III) in the complexes extracted with Cyanex301, Cyanex302 and Cyanex272

**- Direct observation of Cm(III)-fulvate species on fulvic acid-montmorillonite hybrid**

- Sorption behavior of Eu(III) and Cm(III) on the cell surfaces of microorganisms

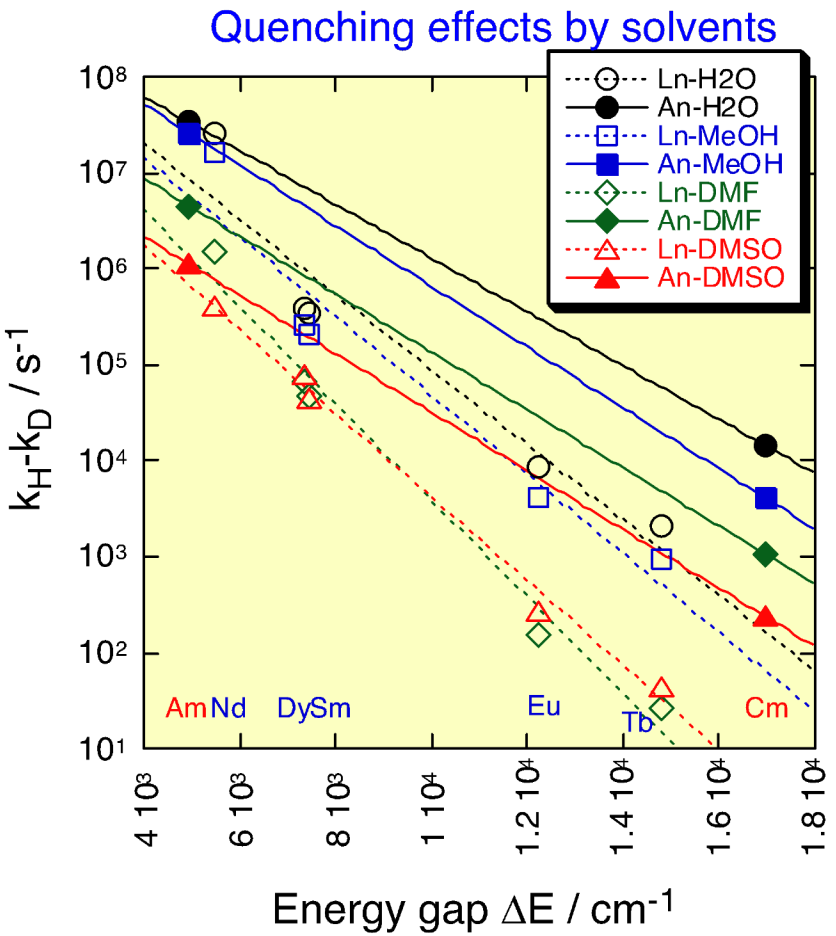
# Lifetimes($\mu$s) in pure solvents

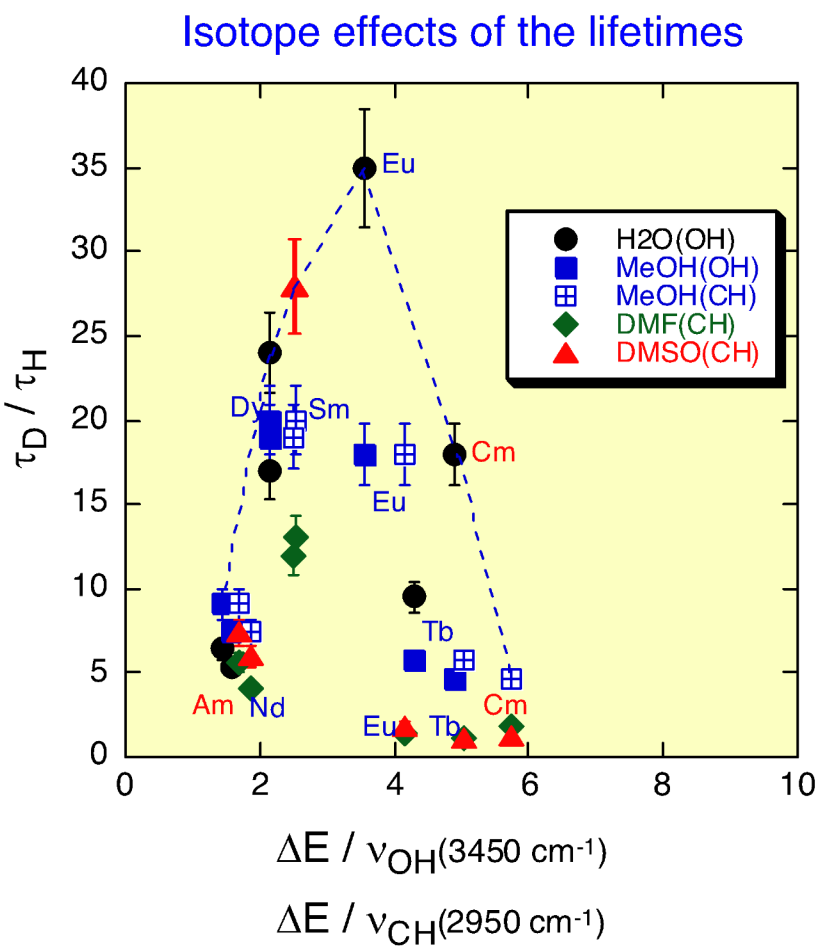
Radiochim. Acta, **89**, 125 (2001).

| | Cm(III) | Tb(III) | Eu(III) | Sm(III) | Dy(III) | Nd(III) | Am(III) |
|---|---|---|---|---|---|---|---|
| $H_2O$ | 65 | 430 | 110 | 2.7 | 2.5 | 0.032 | 0.025 |
| $D_2O$ | 1200 | 4100 | 3900 | 64 | 43 | 0.17 | 0.16 |
| $\tau_D/\tau_H$ | 18 | 9.5 | 35 | 24 | 17 | 5.3 | 6.4 |
| $CH_3OH$ | 190 | 890 | 230 | 4.6 | 3.6 | 0.054 | 0.034 |
| $CD_3OD$ | 880 | 5200 | 4100 | 93 | 69 | 0.40 | 0.31 |
| $\tau_D/\tau_H$ | 4.6 | 5.8 | 18 | 20 | 19 | 7.4 | 9.1 |
| DMF | 420 | 1900 | 1700 | 20 | 14 | 0.49 | 0.18 |
| DMF-$d_7$ | 770 | 2000 | 2300 | 250 | 170 | 2.0 | 1.0 |
| $\tau_D/\tau_H$ | 1.8 | 1.1 | 1.4 | 13 | 12 | 4.1 | 5.6 |
| DMSO | 870 | 2800 | 1700 | 22 | 12 | 2.0 | 0.77 |
| DMSO-$d_6$ | 1100 | 3200 | 3200 | 610 | 330 | 12 | 5.7 |
| $\tau_D/\tau_H$ | 1.3 | 1.1 | 1.9 | 28 | 28 | 6.0 | 7.4 |

[Ln(III)]=1.0x10$^{-2}$ M, [Am(III)]=1.9x10$^{-5}$ M, and [Cm(III)]=1.1x10$^{-6}$ M. $M(ClO_4)_3$ was dissolved in the solvent.
The experimental errors of the lifetimes are about $\pm$2 %.

# Quenching and Isotope effects




- The lifetimes decrease with decreasing ΔE, respectively for An(III) and Ln(III).
- Nonradiative decay rate due to the solvent shows the order of $H_2O$>MeOH>DMF>DMSO.
- The ratios $\tau_D/\tau_H$ give the values of 20 or above when $\Delta E/\nu=2\sim4$, where $\nu$ is the stretching wave number of O-H and/or C-H vibrators of the solvent molecules.

# Preferential solvation in mixed solvents

What kind of solvent is a close friend with An(III) and Ln(III) ?

⇩

Evaluation of preferential solvation by luminescence lifetime measurement

$X_s$: Mole fraction in the bulk solution

$N_{H2O}$: Apparent hydration number

$L_s$: Mole fraction in the first coordination sphere

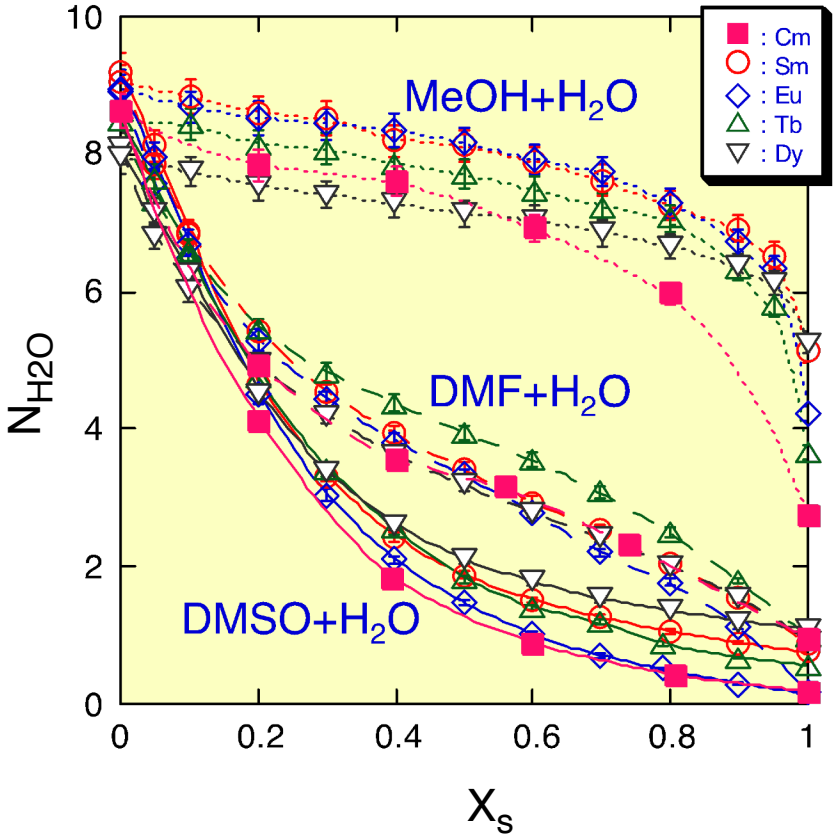
$k_{mix}=L_w k_w+L_s k_s$, $L_w+L_s=1$

$L_s=(k_w-k_{mix})/(k_w-k_s)$

$P_s$: Degree of preferential solvation

$P_s=(L_s/L_w)/(X_s/X_w)$

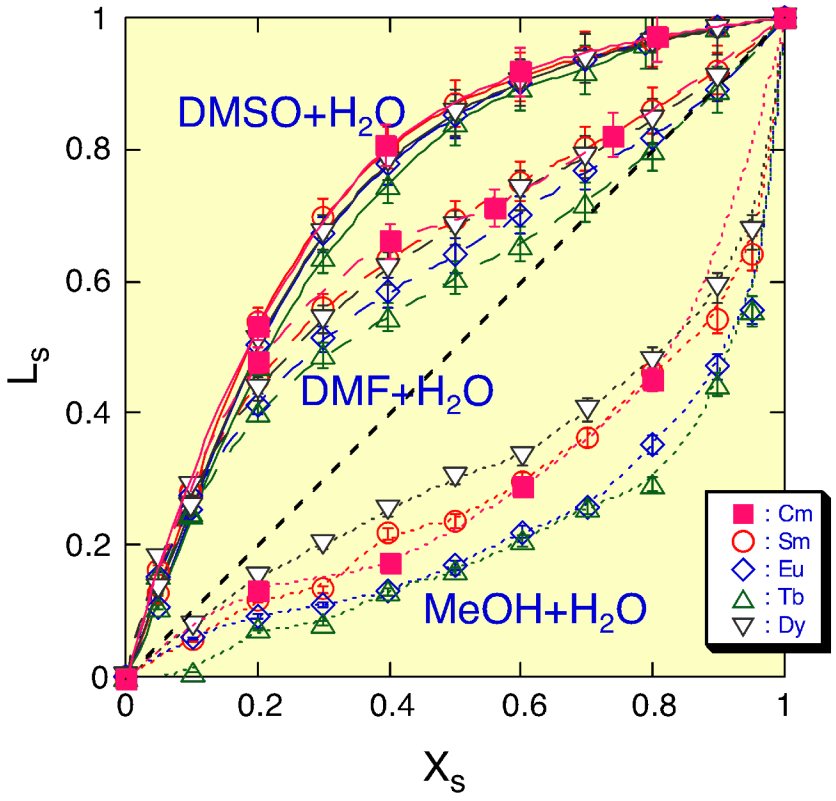
Apparent hydration number



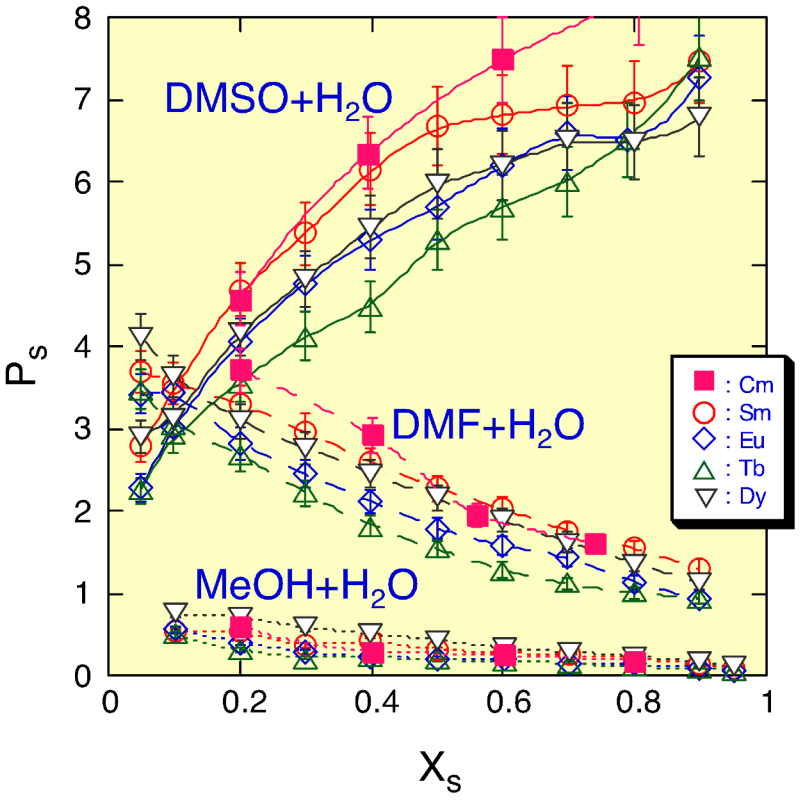

MeOH acts as a quencher of the ions with about half efficiency of $H_2O$, while DMF and DMSO do not.

# $L_s$ vs. $X_s$ and $P_s$ vs. $X_s$

Mole fraction in the first coordination sphere




Degree of preferential solvation




- An(III) and Ln(III) are preferentially solvated by DMSO in DMSO+$H_2O$, by DMF in DMF+$H_2O$, and by $H_2O$ in MeOH+$H_2O$ over the whole range of the solvent composition.
- The degree of preferential solvation varies considerably with the bulk composition.
- The order of the preferential solvation, i.e., DMSO>DMF>$H_2O$>MeOH, is in agreement with the relative basicity of these solvents.

# Separation of An(III) and Ln(III)

Resin: AG 50WX8 (Bio-Rad Lab., Inc.)
Functional group: $-SO_3^-$
Matrix: styrene divinylbenzonate

J. Alloys Compd., **271-273**, 719 (1998).

Separation of An(III)/Ln(III)

by Cation Exchange Resin

HCl : Yes

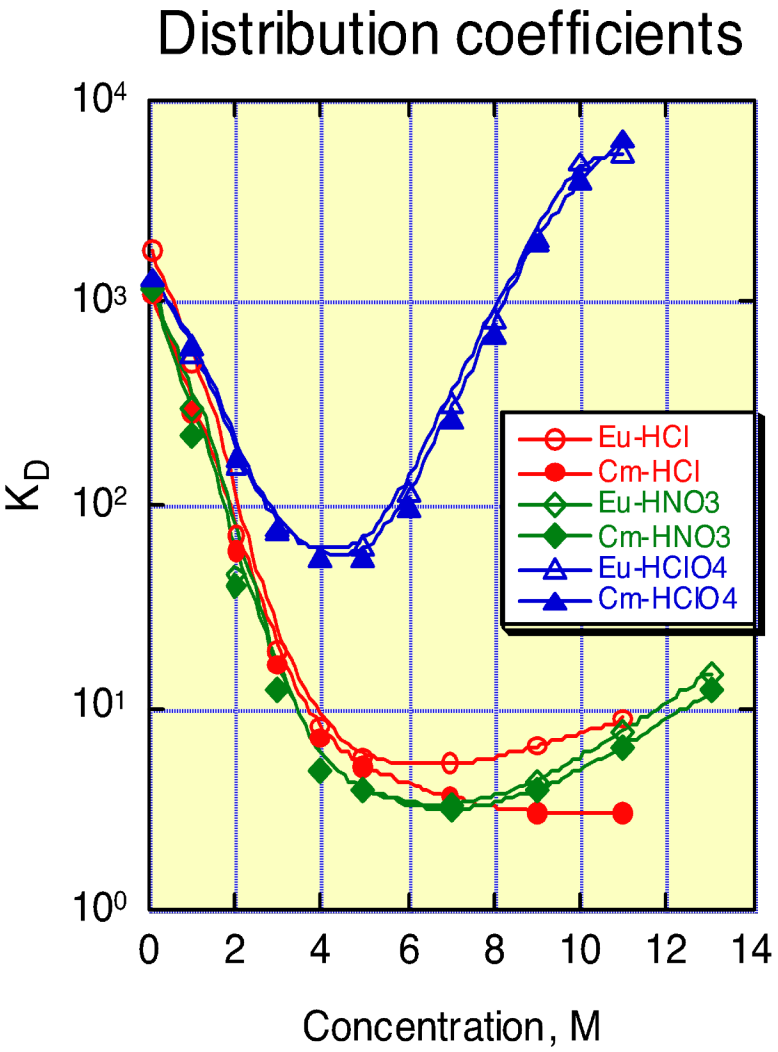
$HNO_3$ or $HClO_4$ : No

Elucidation of the Mechanism

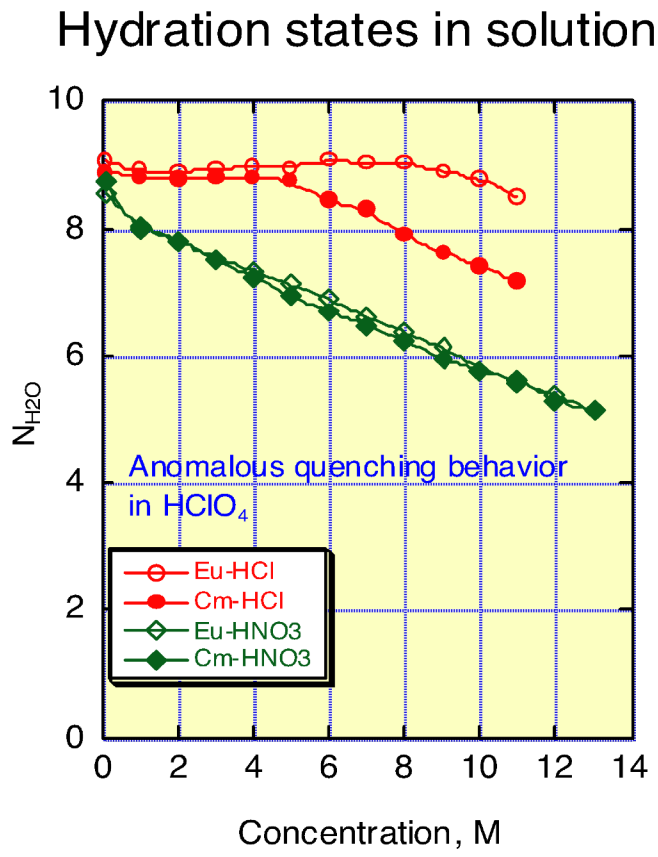
from Hydration States

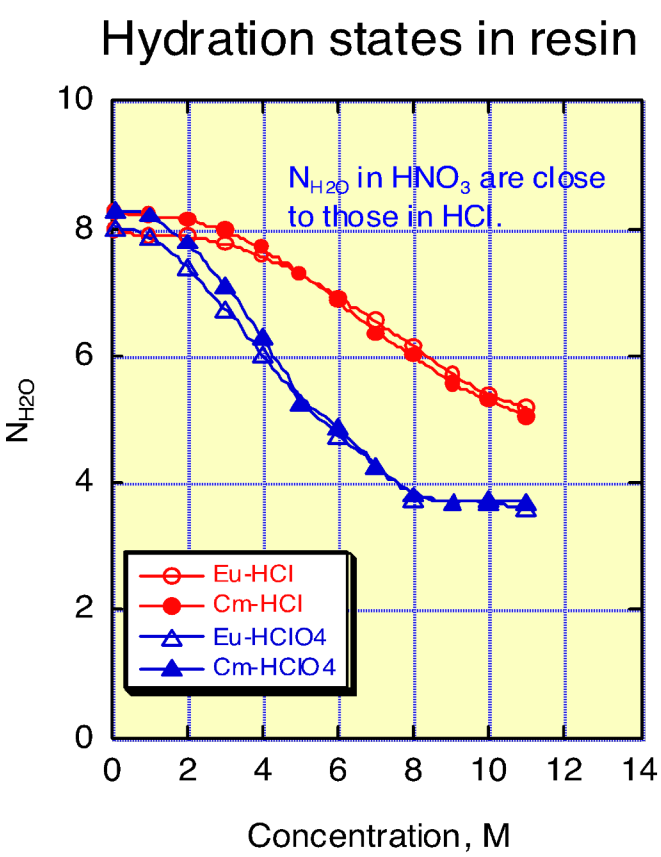
$N_{H2O}$(Solution)⇔ $N_{H2O}$(Resin)

$N_{H2O}$(An) ⇔ $N_{H2O}$(Ln)



# Hydration states of Cm(III) and Eu(III)

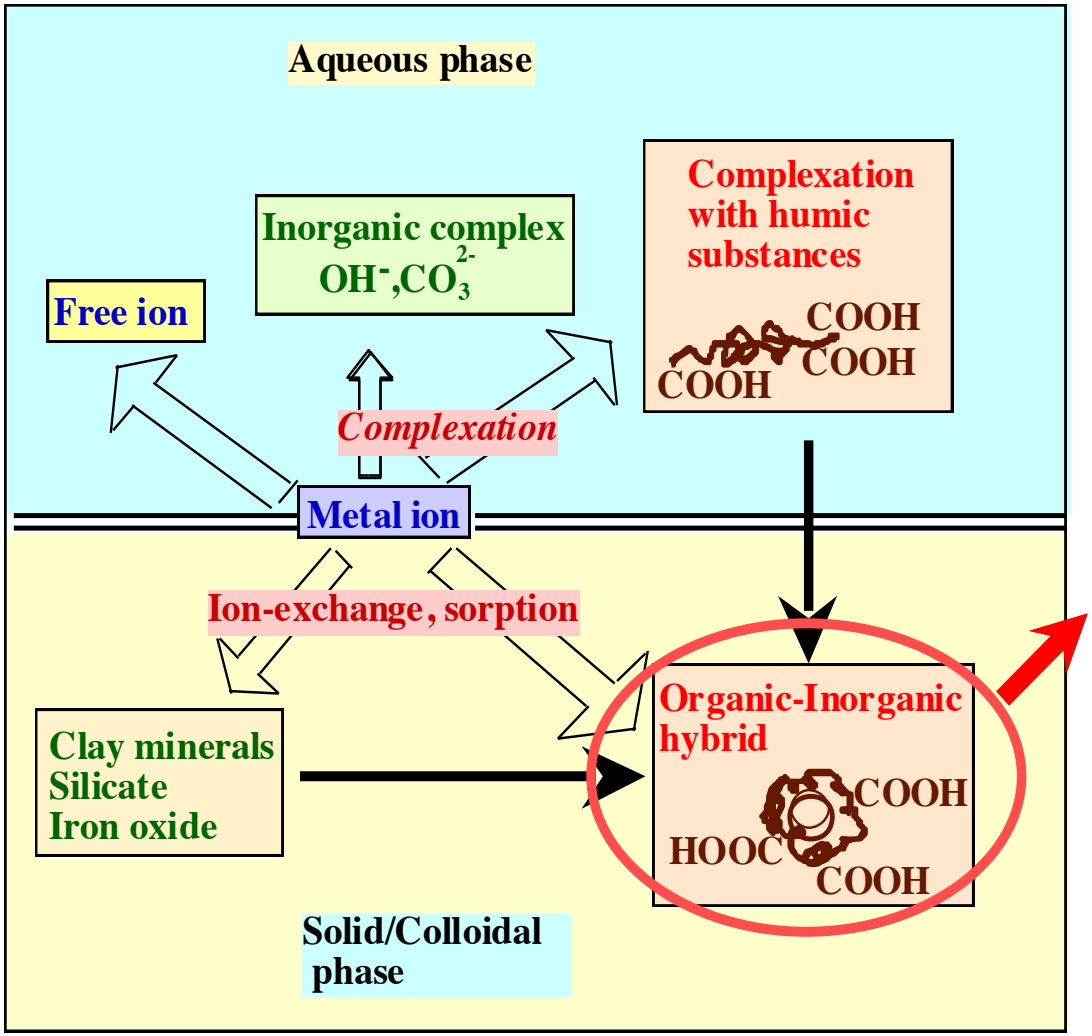



- $K_D$ of An(III)/Ln(III) are well correlated with $N_{H2O}$ in solution.
- $Cl^-$ interacts with An(III) stronger than Ln(III), since $Cl^-$ is a softer donor than $NO_3^-$ or $ClO_4^-$.

# Cm(III) on fulvic acid-montmorillonite

Geochim. Cosmochim. Acta, **66**, 1 (2002).




**Schematic figure on various factors affecting environmental behavior of metal ions.**

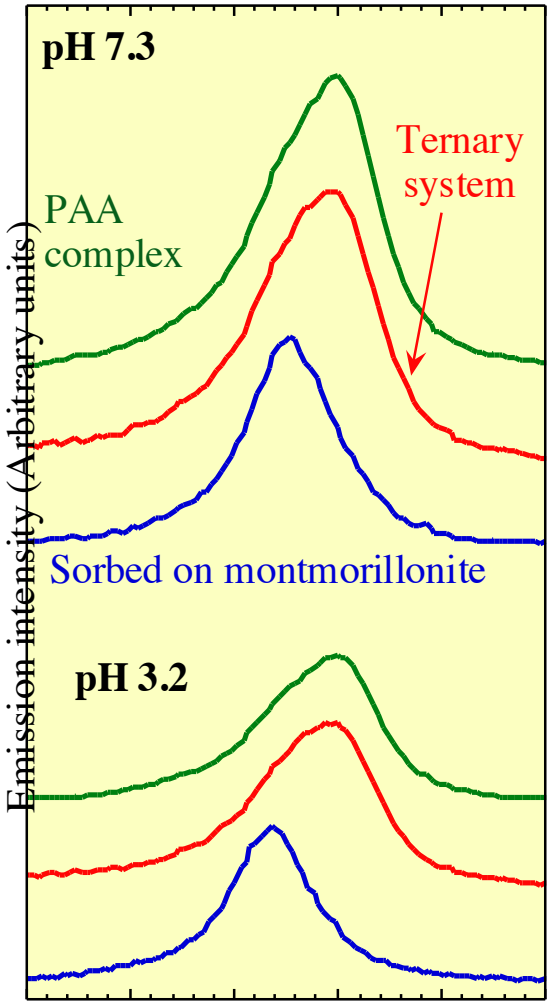
**Sorption on organic-inorganic hybrid**

**Important process for metal ion behavior**

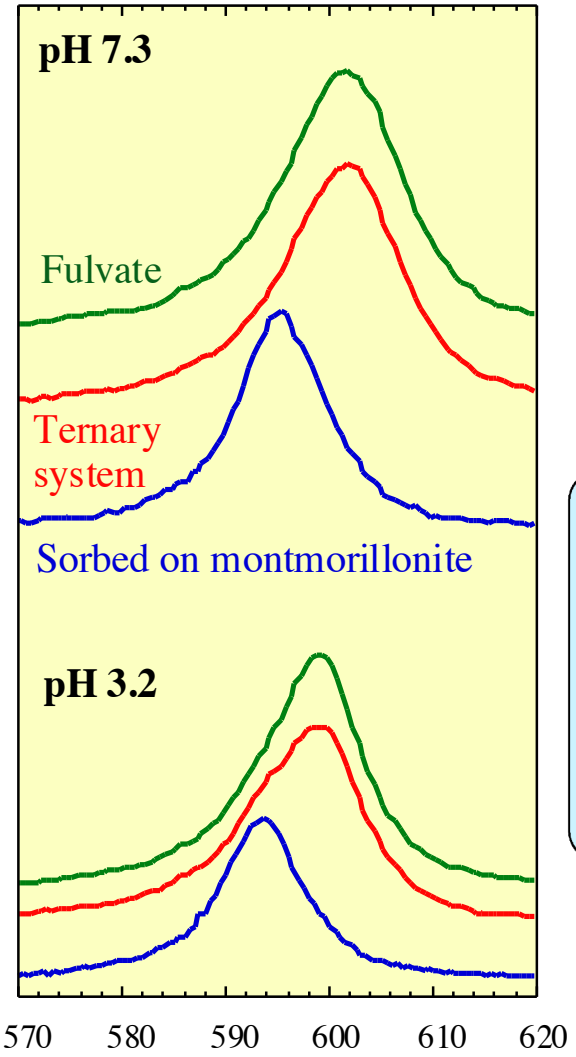
**The chemical-state ?**
**Organic or inorganic ?**

# Emission spectra of Cm(III)

**Cm(III)/PAA/Montmorillonite**



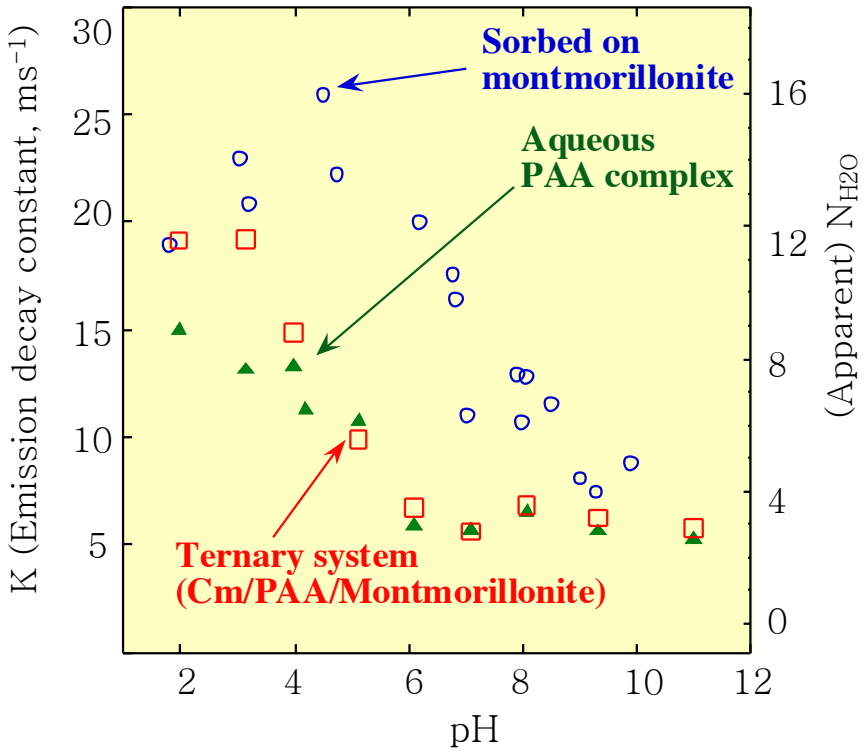

**Cm(III)/FA/Montmorillonite**



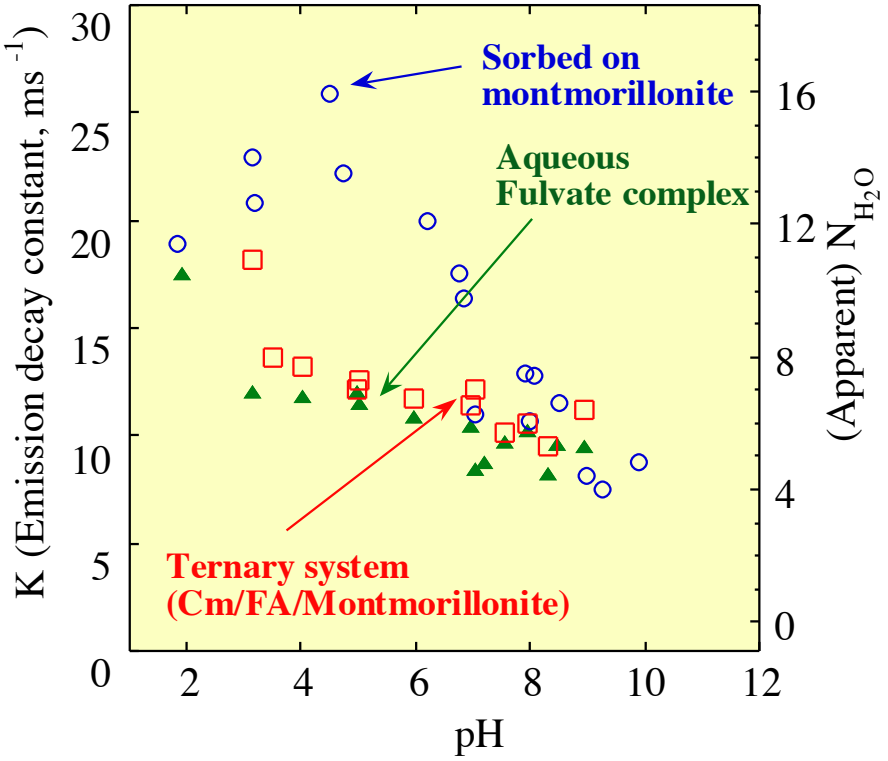

**Cm(III) can be sorbed as PAA or fulvate complex on montmorillonite.**

# Lifetimes of Cm(III)

**Cm(III)/PAA/Montmorillonite system**



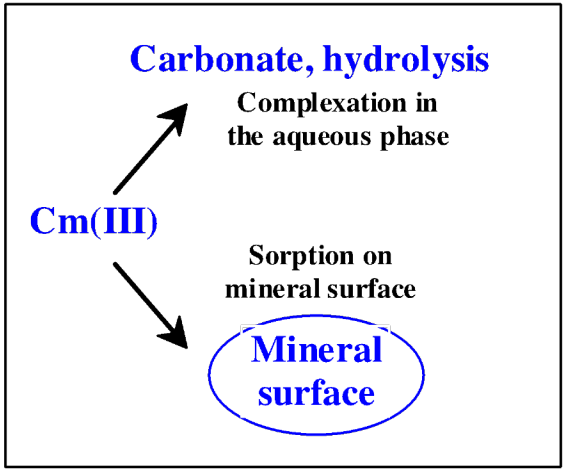

**Cm(III)/FA/Montmorillonite system**




**Cm(III) can be sorbed as PAA or fulvate complex on montmorillonite.**

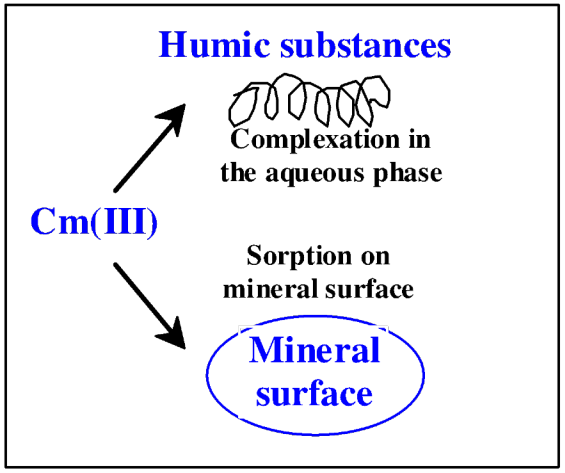
# Cm(III) species in ternary system

**In the absence of humic substances**

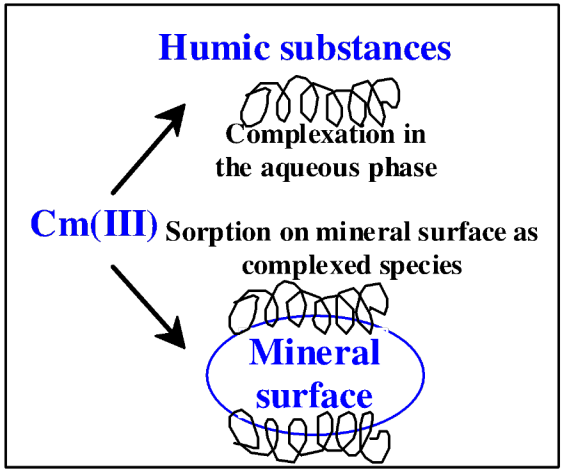



*Competitive*

**In the presence of humic substances**




*Competitive*




*Distribution of humic substances governs that of Cm(III)*

# Conclusion

1. The inner-sphere hydration number $N_{H2O}$ of An(III) [An=Am, Cm] and Ln(III)[Ln=Nd, Sm, Eu, Tb, Dy] can directly be determined by the luminescence lifetime measurement.

2. The determination of $N_{H2O}$ makes it possible to characterize the chemical species of the f-elements in solution, in solid, and at their interface with higher sensitivity and selectivity.

3. This is one of the most promising methods to compare directly the hydration states of An(III) and Ln(III), which can be applied to study the coordination and separation chemistry.

*ご清聴ありがとうございました。*