SPECTROSCOPIC PROPERTIES OF Eu^{3+} FREE IONS UNDER HIGH TEMPERATURE AND HIGH PRESSURE CONDITIONS

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ABSTRACT

An optical cell system for in-situ spectroscopic analysis of aqueous chemical species in high temperature/pressure conditions was developed and applied to study the fluorescence/absorption properties of Eu^{3+} free ions by using time-resolved laser induced fluorescence spectroscopy (TRLFS) and UV/Vis absorption spectroscopy. The temperature effect on the spectroscopic properties was observed in the range of 25 to 170ºC at a constant pressure of 10 MPa. From the temperature dependency of fluorescence lifetime, relevant thermodynamic parameters were determined in the present work based on the Arrhenius equation.

KEY WORDS

Eu^{3+}, High temperature, TRLFS, UV/Vis

1. INTRODUCTION

Deep geological disposal is the internationally preferred method for isolating radioactive waste from the biosphere, utilizing a multi-barrier system consisting of a natural geological barrier and an engineered barrier. To ensure the long-term containment performance of the engineered barrier, repository designs aim to maintain the maximum temperature below 100°C. However, in the near field of the repository, temperatures may rise above 100°C due to radioactive decay heat and the geothermal gradient. Such elevated temperature conditions can significantly affect the retardation and migration behavior of radionuclides in the near field. Although understanding the aqueous chemistry of radionuclides under superheated conditions (T > 100°C) is crucial, the availability of thermodynamic data under these conditions remains limited due to experimental challenges.

In this context, the objective of this study is to develop a high-temperature and high-pressure spectroscopy system and to demonstrate its performance through spectroscopic analysis of Eu^{3+} free ions under superheated conditions.

2. EXPERIMENTAL

2.1 Chemicals

All materials used in the present work were of reagent grade. The initial $Eu(OH)_3$(am, fresh) solid phase was precipitated under alkaline condition in glovebox (O_2 < 5 ppm). Then the stock solution of Eu^{3+} was prepared by dissolution of the precipitated solid phase in 0.1 m $HClO_4$ solution. In four independent samples, the Eu^{3+} stock solution was diluted with 0.18 m $HClO_4$ solution and quantified using ICP-OES to [Eu^{3+}] = 5.03, 15.28, 20.16, and 25.34 mmol/kg_w.

2.2 Spectroscopy system for superheated condition

The experiments were conducted using a custom-developed high-temperature and high-pressure optical cell system, which consists of an accumulator, a pressure regulator connected to an Ar cylinder, cartridge heaters, and a K-type thermocouple (see Fig. 1). The optical cell was constructed from titanium alloy (Ti-6Al-4V, Grade 5) and equipped with sapphire windows, providing an optical path length of 2.32 cm. Using this system, the spectroscopic properties of Eu^{3+} free ions were measured over a temperature range of 25ºC to 170ºC under 10 MPa condition.

In this study, UV/Vis absorption spectra were collected with an absorption spectrometer (SPECORD S 600, Analytik Jena) coupled with a collimating lens-equipped fiber optic system. Moreover, a time-resolved laser-induced fluorescence spectroscopy (TRLFS) system was employed, featuring an pulsed Nd:YAG laser (Brilliant B, Quantel) with a wavelength of 1064 nm and a repetition rate of 10 Hz. The fourth harmonic generator was used to produce a 266 nm laser beam for excitation of Eu^{3+} free ions, with laser pulse energies ranging from 4.2 to 4.6 mJ.

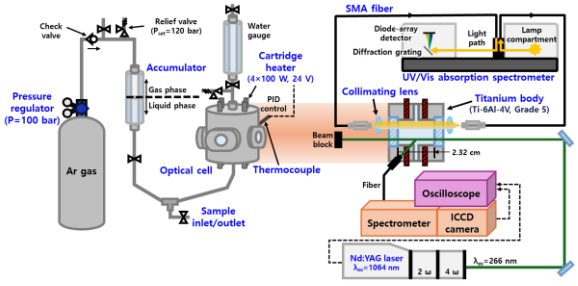

Fig. l: Schematic of TRLFS and UV/Vis spectroscopy system for superheated condition.

Fluorescence emission spectra were recorded using a Czerny-Turner spectrometer (Kymera-328i-A, Andor) coupled with an ICCD camera (DH334T-18F-73, Andor). Fluorescence lifetimes were determined based on the time-dependent fluorescence intensity obtained by controlling the time delay between the laser pulse and ICCD

camera gating through a software program, with the timing monitored using an oscilloscope (Tektronix, TDS7104).

3. RESULTS AND DISCUSSION

As shown in Fig. 2, the molal absorptivity ε of Eu^{3+} free ions decreases with increasing temperature, while the peak positions remain unchanged, consistent with literature data.[2] Compared to the absorption peaks in other wavelength ranges, minor variations were observed at 327, 380.5, and 385 nm, as indicated by the arrows in Fig. 2. These variations are likely due to transitions originating from the $^7F_1$ state, as opposed to those from the $^7F_0$ state.[3]

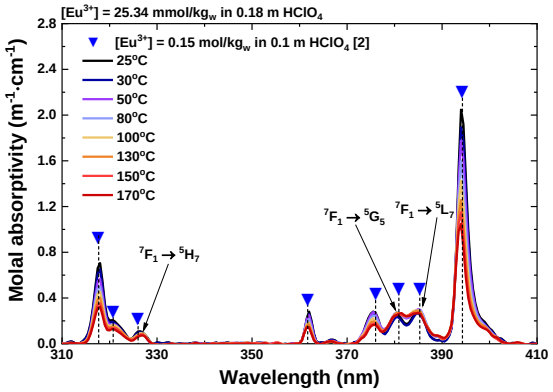

Fig. 2: Molal absorptivity of Eu^{3+} free ions obtained as a function of temperature.

Furthermore, Fig. 3 illustrates the effect of temperature on the fluorescence spectra of Eu^{3+} in 0.18 m $HClO_4$ solution at temperatures ranging from 25ºC to 170ºC under 10 MPa. Fig. 4(a) shows the temperature-dependent mono-exponential decay of fluorescence intensity for Eu^{3+} free ions. The observed de-excitation (*i.e.*, relaxation) rate constant, k_{obs}, defined as the inverse of the fluorescence lifetime, was plotted using the Arrhenius equation (see Fig. 4(b)):

$$k_{obs} = A \cdot \exp(-E_a/RT) \qquad (1)$$

where A is the pre-exponential factor, R is the gas constant, E_a is the activation energy and T is the absolute temperature.

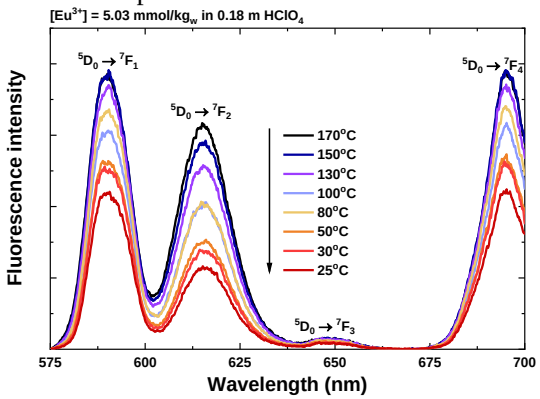

Fig. 3: Fluorescence spectra of Eu^{3+} free ions observed at various temperatures in 0.18 m $HClO_4$.

As shown in Fig. 4(a), the fluorescence lifetime of Eu^{3+} free ions decreases gradually with increasing temperature, aligning with previous study.[4] However, the activation energy calculated in this study is approximately ten times higher than reported one.[4] The observed temperature dependence of fluorescence lifetime and molal absorptivity might be attributed to changes in the number of coordinated H_2O molecules and variations in transition probabilities as a function of temperature.

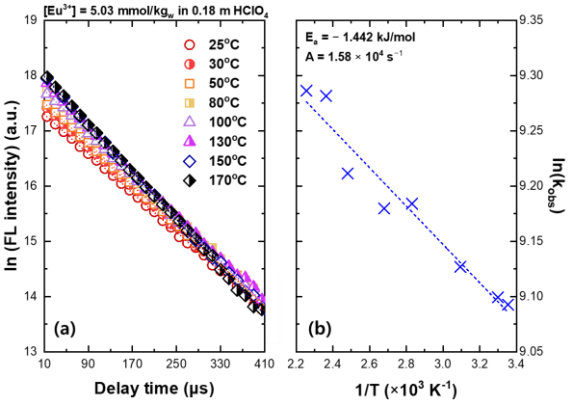

Fig. 4(a): Time-resolved laser fluorescence intensity and (b) Arrhenius plots of the fluorescence decay constant of Eu^{3+} free ion.

4. CONCLUSION

This study presents the development of an in-situ spectroscopic system for analyzing radionuclides under high-temperature and high-pressure aqueous conditions. The system successfully demonstrated its capability for conducting in-situ spectroscopic studies of lanthanides under superheated conditions. However, further studies are necessary to fully understand the phenomena observed in this work, particularly the temperature-dependent fluorescence lifetime. The spectroscopic system developed in this study is expected to be a valuable tool for future investigations into the chemical behavior of radionuclides in superheated environments.

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REFERENCES

1 H. Raiko, Disposal canister for spent nuclear fuel-design report, Posiva 2005-02, (2005).

2 D. C. Stewart, Light absorption of solutions of the trivalent ions of lanthanide and actinide rare earth. I. The lighter lanthanide elements in aqueous perchloric acid, AECD-2389, (1948).

3 S. Ram, O. P. Lamba, H. D. Bist, *Pramana* 23 (1984) 59.

4 T. Kimura, R. Nagaishi, M. Arisaka, T. Qzaki, Z. Yoshida, *Radiochim. Acta* 90 (2002) 715.